Thermodynamics and Phase Behavior of Polycyclic Aromatic Hydrocarbon Mixtures

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Chapter 1. Introduction

Polycyclic aromatic hydrocarbons are common components of petroleum and byproducts of fuels conversion. They are quite regularly found in mixtures of similarly structured compounds and there is surprisingly little in the way of reliable phase behavior information on PAH mixtures in the literature considering the commercial and environmental importance of such mixtures. The research conducted in this laboratory has, for some time, been motivated by this deficiency and aimed at a thorough investigation of the thermodynamics and phase behavior of PAHs and related compounds.

PAHs are produced by both natural and anthropogenic processes. In the latter case, they are quite often associated with the 19th and 20th century production of lighting and heating gas by manufactured gas plants (MGPs). The legacy of these long since abandoned facilities is the inappropriate disposal of PAH-rich tars and non-aqueous phase liquids (NAPLs) that remain a concern still today. Though MGP contamination largely motivated this research, it is important to recognize that PAHs are widely encountered in present industrial and natural settings. The applicability of this study then extends beyond environmental remediation of past contaminants, to present and future risk assessment, disposal, and engineering design.

Based on their adverse health effects and availability, 16 PAHs are listed as priority pollutants by the United States Environmental Protection Agency (EPA, 2010). The movement and final endpoint of such chemical pollutants is commonly
referred to as “fate and transport,” and is dictated both by chemical properties (e.g., vapor pressure, melting point temperature, solubility) and conditions of the surroundings (e.g., temperature, pH, air/water flow). The work presented here addresses the former variable, by measuring and analyzing thermodynamic properties and behavior of PAHs, their mixtures, and related compounds. Properties of main concern were vapor pressure, melting point temperature, fusion enthalpy, microstructure, and aqueous solubility. In addition, the sorption of pure, gas phase PAHs to natural particles is discussed.

Much of this work required unique experimental design, the specifics of which will be given in later sections. It is worth noting though, that gaps in current understanding likely result from inadequacies of traditional experimental techniques. For example, the volatility of PAHs at moderate temperatures is so low that traditional pressure gauges cannot accurately measure equilibrium vapor pressure. Hence, a Knudsen effusion technique was used to indirectly determine the vapor pressure of such compounds and their respective mixtures. Similarly, innovative approaches were employed to measure and characterize the aqueous solubility and gas phase sorption of PAHs.

The work presented in this study will be divided into three main research topics, as was the case in the laboratory. This is not to say that there was no overlap in experiments and analysis, but for the sake of clarity, it is worthwhile to unambiguously walk the reader through the chronological path that was taken in the laboratory. Areas of main concern will be (1) Phase Behavior of PAH mixtures,
(2) Aqueous Solubility of PAH mixtures, and (3) Sorption of PAHs to Natural Particles. Each section will include its own brief review of relevant literature, detailed description of experimental technique, and discussion of the experimental results.

1.1 History of Natural and Anthropogenic PAHs

Polycyclic aromatic hydrocarbons are relatively high molecular weight compounds formed by chemical conversion (usually incomplete combustion) of organic matter. They are composed of at least two, fused, aromatic rings (Wilcke, 2000). The smallest and simplest PAH is naphthalene. Benzene, which has only one aromatic ring, is not classified as a PAH. PAHs gain in complexity as they increase in size and mass, via fusion of additional aromatic rings or by covalently bonding with heteroatoms such as halogens, nitrogen, or oxygen (Goldfarb 2008). To differentiate from traditional PAHs, the hetero-substituted chemicals will, at this point forward, be referred to as polycyclic aromatic compounds (PACs).

PAHs are an abundant organic pollutant and many processes lead to their formation and eventual release into the natural world. Most combustion reactions, especially those associated with open burns, deposit PAHs into the environment. For example, the unenclosed burning of material such as crop residue, tobacco, construction debris, spilled oil, and forests, leads to potentially widespread deposition of PAHs and PACs (amongst other contaminants) into soil, sediment, air, and water (Lemieux et al., 2004). Even the well-engineered combustion reactions of
furnaces and internal combustion engines produce and release byproduct PAHs (Golomb et al., 2001). The reason for this release is that the associated combustion reactions cannot go to completion under the given conditions, so the reactants are not fully converted to carbon dioxide and water. Rather, other products such as soot, particulate matter, light hydrocarbons and semivolatile organic compounds (SVOCs), including PAHs and PACs, are formed in these low-temperature, oxygen-limited systems (Lemieux et al., 2004).

PAHs have long been associated with complex, heterogeneous, liquids or semisolid mixtures, identified as tars and NAPLs. Tars are encountered as solids, semisolids, and/or viscous liquids. They consist of high molecular weight compounds that are nearly insoluble in water and which are solid at room temperature. NAPLs differ in that their comparatively lower molecular weight components are liquid at ambient conditions. This leads to a less viscous, but still water-insoluble and complex liquid-mixture system. In many cases it is difficult to distinguish between tars and NAPLs. It is also important to recognize that tars and NAPLs are comprised of more than PAHs and PACs. Rather, they might contain an abundance of chemicals including metals (e.g., lead, arsenic, mercury), volatile organic compounds (e.g., BTEX), phenols, and sulfur/nitrogen-containing inorganic compounds (Luthy et al., 1994).

Though worldwide production of tar by high temperature pyrolysis originated in the 17th century for purposes of wood preservation, it was not until the birth of manufactured gas plants in the early 1800s that tar was produced in more
appreciable quantities: The demand in urban areas for clean and inexpensive cooking and heating fuel led to widespread production of manufactured gas, or town gas, at 1000 to 2000 manufactured gas plants across the United States (Luthy et al., 1994). In the mid 1900s, pipeline distribution of natural gas took control of the market and led to the eventual closure of all US manufactured gas plants.

During the nearly 150 years of MGP operation, manufactured gas was produced by anaerobic pyrolysis of feedstock such as coke, coal, and oil in furnaces, known as retorts. Light fractions were separated, condensed, collected, and used as combustible gas. Tar, consisting of the high molecular weight fractions including PAHs, was generally considered to be an unwanted byproduct and was produced in all coal carbonization, oil gas, and carbureted water gas processes (Luthy et al., 1994). Due to limited or nonexistent market value, large quantities of these PAH-rich tars were sometimes dumped into nearby water bodies or in unlined waste pits. This intentional discharge, combined with leaks and breaks in waste or storage pits, has produced large tar contamination plumes in soil, mainland and marine sediments, and in groundwater. Even in times when tar byproduct markets or uses existed, releases of various kinds took place.

The processes described above are all related to human activity. The significance of and literature base for such anthropogenic activity can easily overshadow the important reality that PAHs are also formed by natural means. In fact, PAHs and PACs represent a significant fraction of fossil fuels such as crude oil and coal. The PAHs present in these valuable combustible materials are formed
during the very slow degradation, i.e., chemical conversion, of organic material into hydrocarbons. Of course, there is a vast market for products derived from fossil fuel and it is not surprising that the petrochemical industry must consider PAHs when pumping, transporting, and processing such valuable material (Iturbe et al., 2007). For example, gas refineries must separate high molecular weight components in order to meet the specifications of gasoline, engine oil, and diesel fuel. Once removed, the heavy, PAH-containing fractions must be properly disposed of and/or converted by incineration. Additionally, PAH-containing tars and creosote that are present in crude materials must be considered when designing pipeline transportation and numerous other refinery operations.

It should be clear that PAHs are common, naturally derived components of fossil fuels. They are also formed during incomplete combustion or gasification of those fuels and other biomass. Each of these processes forms different groups of PAHs and PACs at varying ratios based upon reaction conditions and feedstock material. This diversity then leads to the existence of PAHs as complicated mixtures in both industrial and environmental settings. Consequently, a mixture from one site will likely vary in components and ratio thereof from another site’s mixture. This, in addition to the notion that PAHs are rarely encountered in pure form, and a concern that thermodynamically ideal behavior may not accurately predict the behavior of such mixtures is what spurred much of this work. These themes will be carried through the remainder of the dissertation as we uncover and analyze non-ideal phase behavior and better define what is actually meant by the term “tar.”
1.2 Availability and Transport of PAH Mixtures

PAHs are ubiquitous environmental pollutants and high concentrations are mainly encountered in subsurface soils and sediments that are contaminated with tars, NAPLs, and fossil fuels (Goldfarb, 2008). Additionally, it is not uncommon for soil contamination to result from atmospheric deposition of PAH-containing particles, derived from combustion processes noted above (Cortes et al., 2000). Soils and sediments readily accept and stabilize PAHs in the condensed phases (solid, liquid) because PAHs have relatively low aqueous solubility and vapor pressure. Furthermore, a soil's organic matter and high surface area provide sorbent sites for organic compounds (Luthy et al., 1997).

Once in the subsurface, PAH-rich tars and NAPLs will migrate though the void volume of the natural particles. In general, their density is greater than that of water and this allows displacement of groundwater as they sink toward and pool at impenetrable bedrock or low porosity soil (Figure 1.1). Tar and NAPL plumes may also move laterally in the subsurface. For example a pooling tar that has reached dense soil may begin to move horizontally along the gradient of the bedrock or clay. Oftentimes this results in movement, similar to that of groundwater, along the slope of the bedrock, towards large bodies of water (Luthy et al., 1994).
Figure 1.1 Cross section of a typical manufactured gas plant site (taken from Luthy et al., 1994).

PAH-rich tars and NAPLs encounter both air and water throughout this sinking and pooling process. In situations involving groundwater flow and vapor intrusion, there is convective air/water flow that may increase the potential for aqueous or vapor phase transport of PAHs. And though PAHs exhibit very low aqueous solubility and vapor pressures at ambient conditions, the levels are not so low that these transport processes can be neglected. In fact, PAHs do both vaporize and partition into water. They then move with a bulk current and/or diffuse. These factors characterize the fate and transport of PAHs in the environment and unabated PAH plumes can contaminate air and water to a point at which human health may be compromised.

Despite the possible vaporization and dissolution of PAHs noted above, the quantity of source material will likely remain nearly unchanged for decades or more. In other words, though the contaminants partition into water and air, the
mass removed from the bulk contamination source is often negligible (Mukherji et al., 1997). Nonetheless, the vapor phase and/or aqueous PAH concentration is significant when considering the risk to human health.

1.3 Polycyclic Aromatics and Human Heath Risk

The inappropriate disposal of manufactured gas plant waste troubled the MGP industry early in the 20th century as acknowledgement of pollution, especially that of water, mounted (Hansen, 1916). The history of such concern is highlighted by the 1919 formation of a “committee on waste disposal” by the American Gas Association and by Blumer’s relatively early, peer-reviewed analyses of soil contamination by PAHs (Blumer, 1961). In his publication, Blumer expressed concern that PAHs may pose a significant health risk to exposed humans and that PAHs could damage fragile subsurface ecosystems.

Carcinogenicity of PAH-containing mixtures was observed and documented as early as 1775 in London chimney sweeps (Douben, 2003). Later records indicate that German coal workers from the late 1800s exhibited skin cancers (Eisler, 1987). These reports led to subsequent studies linking soot, tars, and oils to human and animal cancers (Douben, 2003). Of course, these complicated mixtures are often burdened with PAHs, and now, seven PAHs are classified as probable human carcinogens by the U.S. EPA (Table 1.1). It is commonly understood that other, “nonclassifiable” PAHs and PACs belong on the list. Recent work suggests that even naphthalene, the active ingredient in mothballs, might be carcinogenic (IRIS, 1997).
Furthermore, The National Toxicology Program (NTP) “reasonably anticipates” the human carcinogenicity of six (of the seven) compounds from EPA’s list and an additional nine, high molecular weight PAHs (NTP, 1998). These fifteen PAHs are also regarded as probable and possible human carcinogens by The International Agency for Research on Cancer (IARC, 1987). Table 1.1 summarizes this information. The IARC also lists coal tar as a known human carcinogen, based on both animal and human health effects. There are other risks associated with exposure to PAHs and tars, but cancer risk is the most studied and reported.

The human health risk of these, and all poisonous substances, is quantified by considering both dose and inherent toxicity. This means that an exposure pathway must be present in order for a toxic chemical to affect human health. There is limited toxicological data available for most PAHs, so it is necessary to use toxic equivalency factors (TEFs) when considering the inherent toxicity of PAHs. Since sufficient data exist to quantify the carcinogenic potency factor of benzo[a]pyrene, it is common to estimate the toxicity of other PAHs (dose_i) relative to a benzo[a]pyrene equivalent dose (Peters et al., 1999) as follows:

\[ \text{BaP_{eq}} \text{dose}_i = \text{TEF}_i \times \text{dose}_i \]  

The Office of Health and Environmental Assessment (at the U.S. EPA) provides TEFs for the seven aforementioned probable human carcinogens (EPA, 1993). In addition, Nisbet and LaGoy presented TEFs for all 16 EPA Priority Pollutants (1992). These values are reported in Table 1.1. Their calculations are based on limited data, which report the carcinogenic effects of such PAHs. Hence, these figures are
estimates with a fair amount of uncertainty, but they are nonzero, which is significant. Peters et al. assess the risk of PAH-containing NAPLs by considering that all EPA Priority Pollutant PAHs have the ability to contribute to cancer risk (1999).

From this limited data set, PAH toxicity generally increases with molecular size. PAHs with five or six rings such as benzo[a]pyrene and benzo[b]fluoranthene are more carcinogenic than the smaller compounds, e.g., anthracene and pyrene. In spite of this, one must also consider that the solubility and vapor pressure of the lower molecular weight PAHs is considerably higher than the larger sized molecules. This may lead to potentially higher exposures from dissolution into water or evaporation into air.

The exposure pathways for PAHs are generally understood to include both ingestion and inhalation. Ingestion of PAHs is usually associated with the drinking of contaminated water. The work of Peters et al. (1999) uses experimental solubility of PAHs and the aforementioned TEFs to assess the long-term risk of PAH-contaminated water.
Table 1.1. Categorization and Quantitation of PAH Carcinogenicity (Modified from Peters et al., 1999).

<table>
<thead>
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<th>PAH</th>
<th>EPA Priority Pollutant</th>
<th>EPA Probable Carcinogen</th>
<th>EPA TEF</th>
<th>IARC Carcinogen</th>
<th>NTP Carcinogen</th>
<th>Nisbet/LaGoy TEF</th>
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Exposure by inhalation occurs when breathing contaminated air. In most cases, PAH-containing particles are released to the atmosphere as a result of combustion related processes such as automobile and power plant emissions. These particles consist of dust, soot, ash, etc. For example, diesel fuel engine exhaust contains PAH-laden particulate matter, and the inhalation of such particles is linked
to asthma and allergic breakthrough (Lubitz et al., 2010). Of course, inhalation of PAH-containing diesel fuel emissions may also be a carcinogen exposure pathway.

Also important, albeit little studied, is the risk of PAH inhalation resulting from vapor intrusion; the process in which vaporized, subsurface contaminants are transported through soil/sediment and into indoor-air (Figure 1.2). This may provide an exposure route for even low volatility PAHs that evaporate to and migrate in the vapor phase. There is ongoing research on the movement of volatile organics (e.g. TCE, PCE, benzene) by vapor intrusion (Bozkurt et al., 2009). It has not yet been determined if vapor intrusion of less volatile toxins, e.g., PAHs, can result in poor heath outcomes.

Though only limited toxicological data exist for such vapor phase, inhalation exposures, some relevant exposure limits exist in the literature. For example, the US Occupational Safety and Health Administration (OSHA) regulates “coal tar pitch volatiles” to a permissible exposure limit (PEL) of 0.2 mg/m³ and it is recognized that many PAHs (e.g., pyrene, phenanthrene, anthracene, and benzo(a)pyrene) are included in this category. Furthermore, the European Commission recommends that benzo(a)pyrene exposure be limited to no more than 1 x 10⁻⁶ mg/m³ (Working Group on PAHs, 2001). Of course, the discrepancy in the standards is common and is attributable to limited data reporting the toxic effects of such compounds. Nevertheless, simple calculation using ideal gas theory shows that, at 298 K, the vapor pressures of naphthalene (OSHA PEL 50 mg/m³) and phenanthrene give way to vapor concentrations around 570 and 1.50 mg/m³, respectively, and these exceed
OSHA’s PELs. Moreover, despite its very low volatility, the calculated concentration of benzo(a)pyrene (at \( T = 298 \) K) is around \( 8 \times 10^{-5} \) mg/m\(^3\), and this exceeds the European Commission recommendations. It is worth noting that not all PAHs (e.g., anthracene) exceed the above exposure limits, but PAHs often exist in complicated mixtures and the sum of all individual species vapor pressure may still surpass that recommended by a regulatory agency or research group. The point here is that vapor inhalation via vapor intrusion is not beyond the realm of possibility and could be considered in further risk assessment and/or fate & transport studies.

Figure 1.2 Vapor intrusion schematic (taken from Bozkurt et al., 2009).
1.4 Remediating PAH-Contaminated Sites

The remediation of dense NAPLs and tars presents a sizable challenge to the environmental community, especially to those assessing and cleaning former manufactured gas plants. These challenges are associated with the complexity of the sites, at which large volumes of inhomogeneous contaminants likely exist below the groundwater table and near populated areas. Environmental engineers must be careful not to expose community members (or themselves) to harmful contamination during the remediation process. Furthermore, remediation plans must be versatile enough to respond to the shifting conditions encountered when removing complex mixtures from the subsurface.

In most cases, source material must be removed by excavation or by direct pumping (if possible). Sometimes a portion of this material was abandoned in subsurface structures (e.g., tanks). These structures must be emptied and removed. More frequently though, leaks in the containment structures and/or intentional mixing of tars with backfill has left the soil and sediment soaked with byproduct tar and NAPL. These heavily contaminated soils must be excavated and treated.

Once removed, the source contaminants are generally managed by either stabilization (e.g. in asphalt or cement) or incineration. Land disposal is sometimes the only alternative for heavily contaminated soils (Luthy et al., 1994). Unfortunately, elimination of distinct sources of tarry material may not remove all PAHs from a site. Rather, residual contamination of air and/or water is possible. This may be handled via groundwater pump-and-treat systems, in which
groundwater is recovered and subsequently treated by hydrocarbon-water separation, air stripping, and/or carbon adsorption (Luthy et al., 1994).

The aforementioned processes are extremely time consuming and expensive. Hence, lower cost ex-situ methods, such as thermal desorption (likely between 360 and 830 K), biological treatment, and soil washing have been investigated and used. In cases where contaminated sediments or soils are difficult to access, in-situ remediation and treatment may be more cost-effective and efficient. Contaminants may be difficult to access for a number of reasons. In many situations where subsurface structures or utilities make it difficult to reach the contaminants with excavation equipment, candidate in-situ abatement (PAH destruction or removal) processes include bioremediation, chemical/biological oxidation, steam stripping, and vapor extraction. The latter two techniques may not be adequate, or predictable in terms of efficacy, in cases where high molecular weight, low-volatility compounds are encountered (Luthy et al., 1994).

Sometimes residual tars and NAPLs are relatively inaccessible due to capillary forces and sorption that tightly bind them in the subsurface (Mercer and Cohen, 1990). Surfactant addition and heating can be used to weaken these forces and increase the mobility of the contaminants. This, too, may lead to problems if the movement of mobility-enhanced contaminants cannot be controlled in desired directions (Fountain et al., 1996).

Though many of these more innovative techniques have shown promising results, it is always necessary to consider the kinetics of remediation tools and
respond to unique site conditions. The employed processes can be very slow in many situations. For example, the aqueous solubility of PAHs in tars is so low that hundreds of years would be necessary for total tar removal by most pump-and-treat processes, leading to reports that in situ water flushing of manufactured gas plant tars is impractical (Mackay and Cherry, 1989). Biological treatment may also be too time consuming and ineffective. Hence, the addition of water-miscible polar solvents and surfactants to enhance the solubility and mobility of tar components has been studied (Luthy et al., 1994).

There are a number of approaches in use and under investigation. Not all of them have been reported here and this discussion is meant only to introduce the challenges and techniques linked to tar remediation. The important message is that remediation techniques are grounded in the fundamental chemical and physical characteristics of the contamination. Properties such as reactivity, solubility, and vapor pressure must be well understood in order to properly and effectively remediate these contaminated sites or assess potential long-term risk.
Chapter 2. Background

This chapter will focus entirely on theories developed and reported by others. Its purpose is to set the stage for the experiments, results, and discussions of the subsequent four chapters. The choice of material covered here was based on relevancy to this thesis work.

Sections 2.1 – 2.20 closely follow the work of Smith and coworkers (1987; 2001), and though definitions are always given, the nomenclature used here is nearly analogous to that used in their work. The development of solid-liquid equilibrium and solubility relationships in sections 2.21 and 2.22 is based on similar discussion in thermodynamic textbooks authored by Kyle (1999) and Sandler (2006), respectively. Section 2.23 summarizes sorption theory given by Schwarzenbach et al. (2003). Lastly, the detailed development of Knudsen effusion theory in section 2.24 is grounded in the work of Knudsen himself (1934), and has also been summarized by other workers in this laboratory (Oja and Suuberg 1997; Goldfarb, 2008)

2.1 Internal Energy and The First Law of Thermodynamics

Internal energy is a property from which all thermodynamic theory flows. The scientific study of the field began with (among others) the nineteenth century experiments of James P. Joule who showed that heat is a form of energy, which is quantitatively dependent on work. Joule’s fundamental experiments showed that a
system’s temperature increases when work is done on the working fluid. He also observed that contact with a colder fluid allows the working fluid to cool back to its original temperature. These experiments showed that energy is transferred to a fluid through work and that this energy can be dissipated as heat, i.e., thermal energy. Between absorption and rejection, this energy is stored or contained in the fluid as **internal energy**.

Internal energy is neither work nor heat. Furthermore, energy associated with finite-scale system position (potential energy) or movement (kinetic energy) is not considered to be internal energy. Rather, internal energy is the energy contained in the molecules of the working fluid.

On a microscopic level, molecules internal to a substance have kinetic energy of translation, of rotation, and of internal vibration among others not typically considered in classical thermodynamic analysis (e.g., nuclear). Moreover, intermolecular forces give rise to molecular potential energy. This molecular energy increases with work (if done on a system) and thermal energy (heat into a system), thus increasing the internal energy of the substance.

Thus, internal energy quantitatively defines the energy of a substance on the molecular level, from the larger-scale, macroscopic energies associated with position and movement. This definition includes many modes of energy storage, leading to difficulty in assigning a definite zero point of energy. In other words, there exists no absolute “internal-energy scale” and internal energy is characterized as a thermodynamic primitive in which only changes in level can be characterized.
Absolute values of internal energy cannot be measured or used. Fortunately, thermodynamic analysis only requires that changes in internal energy be known.

The concepts above are the basis for the first law of thermodynamics, which states that energy can be transferred from one form to another, but can never be created or destroyed. This statement of energy conservation demonstrates that total energy of the universe is constant, exists in many forms, and is constantly transformed from one form into another.

Thermodynamic analyses usually require definition of a system and of the surrounding environment. With this in mind, the first law can be expressed by,

$$\Delta E_{\text{system}} + \Delta E_{\text{surroundings}} = 0$$

where $E$ is a broad summation of system energetics.

**Closed systems** are those in which material does not cross the system/surroundings boundary. They do no vary in mass, and thus, internal energy cannot be transported across system borders. Energy exchange can only occur by transfer of heat $Q$ and/or work $W$ to/from the surroundings. This is expressed mathematically by a new expression of the first law:

$$\Delta E_{\text{system}} = Q + W$$

It is worth noting that heat and work always refer to the system and modern thermodynamic sign convention describes transfer into a system as positive.
Eq 2.1.2 can be modified slightly by considering that kinetic and potential energies are never transported to or from closed systems. As a result, total system internal energy $U'$ replaces the broad energy term $E$ of eq 2.1.2:

$$\Delta U' = Q + W \tag{2.1.3}$$

Furthermore, a classical form of the first law can expresses differential changes in internal energy. This is given by

$$dU' = dQ + dW \tag{2.1.4}$$

Here, all properties refer to the entire system. Eq 2.1.4 is the common way to quantitatively express the first law. The differential of internal energy is an exact differential, whereas those for heat and work are inexact, implying path-dependence.

A number of thermodynamic properties are being expressed in these introductory sections and it is important to recognize that these parameters are categorized as either extensive or intensive. Extensive properties such at volume and internal energy depend on the amount of material in a system. Conversely, intensive properties have no dependence on quantity of matter. These include temperature and pressure.

It is oftentimes helpful to think about extensive properties on a molar level, effectively eliminating their dependence on quantity. So from this point forward, any given extensive property $M'$, can be expressed per unit mole by a corresponding
variable $M$. These plain symbols are intensive properties, but can be related back to their corresponding extensive properties by,

$$M' = nM \quad (2.1.5)$$

This gives way to the following expression of eq 2.1.4:

$$d(nU) = dQ + dW \quad (2.1.6)$$

Eq 2.1.6 is important because it relates changes in internal energy, an immeasurable and indefinable property, of a closed system, not in motion, to measurable quantities.

### 2.2 Enthalpy

Differential changes in work of a mechanically reversible closed system depend on pressure and volume and are given by.

$$dW = -Pd(nV) \quad (2.2.1)$$

So, for a constant pressure process, the first law can be rewritten:

$$dQ = d(nU) + Pd(nV) = d[n(U + PV)] \quad (2.2.2)$$

The group $U+PV$ is defined as enthalpy, $H$. Consequently,

$$H = U + PV \quad (2.2.3)$$
So for closed, mechanically reversible, constant-pressure processes, the differential heat transfer is analogous to the differential enthalpy change:

\[ dQ = d(nH) \]  

(2.2.4)

2.3 Equations of State

State variables are a set of thermodynamic parameters that are specified for a given system. The position of such a system is defined by its state variables. Examples include temperature, pressure, and volume. If a system is to return to its original condition, all state variables must be restored to their initial conditions.

This suggests that relationships, i.e., **equations of state** (EOS), can be formed to connect state variables of a given system. Examples include the Van der Waals, virial, and ideal gas equations of state. EOSs are the foundation of the next section, which describes and defines an ideal gas.

2.4 The Ideal Gas

Molecules in real gases interact on the molecular level and, consequently, they can exert forces upon one another, but an **ideal gas is one in which such molecular interactions do not exist.**
Reducing system pressure, thereby increasing the molecular mean free paths (sec 2.24) within a closed space, reduces molecular interactions of gas phase molecules.

Theoretically, a perfectly ideal gas exists only when system pressure approaches zero. In the limiting case where \( P \to 0 \), it has been experimentally observed and theoretically established that the relevant EOS is

\[
PV = RT
\]  

(2.4.1)

The internal energy and the enthalpy of an ideal gas are solely dependent on temperature and not at all on pressure. Generally, internal energies vary with both temperature and pressure \( U = U(T, P) \). This dependence on pressure is a consequence of molecular interaction and thus, is negligible in situations involving ideal gases. So, the internal energy of an ideal gas depends only on temperature \( U^\text{ig} = U^\text{ig}(T) \) and it follows that,

\[
H = U(T, P) + PV
\]

(2.4.2)

\[
H^\text{ig} = U^\text{ig}(T) + RT = H^\text{ig}(T)
\]

(2.4.3)

2.5 Equilibrium Vapor Pressure and Partial Pressure

Chemicals in condensed phases, i.e., liquids and solids, have a propensity to vaporize (and also to recondense) until the conditions of equilibrium are satisfied. Therefore, closed systems will equilibrate with some quantity of evaporated or
sublimed material in the vapor headspace, and these gas-phase molecules will induce a certain pressure in the system (from the kinetic theory of gases). This pressure is known as the \textit{equilibrium vapor pressure} and is specific to each pure compound or mixture thereof. Vapor pressure is a fundamental property because it governs transport into the gas phase, and thus, is significant whenever the propensity of a material to exist as a vapor is important.

Liquids and solids that evaporate quickly have a relatively high vapor pressure and are termed “volatile.” Conversely, compounds with lower evaporative tendencies are known as semi- or non-volatile. High vapor pressure substances include light organics such as benzene, toluene, ethylbenzene, and xylene (BTEX). Higher molecular weight organics, e.g., polycyclic aromatics hydrocarbons, are not nearly as volatile. In fact, PAHs are categorized at semi-volatile organic compounds, based on their low vapor pressure.

The vapor pressure of any material is a strong function of temperature. The details of this association will be discussed later, but it important to note here that vapor pressure increases (non-linearly) with temperature. At ambient conditions, evaporation generally occurs from the surface of the condensed phase and the equilibrium vapor pressure of the liquid does not exceed ambient pressure. For example, water molecules at room temperature evaporate from the surface of the liquid. In cases where the equilibrium vapor pressure exceeds ambient pressure (usually at very high temperatures), the liquid will boil because gas molecules are able to displace the surrounding liquid.
Now consider an equilibrated, multiple-phase, multi-component, closed system. All condensed species will evaporate and coexist as a mixture in the vapor phase. The pressure of each independently acting vapor species $P_i$ is known as that component’s **partial pressure**. This can be described mathematically using the ideal gas law. For $n$ moles of an ideal gas, the total system pressure is given by:

$$P = \frac{nRT}{V_{\text{total}}} \quad (2.5.1)$$

Given that each species present in the mixture occupies the same total volume, partial pressure can be described as follows.

$$P_i = \frac{n_iRT}{V_{\text{total}}} \quad (2.5.2)$$

Since each independently acting gas contributes to the total pressure,

$$P = \sum_i P_i \quad (2.5.3)$$

and the fractional contribution of each gas is $P_i/P = n_i/n$, and $n_i/n = y_i$, the vapor phase mole fraction. Hence,

$$P_i = y_iP \quad (2.5.4)$$
2.6 Entropy and The Second Law of Thermodynamics

The first law of thermodynamics is a statement of energy conservation and transport. It is limited because it gives no guidance on the direction of energy transport processes. Nonetheless, there exists a preferential direction for energy transfer and the second law of thermodynamics gives definition to this observation.

To begin with, experience demonstrates that heat is transferred through matter from hot sources to colder sinks. These processes never occur in reverse. Furthermore, Joule’s experiments and others showed that work can easily be converted into other forms of energy, such as potential, kinetic, thermal, and electric. On the other hand, transfer of heat to other forms of energy, e.g., work, is quite difficult.

**Entropy** $S$, a new thermodynamic property, is born from these considerations, and differential changes in total entropy are given by,

$$dS' = \frac{dQ_{rev}}{T}$$  \hspace{1cm} (2.6.1)

where

$$\Delta S' \geq 0$$  \hspace{1cm} (2.6.2)

It should be clear that no finite definition of entropy exists and eq 2.6.1 is used only to correlate entropy to measurable properties.
The significance of the second law and the derivation/characterization of entropy, is that processes always move in a direction of higher total entropy, thereby satisfying eq 2.6.2. In a sense, total entropy is a measure of disorder that gives directionality to thermodynamic processes.

2.7 Gibbs Free Energy

The first law for a reversible process can be written as,

\[ d(nU) = dQ_{\text{rev}} + dW_{\text{rev}} \]  \hspace{1cm} (2.7.1)

Substitution of eq 2.2.1 and the definition of entropy (eq 2.6.1) yields the combined first and second laws, which contains only properties (state functions):

\[ d(nU) = Td(nS) - Pd(nV) \]  \hspace{1cm} (2.7.2)

The Helmholtz energy \( A \) is given by

\[ A \equiv U - TS \] \hspace{1cm} (2.7.3)

and the Gibbs free energy \( G \) is defined by

\[ G \equiv H - TS \] \hspace{1cm} (2.7.4)

The fundamental property relations similar to eq 2.7.2, with reference to these thermodynamic functions are.

\[ dU = TdS - PdV \] \hspace{1cm} (2.7.5)
\[ dH = TdS + VdT \] \hspace{1cm} (2.7.6)

\[ dA = -PdV - SdT \] \hspace{1cm} (2.7.7)

\[ dG = VdT - SdT \] \hspace{1cm} (2.7.8)

Systems at constant temperature and pressure drive towards minimum Gibbs free energy during equilibration, and this is equivalent to maximizing their total entropy under conditions of constant temperature and pressure.

The total Gibbs free energy of any closed system can be related to temperature and pressure by

\[ d(nG) = (nV)dP - (nS)dT \] \hspace{1cm} (2.7.9)

When a closed system is nonreactive and is comprised of only a single-phase, its composition is constant, and the following partial derivatives characterize the change in Gibbs function with pressure or temperature.

\[ \left[ \frac{\partial(nG)}{\partial P} \right]_{T,n} = nV \quad \text{and} \quad \left[ \frac{\partial(nG)}{\partial T} \right]_{P,n} = -nS \] \hspace{1cm} (2.7.10)

### 2.8 Gibbs Free Energy and Phase Equilibria

Eq 2.7.9 describes the total Gibbs free energy of any closed system. Consider now that spontaneous vaporization and condensation occur within a closed, multi-phase system. These differential phase changes can be described by integration of eq 2.7.9 from one phase \( \alpha \) to the next \( \beta \). For a closed system at constant
temperature, pressure, and mole number \( n \), \( dG = 0 \), and thus, for two phases in equilibrium,

\[
G^\alpha = G^\beta
\]  
(2.8.1)

This result implies that the molar Gibbs free energy of each phase is equivalent.

### 2.9 Multicomponent Systems

Consider now the composition change of a single-phase, open system that can exchange chemical species (of the same phase) with its surroundings. In this case, the Gibbs free energy is related not only to temperature and pressure, but also to the composition: \( nG = nG(P,T,n_1,n_2,...) \). The total differential describing the Gibbs function (eq 2.7.9) then becomes,

\[
d(nG) = \left[ \frac{\partial(nG)}{\partial P} \right]_{T,n} dP + \left[ \frac{\partial(nG)}{\partial T} \right]_{P,n} dT + \sum_i \left[ \frac{\partial(nG)}{\partial n_i} \right]_{P,T,n} dn_i
\]  
(2.9.1)

All mole numbers are held constant in the third partial derivative, apart from the species \( i \). This derivative is known as the **chemical potential**, \( \mu \) of species \( i \) where

\[
\mu_i = \left[ \frac{\partial(nG)}{\partial n_i} \right]_{P,T,n}
\]  
(2.9.2)

Eq 2.9.1 can then be rewritten

\[
d(nG) = (nV)dP - (nS)dT + \sum_i \mu_i dn_i
\]  
(2.9.3)
Eq 2.9.3 is the **fundamental property relation for a multicomponent system**.

Written in terms of intensive variables alone, the fundamental property relation is

\[
dG = VdP - SdT + \sum_i \mu_i dx_i
\]

(2.9.4)

### 2.10 Chemical Potential and Phase Equilibria

Now consider an equilibrated, multiple-phase, closed system. Although several phases may exist, the following discussion is simplified by reducing the number of phases to just two, e.g., here a liquid and a vapor phase. Analogous descriptions are valid for systems of any number of phases.

Envision that each phase in the closed system is its own separate open system. In other words, each phase can exchange chemical species with the surrounding phases, but all phases are contained inside one, larger closed system. Under these conditions, the fundamental property relation can be written separately for each phase where superscripts \( l \) and \( v \) denote liquid and vapor phases, respectively:

\[
d(nG)^l = (nV)^l dP - (nS)^l dT + \sum_i \mu_i^n dx_i
\]

(2.10.1)

\[
d(nG)^v = (nV)^v dP - (nS)^v dT + \sum_i \mu_i^n dx_i
\]

(2.10.2)

Since the total change in Gibbs free energy is the summation of the individual phase \( \Delta G \)'s, eqs 2.10.1 and 2.10.2 may be combined:
\[ d(nG) = (nV)dp - (nS)dT + \sum_i \mu_i^l dn_i^l + \sum_i \mu_i^v dn_i^v \]  \hspace{1cm} (2.10.3)

And since the system under consideration is closed, the constraint on total Gibbs free energy given by eq 2.7.9 is applicable. When combined, eqs 2.7.9 and 2.10.3 give

\[ 0 = \sum_i \mu_i^l dn_i^l + \sum_i \mu_i^v dn_i^v \]  \hspace{1cm} (2.10.4)

The derivative terms of eq 2.10.4 describe the constraints on mass transfer of species between phases. By continuity \(-dn_i^l = dn_i^v\), so equation 2.10.4 can be rewritten:

\[ 0 = \sum_i (\mu_i^l - \mu_i^v)dn_i^l \]  \hspace{1cm} (2.10.5)

Given that \(dn_i^l\) is arbitrary and not necessarily zero, the term within the parentheses (of eq 2.10.5) must be zero. This leads to the fundamental requirement of solution thermodynamics, which states that the **chemical potential of each equilibrated species must be identical in all phases**. This is expressed symbolically as,

\[ \mu_i^l = \mu_i^v \quad (i = 1, 2, ..., N) \]  \hspace{1cm} (2.10.6)

Hence the earlier result for a pure, single component system is here generalized to a multicomponent system.

Derivation of eq 2.10.6 was based on the assumption of a two-phase, vapor/liquid system. However, as discussed above, this work can be generalized for all phases as follows:
\[ \mu_i^G = \mu_i^\beta = \ldots = \mu_i^\zeta \quad (i = 1, 2, \ldots, N) \quad (2.10.7) \]

2.11 Chemical Potential of an Ideal Gas

The Gibbs free energy of an ideal gas and the corresponding partial molar Gibbs energy may be written:

\[ G_{ig} = H_{ig} - T S_{ig} \quad \& \quad \mu_i^{ig} = \mu_i^{ig} = H_i^{ig} - T S_i^{ig} \quad (2.11.1) \]

Modification of these equations into a more practical form requires further exploitation of the enthalpy and entropy of ideal gases.

Bear in mind that, in cases of ideal-gas mixtures, the partial molar properties, excluding volume, of each species are equivalent to the corresponding molar properties at the mixture \( T \) and \( P \). Here, \( T \) is the system temperature and \( P \) is the partial pressure of component \( i \) in the mixture. This can be described algebraically for enthalpy and entropy as follows:

\[ \overline{H}_i^{ig} (T, P) = H_i^{ig} (T, P) \quad (2.11.2) \]

\[ \overline{S}_i^{ig} (T, P) = S_i^{ig} (T, P) \quad (2.11.3) \]

Since the enthalpy of an ideal gas does not depend on system pressure by eq. 2.4.3, the dependence on partial pressure is trivial and,

\[ H_i^{ig} (T, P) = H_i^{ig} (T, P) \quad (2.11.4) \]
Moreover, because the molecular species in an ideal gas do not energetically interact, the enthalpy of an ideal gas may be written as a weighted summation of pure species enthalpies:

\[ H_{ig} = \sum_i y_i H_{ig} \]  

(2.11.5)

Unlike enthalpy, the entropy of an ideal gas does depend upon pressure. Rearrangement of eq 2.7.2 for a molar quantity of vapor gives

\[ dS = \frac{dU}{T} + \frac{PdV}{T} \]  

(2.11.6)

and differentiation of eq 2.4.2 shows that

\[ dH = dU + PdV + VdP \]  

(2.11.7)

When the previous two equations are rearranged and combined, it becomes clear that

\[ dS = \frac{dH}{T} - \frac{VdP}{T} \]  

(2.11.8)

The enthalpy of an ideal gas as a function of heat capacity \( C_P \) is defined as.

\[ dH = C_P^{ig} dT \]  

(2.11.9)

Substitution of eq 2.11.9 and the ideal gas EOS into eq 2.11.8 produces a relationship for the differential entropy change of an ideal gas system:

\[ dS = \frac{C_P^{ig}}{T} dT - \frac{R}{P} dP \]  

(2.11.10)
So, for a given species $i$ at constant temperature,

\[ dS^\text{ig}_i = -R \frac{dP}{P} = -R \ln P \]  

(2.11.11)

and subsequent integration from $P_i$ to $P$ gives,

\[ S^\text{ig}_i(T, P) - S^\text{ig}_i(T, P_i) = -R \ln \frac{P}{P_i} = -R \ln \frac{P}{y_i P} = R \ln y_i \]  

(2.11.12)

or

\[ S^\text{ig}_i(T, P) = S^\text{ig}_i(T, P_i) - R \ln y_i \]  

(2.11.13)

Now consider and apply eq 2.11.3 to the previous relationship to produce a definition of the partial molar entropy of an ideal gas (at some $T$ and $P$):

\[ \overline{S}^\text{ig}_i = S^\text{ig}_i - R \ln y_i \]  

(2.11.14)

The total entropy of an ideal gas is

\[ S^\text{ig} = \sum_i y_i S^\text{ig}_i - R \sum_i y_i \ln y_i \]  

(2.11.15)

These new terms for enthalpy (eq 2.11.4) and entropy (eq 2.11.14) of species $i$ in ideal gas mixtures can be substituted into eq 2.11.1 to give the following expression:

\[ \mu^\text{ig}_i = H^\text{ig}_i - TS^\text{ig}_i + RT \ln y_i \]  

(2.11.16)
Finally, recall that $G_{i}^{ig} = H_{i}^{ig} - TS_{i}^{ig}$. Substitution into eq 2.11.16 gives the chemical potential of an ideal gas:

$$\mu_{i}^{ig} = G_{i}^{ig} + RT \ln y_{i}$$

(2.11.17)

### 2.12 Chemical Potential of an Ideal Solution

The chemical potential of an ideal solution is quite similar to that of an ideal gas. In fact, the equations describing both properties can be derived by related means. There is, however, one unique consideration that must be made concerning the possible existence of an ideal solution not only in the vapor phase, but in condensed phases as well.

**Ideal solutions consist of structurally comparable molecules that impose a net force on one another that does not depend upon composition.**

The total molar volume of an ideal gas mixture is given by the weighted sum of all pure component molar volumes as ideal gases $V_{i}^{ig}$:

$$V^{ig} = \sum_{i} y_{i} V_{i}^{ig}$$

(2.12.1)

This implies that the molar volume of each ideal gas component is unaffected by the process of mixing. In other words, the ideal gas law ($V_{i}^{ig} = RT/P$) applies to each species in the vapor phase mixture.
A liquid solution that meets the requirements of ideality follows the same rule, even if the intermolecular interactions are no longer negligible.

\[ V^{id} = \sum x_i V_i \]  

(2.12.2)

Given this (and the fact that composition of an ideal solution has no effect on molecular energetics), the enthalpy and entropy of ideal solutions can be written in terms of actual molar properties:

\[ H^{id} = \sum x_i H_i \]  

(2.12.3)

\[ S^{id} = \sum x_i S_i - R \sum x_i \ln x_i \]  

(2.12.4)

Eqs 2.12.3 and 2.12.4 can be substituted into the expression \( G^{id} = H^{id} - TS^{id} \), and subsequent differentiation according to the definition of chemical potential (eq 2.9.2) produces an expression for the chemical potential of an ideal solution:

\[ \mu_i^{id} = G_i + RT \ln x_i \]  

(2.12.5)

2.13 Raoult’s Law

In 1882 Francois-Marie Raoult developed a simple model that relates the equilibrium vapor pressure of a solution and of the components therein to the solution composition. The relationship is now commonly known as Raoult’s Law and requires that the following conditions are met:
(1) The condensed phase (i.e., the liquid mixture) is an **ideal solution**.

(2) The vapor phase is an **ideal gas**.

These assumptions imply that Raoult's law is valid only for ideal vapor/liquid equilibrium scenarios, but these conditions are widely, though by no means universally, approximated.

First consider ideal, liquid- and gas-phase solutions of \( N \) components contained in a closed system at a given temperature and pressure. The system will tend towards equilibrium, or the point at which

\[
\mu_i^v = \mu_i^l \quad (i = 1, 2, ..., N) \tag{2.10.6}
\]

The chemical potential of ideal gases and solutions can be described by the following two, previously derived equations:

\[
\mu_i^v = G_i^g + RT \ln y_i \tag{2.11.17}
\]

\[
\mu_i^l = G_i^l + RT \ln x_i \tag{2.12.5}
\]

When combined according to eq. 2.10.6,

\[
G_i^{\text{eq}}(T, P) + RT \ln y_i = G_i^l(T, P) + RT \ln x_i \tag{2.13.1}
\]

Here, the Gibbs free energies are dependent on system temperature and total pressure. It is desirable to show dependence instead on temperature and equilibrium vapor pressure of species \( i \).
The effect of pressure on the Gibbs free energy of the condensed phase is considered to be negligible (i.e., the Poynting correction is negligible) and,

\[ G_i^l(T,P) = G_i^l(T,P_{i\text{sat}}) \]  

(2.13.2)

Then, for each species in the constant temperature, ideal gas mixture,

\[ dG_i^{ig} = V_i^{ig} dP - S_i^{ig} dT = \frac{RT}{P} dP \]  

(2.13.3)

Upon integration from \( P \) to \( P_{i\text{sat}} \),

\[ G_i^{ig}(T,P_{i\text{sat}}) - G_i^{ig}(T,P) = \int_P^{P_{i\text{sat}}} \frac{RT}{P} dP = RT \ln \frac{P_{i\text{sat}}}{P} \]  

(2.13.4)

Combination of eqs 2.13.1 and 2.13.4 gives,

\[ RT \ln \frac{y_i}{x_i} = G_i^l(T,P_{i\text{sat}}) - G_i^{ig}(T,P_{i\text{sat}}) + RT \ln \frac{P_{i\text{sat}}}{P} \]  

(2.13.5)

It is understood that at the equilibrium vapor pressure (\( P_{i\text{sat}} \)), the Gibbs free energies of liquid-\( i \) and vapor-\( i \) are equivalent. So \( G_i^l(T,P_{i\text{sat}}) - G_i^{ig}(T,P_{i\text{sat}}) = 0 \) and eq 2.13.5 reduces to Raoult’s law (eq 2.13.7).

\[ RT \ln \frac{y_i}{x_i} = RT \ln \frac{P_{i\text{sat}}}{P} \]  

(2.13.6)

\[ y_i P = x_i P_{i\text{sat}} \]  

(2.13.7)
Raoult’s law is a simple and useful equation that relates system pressure and vapor composition to solution composition where $P_{i}^{sat}$ is the equilibrium vapor pressure of each pure species. The left hand side of eq 2.13.7 represents the partial pressure of species $i$ above the solution. Furthermore, the total system pressure is the sum of partial pressures, and hence:

$$P = \sum_{i}^{N} x_i P_{i}^{sat}$$

(2.13.8)

### 2.14 The Clapeyron Equation

Apart from the chemical potential and temperature, which are equal across phase boundaries, most thermodynamic properties of equilibrated species vary significantly from one phase to another. For example, the molar internal energy, entropy, enthalpy, and volume of a species in the liquid phase are all very different from those of the same species in the vapor phase.

Benoit Paul Emile Clapeyron took advantage of the equality of chemical potential and used it to derive an expression for the slope of the pressure/temperature coexistence curve of any single component, multi-phase system. The $P/T$ coexistence curve is the line that separates two phases on a $P/T$ diagram. It is significant because it represents the equilibrium coexistence, or “saturation”, of two phases.
Consider a closed system whose temperature and pressure are adjusted in such a way that the system always remains at equilibrium. Another way to envision this is to imagine that the system equilibrates instantaneously after a modification of temperature or pressure. Eq 2.8.1 must always be satisfied under these conditions, and in order to fulfill this requirement, any differential changes in molar Gibbs free energy resulting from movement from one phase to another must also be equivalent:

\[ dG^\alpha = dG^\beta \]  \hspace{1cm} (2.14.1)

Then substitution of eq 2.7.9 gives the following expression:

\[ V^\alpha dP^\text{sat} - S^\alpha dT = V^\beta dP^\text{sat} - S^\beta dT \]  \hspace{1cm} (2.14.2)

Algebraic rearrangement yields,

\[ \frac{dP^\text{sat}}{dT} = \frac{S^\beta - S^\alpha}{V^\beta - V^\alpha} = \frac{\Delta S^\alpha\beta}{\Delta V^\alpha\beta} \]  \hspace{1cm} (2.14.3)

where the \( \Delta S \) and \( \Delta V \) terms represent differential changes in the respective molar properties and the superscript \( \alpha\beta \) denotes a phase change from \( \alpha \) to \( \beta \).

Consider now that because at equilibrium \( \Delta G^{\alpha\beta} = 0 = \Delta H^{\alpha\beta} - T\Delta S^{\alpha\beta} \), then

\[ \Delta H^{\alpha\beta} = T\Delta S^{\alpha\beta} \]  \hspace{1cm} (2.14.4)

or

\[ \Delta S^{\alpha\beta} = \frac{\Delta H^{\alpha\beta}}{T} \]  \hspace{1cm} (2.14.5)
Substitution of eq 2.14.5 into 2.14.2 gives a fundamental relationship:

$$\frac{dP_{sat}}{dT} = \frac{\Delta H^{\alpha\beta}}{T\Delta V^{\alpha\beta}}$$  \hspace{1cm} (2.14.6)

Eq 2.14.6 is the **Clapeyron equation** expressing the temperature dependence of vapor pressure in terms of changes in state variables upon phase change. The changes in enthalpy and volume are not necessarily constant and may vary with temperature, leading to potentially complicated integration.

The Clapeyron equation is the basis of most equilibrium vapor pressure prediction and calculation. It is quite general and, consequently, can be applied to a variety of situations with varied equilibrium conditions. Its level of complexity depends on the situation at hand and on permissible assumptions.

### 2.15 The Clausius-Clapeyron Equation

Integrated forms of the Clapeyron equation are used in a variety of circumstances. The purpose of this section is to consider common integrations of the Clapeyron equation. The process will lead to the development of the Clausius-Clapeyron equation.

**Case 1** - In systems for which both $\Delta H^{\alpha\beta}(T)$ and $\Delta V^{\alpha\beta}(T)$ vary with temperature, the species-specific enthalpy of phase transition is often described by a polynomial expression of the following form:
\[ \Delta H(T) = \Delta aT + \frac{\Delta bT^2}{2} - \frac{\Delta c}{T} + \Delta d \]  

(2.15.1)

These polynomials and their respective constants (i.e., \(a\), \(b\), \(c\), and \(d\)) arise from heat capacities that vary with temperature. The constants must be experimentally determined and are tabulated for many substances. The details are not pertinent to the discussion at hand, but are readily available in most thermodynamic reference books.

The complexity of case 1 is exacerbated by temperature- and pressure-dependent molar volume changes \(\Delta V^{\text{eqi}}\), generally associated with system pressures that exceed 10 atm. It is necessary in these cases to develop or obtain an expression for \(\Delta V^{\text{eqi}} = f(T, P)\) using coefficients of thermal expansion and isothermal compressibility. Once developed, the expressions are substituted into the Clapeyron equation, resulting in potentially complicated integrations. The details are system-specific and thus, will not be described further. Rather, we will make use of reasonable approximations to develop more widely applicable expressions.

**Case 2** – Complexity is reduced for systems consisting of a condensed phase (either a liquid or a solid) in equilibrium with an ideal vapor. The following approximation can often be used for such cases:

\[ V^g - V^{l,s} = V^g = \frac{nRT}{P} \]  

(2.15.2)

Here, the molar volume of the gas is often orders of magnitude greater than that of the condensed phase and the contribution of the latter to \(\Delta V\) becomes negligible.
Substitution of eq 2.15.2 into the Clapeyron equation affects only the denominator (of eq 2.14.6). The latent heat of vaporization may still vary with temperature (eq 2.15.1). Thus,

$$\frac{dP_{\text{sat}}}{dT} = \frac{\Delta H_{lv}^\text{v}(T)}{RT^2/P_{\text{sat}}}$$  \hspace{1cm} (2.15.3)

**Case 3** – Now consider the system of case 2, but assume that $\Delta H_{\alpha\beta}^\text{v} \neq f(T)$. In other words, the latent heat of vaporization is constant in the temperature range of interest such that the expression may be rewritten with a right hand side term that is a constant:

$$\frac{dP_{\text{sat}}/P_{\text{sat}}}{dT/T^2} = \frac{\Delta H_{lv}^\text{v}}{R}$$  \hspace{1cm} (2.15.4)

This is more commonly rewritten recognizing $d\left(\frac{1}{T}\right) = -\frac{1}{T^2} dT$ and $d\ln P = \frac{dP}{P}$. Thus,

$$\Delta_{\text{vap}} H = -R \frac{d\ln P_{\text{sat}}}{d(1/T)}$$  \hspace{1cm} (2.15.5)

This expression is commonly known as the **Clausius-Clapeyron equation**. It is an approximation that relates the latent heat of vaporization to the slope of the vapor pressure curve. Plotting vapor pressure as $\ln P$ vs. $1/T$, makes apparent that the enthalpy of vaporization is proportional to the slope of that curve. Note that since the $\Delta H$ and $\Delta V$ were expressed in the direction of vaporization, and since the enthalpy of the vapor state is greater than that of the condensed state, the above requires that vapor pressure increase with temperature.
This derivation has been carried out for vaporization (l to v) processes, but equally holds true for sublimation (s to v):

\[ \Delta_{\text{sub}}H = -R \frac{d \ln P^{\text{sat}}}{d(1/T)} \]  

(2.15.6)

The most widely used integrated form of the Clausius-Clapeyron equation is reliant on the assumption that latent heat is relatively independent of temperature. This is rarely true for real systems. In fact, \( \Delta H^{\text{al}}(T) \) decreases with increasing temperature and becomes zero at the critical point. Hence, the integrated form of the Clausius-Clapeyron equation shown below should only be applied for low-pressure systems (because of the assumption of ideal vapor and \( \Delta V = V^g \)) and over a narrow range of temperature (for which enthalpy of vaporization is about constant).

Indefinite integration of the Clausius-Clapeyron equation yields

\[ \ln P = \frac{\Delta_{\text{vap}}H}{RT} + C \]  

(2.15.7)

The constant of integration \( C \) will be discussed in the next section. Integration between defined states 1 and 2 gives

\[ \ln \frac{P_2}{P_1} = -\frac{\Delta_{\text{vap}}H}{R} \left( \frac{1}{T_2} - \frac{1}{T_1} \right) \]  

(2.15.8)
Case 4 – When both phases are condensed and $\Delta S^{\alpha \beta}, \Delta H^{\alpha \beta}, \Delta V^{\alpha \beta} \neq f(T)$, integration of the Clapeyron equation leads to the following expression. For coexisting condensed phases,

$$\frac{P - P_o}{T - T_o} = \frac{\Delta H^{\alpha \beta}}{T_o \Delta V^{\alpha \beta}}$$

(2.15.9)

The assumption of temperature independence of properties is again somewhat restrictive.

2.16 Entropy and the Clausius-Clapeyron Equation

The vapor pressure curve on a Clausius-Clapeyron plot is a straight line with an intercept of constant value. It may be immediately recognized that the integrated form (eq 2.15.7) requires the constant $C$ to have a special form that makes the equation dimensionally homogeneous (i.e., the vapor pressure has units, and the value of $C$ will depend upon that choice). Suppose we define a reference state at a temperature $T_1$, yielding a vapor pressure $P_1$. Then

$$\ln P_1 = -\frac{\Delta_{vap}H}{RT_1} + C$$

(2.16.1)

Now, use the fact that at equilibrium $\Delta_{vap}G = \Delta_{vap}H - T\Delta_{vap}S = 0$ such that

$$\ln P_1 = -\frac{\Delta_{vap}S}{R} + C$$

(2.16.2)
This immediately shows the nature of $C$ to be a measure of entropy of vaporization at some reference condition. Substituting this into eq 2.15.7 gives

$$\ln\left(\frac{P}{P_1}\right) = -\frac{\Delta_{\text{vap}} H}{RT} + \frac{\Delta_{\text{vap}} S}{R}$$

(2.16.3)

Thus, we can see the influence of enthalpy of vaporization – all else equal, the higher the required enthalpy, the lower the vapor pressure. By the same token, the higher the entropy increase, the greater the vapor pressure.

It is worth noting in passing that if $P_1$ is chosen as the normal boiling point, then

$$\frac{\Delta_{\text{vap}} H}{T_1} = \frac{\Delta_{\text{vap}} H}{T_{\text{BP}}} = \Delta_{\text{vap}} S$$

(2.16.4)

For a great many compounds, $\Delta_{\text{vap}} S = 88$ Jmol$^{-1}$K$^{-1}$, or $\frac{\Delta_{\text{vap}} S}{R} = 10.63$, which is the noted “Trouton’s Rule.” This approximation holds well for small, non-polar species, but does not hold for larger or more polar compounds. Empirical approximations have been proposed by Riedel (1954) and Watson (1943) that involve corrections using critical parameters, but discussion of this is beyond the scope of this thesis.
2.17 The Antoine Equation

The Clausius-Clapeyron equation is extremely powerful because it can be used to calculate latent heat and entropies of vaporization given vapor pressure data. The Clausius-Clapeyron equation can be rewritten in the following form:

\[
\ln P_{\text{sat}} = A - \frac{B}{T} \tag{2.17.1}
\]

where \( A \) and \( B \) are species-specific constants as already discussed. This equation provides a fair approximation of vapor pressure over the entire temperature range, from the triple point to the critical point, and interpolation between points is possible.

The Antoine equation (eq 2.17.2) is an empirical modification of eqs 2.16.3 and 2.17.1. It is widely used because it better captures the temperature dependence of vapor pressure, bearing in mind that eq 2.17.1 was subject to a restrictive assumption regarding the constancy of \( \Delta v_{\text{ap}}H \).

\[
\ln P_{\text{sat}} = A - \frac{B}{T + C} \tag{2.17.2}
\]

Antoine equation parameters are determined experimentally. They have been tabulated for a wide variety of substances, making this model one of the easier and more widely used approaches to vapor pressure correlation. Furthermore, the Antoine equation can be more precise than eq 2.17.1 because often constants are available for relatively well-defined temperature intervals.
This and the previous three sections should provide a basis for vapor pressure correlation with varying degrees of complexity and assumption. These forms continue to be powerful tools for calculation and experimental design related to energetics of phase transitions and to vapor pressure prediction.

2.18 Azeotropy

Thus far, the main emphasis has been on various idealized systems. Raoult's law is derived from ideal gas and ideal solution theory. Furthermore, the integrated Clausius-Clapeyron equation follows from ideal gas and constant enthalpy assumptions. Ideal theory serves as an essential baseline for all thermodynamic analysis, but deviations from ideality are quite common. These deviations will be briefly covered here and in sections 2.19 and 2.20, and they are covered in greater detail in any number of classical thermodynamic reference texts.

Non-ideality in the form of azeotropy is encountered and extensively discussed in this dissertation. An azeotrope is a mixture vaporizing at constant composition. Ideal theory, i.e. Raoults law, states that condensed-phase mixtures will evaporate according to a weighted average of pure component vapor pressures. So as an ideal mixture evaporates, it will become enriched in its less volatile components. In the case of azeotropy, mixtures reach a composition at which they evaporate at constant molar ratio. Therefore, the mixture composition does not change during evaporation and vapor pressure above the mixture is held constant.
This is most often encountered in cases of strong molecular interaction. It is most often seen in liquid-vapor equilibrium systems, but the experiments of this study report azeotropy in solid-vapor systems, which has not otherwise been reported.

2.19 The Activity Coefficient

Recall that Raoult’s law, given by eq 2.13.7,

\[ y_i P = x_i P_i^{sat} \]  \hspace{1cm} (2.13.7)

assumes that the given condensed phase is an ideal solution. Oftentimes, this is not the case for real situations where, at low to moderate pressures, non-ideal molecular interaction exists between molecules of the liquid or solid phases.

This deviation from ideal behavior is accounted by the following modification of Raoult’s law:

\[ y_i P = x_i \gamma_i P_i^{sat} \]  \hspace{1cm} (2.19.1)

The new term \( \gamma_i \) is called the activity coefficient. Of course, an activity coefficient of unity implies that a given solution is ideal (eq 2.19.1 reduces to Raoult’s law), while positive and negative deviations from \( \gamma_i = 1 \) infer the existence of non-ideal condensed phase molecular interaction. The absolute magnitude of deviation is related to the degree of non-ideality of molecular interactions. Activity coefficients
differing from unity can significantly affect the partial pressure of a given species \( i \) above a mixture.

It is worth mentioning that activity coefficients are largely defined via experimental analysis. Though predictive models exist, the values are normally established experimentally. Activity coefficients are widely reported in thermodynamic texts and peer reviewed literature.

### 2.20 Fugacity and The Fugacity Coefficient

Section 2.10 outlined the fundamental criteria for thermodynamic equilibrium and eq 2.10.7 implied that the chemical potentials of a given substance must be equivalent in all phases present at equilibrium. Though this is a significant result, chemical potential, like molar Gibbs energy, is described by two indefinite primitives, internal energy and entropy. As a result, no absolute values of \( \mu_i \) exist. The chemical potential of an ideal gas is given by,

\[
\mu_{ig}^i = \mu_i^o(T) + RT \ln P
\]

or

\[
G_{ig}^i = RT \ln P + \mu_i^o(T)
\]

reminding us of the equivalence of chemical potential and molar Gibbs free energy for an ideal gas. The latter relationship is only valid for pure species \( i \) in the ideal gas state. Therefore, to correct eq 2.20.1 for the real gas state, fugacity \( f_i \) is introduced
upon replacement of $P$ by an empirical corrected pressure parameter. Fugacity $f_i$ has units of pressure. Consequently, the Gibbs energy of a real fluid is expressed by the following relationship:

$$G_i^{\text{real}} = RT \ln f_i + \mu_i^c(T)$$  \hspace{1cm} (2.20.3)

Subtraction of eq 2.20.2 from eq 2.20.3 is carried out in eq 2.20.4 and quantifies the difference in free energy between real and ideal states. This difference is termed the **residual Gibbs free energy** and is defined as follows:

$$G_i^{\text{real}} - G_i^{\text{ig}} \equiv G_i^R = RT \ln \left( \frac{f_i}{P} \right) = RT \ln \phi_i$$  \hspace{1cm} (2.20.4)

A dimensionless parameter $\phi_i$ is introduced, which is called the **fugacity coefficient** and is defined by,

$$\phi_i \equiv \frac{f_i}{P}$$  \hspace{1cm} (2.20.5)

The fugacity of an ideal gas is equal to its pressure (i.e., there is no correction needed, since one is in the ideal state):

$$f_i^{\text{ig}} = P$$  \hspace{1cm} (2.20.6)

For an ideal gas, the residual Gibbs energy is zero, the fugacity coefficient is unity, and eq 2.20.2 is recovered from eq 2.20.3. The fugacity coefficient $\phi$ is obtained from experimental P/V/T data and application of the definition of $G$ in terms of these properties:
\[
\phi = \exp \left[ \frac{1}{RT} \int_0^P \left( V - \frac{RT}{P} \right) dP \right]
\]  

(2.20.7)

Thus far, fugacity has been considered for pure species. Analogous equations can be developed for substances in solution. For example, the chemical potential of real species \( i \) in a real solution is given by

\[
\mu_i = RT \ln \hat{f}_i + \mu_i^o(T)
\]

(2.20.8)

where \( \hat{f}_i \) is the fugacity of species \( i \) in solution. Eq 2.20.8 is not limited to ideal solution theory. Rather, it applies to real mixtures of gases or liquids.

Recall now that phase equilibrium is characterized by equality of chemical potentials (eq 2.10.7) and impose this constraint on eq 2.20.8 to uncover a parallel assertion for the fugacities of species in solution. For example, the chemical potential of a system at vapor/liquid equilibrium can be written as

\[
RT \ln \hat{f}_i^L + \mu_i^o(T) = RT \ln \hat{f}_i^V + \mu_i^o(T)
\]

(2.20.9)

It follows then that

\[
\hat{f}_i^L = \hat{f}_i^V, \text{ or more generally that } \hat{f}_i^\alpha = \hat{f}_i^\beta = \ldots = \hat{f}_i^\pi
\]

(2.20.10)

This illustrates that the fugacity of any equilibrated species will be the same for all phases present in the system. This result is analogous to that stated for chemical potential, but may be more practical because absolute values of fugacity exist, or may be obtained experimentally.
Relationships and definitions similar to those of eq 2.20.4 – 2.20.6 can be developed for real solution systems. So for example, the **partial residual Gibbs energy** is given by

\[ G_i^R = RT \ln \hat{\phi}_i \]  

(2.20.11)

and the **fugacity coefficient of species i in solution** \( \hat{\phi}_i \) is given by

\[ \hat{\phi}_i = \frac{\hat{f}_i}{y_i P} \]  

(2.20.12)

Furthermore, for the special case of an ideal gas mixture, the fugacity of species i in solution is equivalent to the partial pressure of that species; a special case of the Lewis-Randall rule.

\[ \hat{f}_i^{ig} = y_i P \]  

(2.20.13)

As was the case for the pure species, an ideal gas mixture will have no partial residual Gibbs energy and the fugacity coefficient of species i in solution will be unity.

### 2.21 Solid-Liquid Equilibrium and Formation of Eutectic Phases

A significant portion of the theory described in this chapter has been used to develop relationships that describe vaporization of solids and liquids. To more fully cover the systems that will be encountered in later chapters, we now turn our focus towards solid-liquid equilibria, i.e., melting and fusion phenomena. These processes...
are often best described graphically (Figure 2.1) on constant pressure phase diagrams, which map saturation curves with respect to composition.

An example of such a plot is given in Figure 2.1 for a binary, solid-liquid system that exhibits eutectic behavior. In other words, to maintain chemical equilibrium, certain solid mixtures melt and solidify at temperatures lower than the pure phase melting temperatures (given by points A and B). The AEB curve is the liquidus line, above which only liquid exists. Point E is the eutectic point. Below the eutectic temperature, i.e., at temperatures below the CED curve, multiple solid phases exist. The CED curve is sometimes referred to as the thaw line because it represents the point at which solid phase(s) begin to melt (as temperature is increased). Liquid and solid phases coexist between the thaw and liquidus curves.

Figure 2.1. Phase diagram used to describe the solid-liquid equilibrium behavior of a binary, eutectic system. Constant pressure is implied. (Taken from Kyle, 1999)
Phase diagrams are unique to each mixture system. Figure 2.1 is presented as a general example and is not meant to describe all binary solid-liquid equilibrium behavior. Though phase diagrams are often determined experimentally (this will be shown in later chapters), it is also worthwhile to develop some general relationships to describe solid-liquid equilibrium in terms of thermodynamic theory and measurable parameters:

As described in earlier sections, the chemical potential of a given species in a closed, equilibrated system must be equal for all phases present in that system. This is valid for both single- and multi-component systems and can be expressed as follows. Superscripts $S$ and $L$ correspond to solid and liquid phases.

$$\hat{\mu}_i^S = \hat{\mu}_i^L \quad (2.21.1)$$

The chemical potential of species $i$ in a liquid mixture can be given in terms of pure species chemical potential, mole fraction, and activity coefficient, where

$$\hat{\mu}_i^L - \mu_i^L = RT \ln x_i + RT \ln \gamma_i \quad (2.21.2)$$

or

$$\hat{\mu}_i^L = \mu_i^L + RT \ln x_i \gamma_i \quad (2.21.3)$$

Analogous equations are valid for species in solid phase mixtures as well. These relationships can be combined to describe equilibrium between saturated solid and saturated liquid phases (eq 2.21.4) where $x_{is}$ and $X_{is}$ are mole fractions in the liquid
and solid phases, respectively. Similarly, $\gamma_{is}$ and $\Gamma_{is}$ are activity coefficients that correspond to respective liquid and solid phases.

\[
\mu^L_i + RT \ln x_i \gamma_{is} = \mu^S_i + RT \ln X_i \Gamma_{is} \tag{2.21.4}
\]

Eq 2.21.4 can be rearranged to describe the change in pure species chemical potential upon solidification:

\[
\mu^S_i - \mu^L_i = RT \ln \left[ \frac{x_i \gamma_{is}}{X_i \Gamma_{is}} \right] \tag{2.21.5}
\]

Evaluation of the left hand side of this relationship at temperature $T$ is assisted by considering the path of the solidification process to be defined as follows. Consider first that pure liquid $i$ exists at some temperature $T$. This liquid then cools to the melting temperature of species $i$, $T_{mi}$. The liquid then solidifies at $T_{mi}$ and this pure solid is then heated back to the original temperature $T$.

Recall that for constant pressure processes,

\[
d\mu = VdP - SdT = -SdT \ @ \ dP = 0 \tag{2.21.6}
\]

Substitution yields a new equality describing the left hand side of eq 2.21.5 in terms of entropy and temperature changes described by the pathway given above:

\[
\int_{\mu^L_i}^{\mu^S_i} d\mu = \mu^S_i - \mu^L_i = -\int_{T_{mi}}^{T} S^L_i dT + 0 - \int_{T_{mi}}^{T} S^S_i dT \tag{2.21.7}
\]

This relationship can be rewritten:
\[ \mu_i^S - \mu_i^L = \int_{T_w}^{T} (S_i^L - S_i^S) dT \]  

(2.21.8)

Substitution of eq 2.21.8 into eq 2.21.5 yields

\[ RT \ln \left( \frac{X_{is}^L \gamma_{is}}{X_{is}^S \Gamma_{is}} \right) = \int_{T_w}^{T} (S_i^L - S_i^S) dT \]  

(2.21.9)

To be practically useful, the entropy change described in eq 2.21.9 should be expressed in terms measurable parameters. Recall that

\[ \Delta S = \int \frac{dQ_{rev}}{T} \quad \text{and also that} \quad dQ_{rev} = dH = C_p dT \]

So then, the entropy terms of eq 2.21.9 can be replaced by heat capacities or, in the case of crystallization at constant \( T_{mi} \), latent heat of solidification \( L_{mi} \). Notice that each of the three terms of eq 2.21.10 describes a step in the crystallization path given above.

\[ S_i^S - S_i^L = \int_{T}^{T_{mi}} \frac{C_{pi}^L}{T} dT - \frac{L_{mi}}{T_{mi}} + \int_{T_w}^{T} \frac{C_{pi}^S}{T} dT \]  

(2.21.10)

This can be further written as:

\[ S_i^L - S_i^S = \frac{L_{mi}}{T_{mi}} + \int_{T_w}^{T} \frac{(C_{pi}^L - C_{pi}^S)}{T} dT \]  

(2.21.11)

Finally, substitution of eq 2.21.11 into eq 2.21.9 yields a general relationship that fully describes solid-liquid equilibrium phenomena.
Further analysis requires that heat capacities of liquids below their freezing points and of solids above their melting points be known. These values are rarely available, but it is reasonable to approximate that $\Delta C_p = C_p^L - C_p^S$ is independent of temperature. Implementation of this assumption and subsequent integration of eq 2.21.12 yields

$$ RT \ln \left[ \frac{x^L}{x^S} \right] = L_m (T - T_m) \left[ \frac{T}{T_m} \right] + \int_{T_m}^{T} C_p \ln \left[ \frac{T}{T_m} \right] dT $$

(2.21.13)

It follows that

$$ RT \ln \left[ \frac{x^L}{x^S} \right] = L_m (T - T_m) \left[ \frac{T}{T_m} \right] + T \Delta C_p \ln \left[ \frac{T}{T_m} \right] + \Delta C_p (T_m - T) $$

(2.21.14)

Eq 2.21.14 is a relationship describing conditions of solid-liquid equilibria in terms of only pure component properties and temperature. In cases where equilibrium exists between a liquid solution and a pure solid phase, the denominator of the left hand side of eq 2.21.4 is unity. This yields the following, simplified form of eq 2.21.14:

$$ RT \ln \left[ \frac{x^L}{x^S} \right] = \frac{L_m (T - T_m)}{T_m} + T \Delta C_p \ln \left[ \frac{T}{T_m} \right] + \Delta C_p (T_m - T) $$

(2.21.15)

Generally, the first term on the right hand side of eq 2.21.15 dominates in magnitude, so
\[
\ln[x_i, \gamma_{is}] = \frac{L_{mi}}{RT} \left( \frac{T}{T_{mi}} - 1 \right) \quad (2.21.16)
\]

If \( \gamma_{is} = 1 \), the ideal solubility of \( i \) at a temperature \( T \) is easily estimated. Of course, \( \gamma_{is} \) will often not be unity in real systems. In these more complex systems, it will be necessary to utilize empirical expressions, such as the Margules equation, to represent the \( \gamma_{is} \) and \( I_{is} \) values, e.g.

\[
\ln \gamma_{is} = \frac{A}{RT} (1 - x_i)^2 \quad (2.21.17)
\]

### 2.22 Solubility of Solids in Liquids

Though processes involving dissolution of solid solutes in liquid solvents are described by quantitative thermodynamic analysis in many reference texts, solubility phenomena are oftentimes complex and hence, difficult to describe theoretically. Description and understanding of solid to liquid solubility behavior may require a combination of general thermodynamic theory, system-specific analysis, qualitative considerations, and experimental observations. For that reason, the details of other analyses regarding dissolution of PAHs from mixtures will be described as a literature review in the introductory section of Chapter 5. Nevertheless, it is worth briefly introducing qualitative and quantitative theory available in introductory texts, and to explain why such a model might not hold true for the mixtures examined in this study.
In general, dissolution of a pure solid into a liquid can be qualitatively linked to that solid’s melting temperature and enthalpy of fusion. Since entropy is defined in relation to such properties, dissolution processes might also be correlated to a compound’s entropy of fusion. The general trend is that when other factors (e.g., intermolecular forces) are held constant, the solubilities of various pure solids decrease with increasing melting temperature. Accordingly, a higher enthalpy of fusion often indicates decreased solubility. These trends are general and do not necessarily apply to all solute-solvent systems. Nevertheless, this qualitative description is consistent with the concept that solid species with higher melting temperatures and fusion enthalpies have reached a lower energy configuration and hence, are more stable with regards to solid to liquid phase change associated with dissolution.

Binary systems consisting of one, pure solid solute and one, pure liquid solvent might be quantitatively described by the following thermodynamic relationship, the derivation of which is based on solid-liquid equilibrium theory given in section 2.21. Notice the similarity to eq 2.21.15.

\[
\ln \gamma_{2x_2} = \frac{-\Delta_{fus}H}{RT} \left(1 - \frac{T}{T_t}\right) + \frac{\Delta C_p}{R} \left(\frac{T_t - T}{T}\right) - \frac{\Delta C_p}{R} \ln \frac{T}{T_t}
\]

(2.22.1)

Here, subscript 2 refers to the solute, \(x_2\) is the equilibrium solubility (given as mole fraction), \(T_t\) is the triple point temperature, and

\[
\Delta C_p = C_p \text{ (subcooled liquid solute)} - C_p \text{ (solid solute)}
\]

(2.22.2)
The following approximations might then be applied to eq 2.22.1: (1) The normal melting temperature \( T_m \) is nearly equivalent to the triple point temperature, (2) \( \Delta_{\text{fus}}H \) at \( T_m \) and \( T_t \) are essentially equal, and (3) the first term on the right hand side (of eq 2.22.1) is much more significant than the remaining terms. These approximations and the definition of entropy \( \Delta S = \Delta H / T \) give rise to the following simplified solubility relationship:

\[
\ln \gamma_2 x_2 = \frac{-\Delta_{\text{fus}}S}{RT} \left( \frac{T_m}{T} - 1 \right) \quad (2.22.3)
\]

The calculations and assumptions associated with relationships 2.22.1 and 2.22.3 rely on the assumptions that the solid solute is a pure species and that no solvent dissolves into the solute. Since the systems examined in this study are mixtures, they do not necessarily obey the former assumption. Where these assumptions do not apply, methods such as those described at the end of section 2.21 need to be applied to estimate the \( \gamma_{is} \) and \( I_{is} \) (since there will no longer be a clear distinction between solute and solvent).

**2.23 Sorption Processes**

Substances, often in either dissolved or vapor phases, sometimes have the propensity to associate with surrounding solid media. This process is generically referred to as sorption. The terms adsorption and absorption are specific types of sorption processes. The former, adsorption, is a surface phenomenon and is generally thought of as a two-dimensional process, in which chemicals adhere only
to the surface of a solid. In contrast, absorption, describes three-dimensional association, in which species infiltrate a solid matrix.

Sorption analysis is crucial to the understanding of fate and transport of chemical species in the environment and beyond. In many cases, such as those dealing with PAHs, sorption effects can be a governing factor in bioavailability, bioremediation, vapor pressure, solubility, etc. In other words, introduction or availability of a sorbent may greatly affect environmental and/or industrial procedures and outcomes, and it is important to consider that traditional behavior-predicting techniques and calculations may not apply in situations where affinities between sorbates and sorbents exist.

Although this chapter is meant to provide a general and nonspecific overview of pertinent concepts and theories, the present study is aimed at understanding a group of chemicals (PAHs and PACs) that exist in the natural world, and so, the complexity and heterogeneity of such systems must be acknowledged. The overall point is that sorption of subsurface contaminants to natural particles is not easily predicted. For example, subsurface soil and sediment systems are, by nature, highly complex. Soil particles vary in size, shape, and origin and are rarely homogenous. They consist of both organic and inorganic matter at varying degrees of decomposition. In many cases, fractions with high carbon content, and frequently, high porosity account for strong sorption effects. Other variable soil properties include, but are not limited to, pH, cation exchange capacity, moisture content, dissolved organic matter content, and soil gas content.
Soil-contaminant systems are further complicated by the lack of chemical homogeneity in natural settings. In addition to sorbent variability, there are the complexities of the sorbates themselves because chemicals rarely exist in nature as a single species. Rather, like in the cases of PAHs, they may occur as complicated mixtures in multiple phases.

The lack of homogeneity discussed in the previous two paragraphs gives rise to a number of sorption mechanisms and processes that exist in the natural environment. These mechanisms work concurrently at a microscopic level and produce some difficult to predict macroscopic result. Despite these difficulties, there do exist some methods to predict sorption equilibrium and kinetics in natural systems. The remainder of this section will focus on these predictive methods with regard to the sorption of chemicals from aqueous solution and air to solid particles.

**Sorption isotherms** are relationships that correlate the total sorption \( C_{is} \) (quantity of sorbate per mass sorbent) with bulk solution concentration \( C_{iw} \) (quantity of chemical per volume solvent). Sorption isotherms characterize the equilibrium distribution of a sorbate, without consideration of kinetics. It is worth mentioning that the definition of equilibrium needs to be carefully considered because desorption kinetics can be very slow and endpoints can be difficult to determine. This issue will be discussed again in a later chapter.

Isotherms are often system and/or chemical specific and must be determined experimentally. They can be roughly categorized into three main forms. The first and most straightforward isotherm is that which describes a system of constant
sorbate-sorbent affinity over an observed concentration range. This is called a **linear isotherm** because the $C_{is}$ vs. $C_{iw}$ curve is a straight line of positive slope.

Oftentimes, sorption sites in a given system are limited, and can become filled to capacity. When this occurs, the affinity for sorbates naturally decreases with concentration. Thus, the second, most commonly observed sorption isotherm occurs when sorbate-sorbent affinity decreases with increasing solution concentration. This results in an isotherm whose slope decreases with $C_{iw}$. In some cases, the sorbent can become completely saturated and the isotherm slope will become zero at some $C_{is,max}$.

The third and least commonly observed isotherm describes a system in which sorbate-sorbent affinity increases with solution concentration. This occurs in cases where high sorbate concentrations cause a chemical or physical modification of the sorbent that increases its sorption capacity.

Multiple sorption mechanisms may exist in natural settings where heterogeneous organic matter is present. These molecular-level processes occur simultaneously, and consequently, macroscopically observed trends probably represent some combination or summation of independent isotherms. Thus, in many real situations, isotherms may be difficult to categorize according to the simple forms noted above.

Sorption isotherms can often be described quantitatively by fitting experimentally determined sorption data to an equation called the **Freundlich**
isotherm, which contains a minimum number of adjustable parameters and is given by,

\[ C_{is} = K_{if} C_{iw}^{n_i} \]  \hspace{1cm} (2.23.1)

Here, \( K_{if} \) is Freundlich constant capacity factor and \( n_i \) is the Freundlich exponent. Both of these parameters are species specific. Since \( C_{is} \) and \( C_{iw} \) are expressed in units of concentration, the value of \( K_{if} \) must have correspondingly appropriate units.

The Freundlich exponent \( n_i \) quantifies the variability of free energies associated with heterogeneous sorbate-sorbent systems. Hence, the Freundlich isotherm accounts for the diversity of mechanisms associated with natural sorption processes. When \( n_i = 1 \), the system is marked by constant free energies over the observed concentration range, and the isotherm is linear. When \( n_i < 1 \), the free energies of sorption decrease as sorption sites are filled. This leads to an isotherm that decreases in slope with increasing solution concentration, that is, the isotherm is a downward-concaving curve. Lastly when \( n_i > 1 \), the free energies of sorption increase as sorption sites are filled. This results in an upward-concaving curve.

The Freundlich isotherm can be written in logarithmic form as follows:

\[ \log C_{is} = n_i \log C_{iw} + \log K_{if} \]  \hspace{1cm} (2.23.2)

When sorption data are plotted as such, the slope and intercept of the linear regression represent the Freundlich exponent and constant capacity factor, respectively.
In some situations, the Freundlich isotherm cannot fit the data and other models must be used. For example, in cases where a sorbent can become saturated in a given range of solution concentration the **Langmuir isotherm**, given by eq 2.23.3, may be preferred.

\[
C_{is} = \frac{\Gamma_{\text{max}} K_{il} C_{iw}}{1 + K_{il} C_{iw}}
\]  

(2.23.3)

Here \(\Gamma_{\text{max}}\) represents the sorbent capacity as a total number of sorption sites per mass of sorbent. Since sorbates vary in size and shape, this parameter is not constant for all chemicals. Hence it is sometimes written as \(C_{i,\text{max}}.\) \(K_{il}\) is the Langmuir constant, which assumes some constant sorbate-sorbent affinity for all sorption sites. These parameters can be quantified by fitting experimental data using the following form:

\[
\frac{1}{C_{is}} = \frac{1}{C_{is,\text{max}} K_{il} C_{iw}} + \frac{1}{C_{is,\text{max}}}
\]

(2.23.4)

Here \((1/C_{is,\text{max}} K_{il})\) and \((1/C_{is,\text{max}})\) are the slope and intercept of the curve, respectively.

In cases where sorption data cannot be fit to either of the aforementioned relationships, combinations of isotherms can sometimes be used. These combined relationships are called **distributed models** and usually involve some combination of linear, Freundlich, and Langmuir isotherms. For example, the equation

\[
C_{is} = K_{lp} C_{iw} + \frac{C_{is,\text{max}} K_{il} C_{iw}}{1 + K_{il} C_{iw}}
\]

(2.23.5)
is a combination of linear adsorption isotherms (with $K_p$ as the partition coefficient) and a site-limited, Langmuir isotherm. A number of these semi-empirical equations exist and some will be discussed in a later section.

2.24 Rarefied Gas Flow and Development of the Knudsen Effusion Technique

Much of the experimental data from this study rely on an indirect vapor pressure measurement technique called the Knudsen effusion technique. The experimental method and theory thereof is based upon rarefied gas flow, a special case of the kinetic theory of gases.

The kinetic theory of gases itself relates the macroscopic properties of a gas, e.g., pressure, volume, and temperature, to corresponding molecular scale behavior. It postulates that the molecules of gases are always in rapid and random motion, and that these molecules frequently experience collisions with one another and with the walls of a surrounding container. It is these molecular collisions that produce pressure. The kinetic theory for an ideal gas is based on the following three postulates:

1. Gases are composed of a large number of very small molecules, the size of which is always much smaller than the distance between them.

2. These molecules have kinetic energy because they are in constant motion.

3. There exist no intermolecular forces between gas molecules. In other words, repulsive and attractive forces are not exhibited, except during collision.
So then, ideal kinetic theory is based upon the statistical treatment of a large number of spherical particles, with negligible volume and perfectly elastic intermolecular collisions. Furthermore, the kinetic energy and thus velocity of the gas molecules is a strong function of temperature. This simplified, ideal model is the foundation upon which more realistic theories, such as the Boltzmann and Knudsen effusion theories, are based. Though ideal theory is a plausible estimate for many gases the Boltzmann and Knudsen models relax the assumptions noted above for systems of high and low density gases, respectively.

Both rarefied gas flow and effusion describe movement of very low-density gas molecules. Rarefied gas flow is described as the movement of gas molecules at sub-atmospheric pressures, in which molecular collisions are not frequent. Effusion is the movement of gases in passageways that are small when compared to the average distance molecules travel between molecular collisions, as characterized by the mean free path, $\lambda$. For a given passageway with diameter $d$, effusion theory applies only if

$$d << \lambda$$

(2.24.1)

The development and application of the Knudsen effusion technique first require an experiment-specific estimate and comparison of molecular mean free path and passageway size. The molecular mean free path for billiard-ball molecules is given by

$$\lambda = \frac{V}{\sqrt{2} \pi d^2 N_A} = \frac{k_b T}{\sqrt{2} \pi d^2 P}$$

(2.24.2)
where \( d_A \) is the characteristic molecular diameter, \( N_A \) is the total number of A molecules in the system, \( n \) is the total number of moles in the system, and \( k_b \) is the Boltzmann constant. The mean free path estimated and used in this study for the relevant experimental conditions \((T > 300 \, \text{K}, \, P < 10^{-4} \, \text{Pa}, \, d_A \approx 0.60 \, \text{mm})\) is on the order of 30 cm. This is much larger than the typical passageway diameter of 0.06 cm, and hence the development of the Knudsen effusion technique is appropriate for this experimental study.

The development of Knudsen effusion theory requires that a number of relationships be considered and simultaneously combined. The kinetic theory of gases estimates average molecular speed as

\[
\bar{c} = \sqrt{\frac{8k_bT}{\pi m}} = \sqrt{\frac{8RT}{\pi m}}
\]

(2.24.3)

where \( m \) is molecular mass and \( M \) is molar mass. Next, the ideal gas law can be written in the new form

\[
P V = N_A k_b T
\]

(2.24.4)

and therefore, in terms of number density \( n \),

\[
P = nk_bT
\]

(2.24.5)

Next consider that collision frequency of gas molecules on any portion of a container wall is given by

\[
Z_{\text{wall}} = \frac{n \bar{c}}{4}
\]

(2.24.6)
If the previously discussed effusion passageway is projected two-

dimensionally on a surface of the container wall, then the number molecular

collisions with this projection during time $t$ is given by,

$$\omega = Z_{\text{wall}}At$$  \hspace{1cm} (2.24.7)

where $A$ is the surface area of the projection. Now, in the case of Knudsen effusion,
this hypothetical projection actually represents a hole in some container. Thus

equation 2.24.7 actually describes the number of molecules that escape from a
container through a hole of area $A$ during a given time $t$ and the total mass lost is
given by

$$g = \omega m$$  \hspace{1cm} (2.24.8)

Combination of the parameters given above allows development of the Knudsen
effusion working equation. First,

$$n = \frac{4z_{\text{wall}}}{c} = \frac{4g}{mAt} \sqrt{\frac{\pi m}{8k_b T}} = \frac{g}{At} \sqrt{\frac{2\pi}{k_b m t}}$$  \hspace{1cm} (2.24.9)

Then,

$$P = nk_b T = \frac{g}{At} \sqrt{\frac{2\pi k_b T}{m}} = \frac{g}{At} \sqrt{\frac{2\pi RT}{M}}$$  \hspace{1cm} (2.24.10)

This is the theoretical working equation for the Knudsen effusion technique, in
which gas molecules at pressure $P$ escape from a confining container through a very
small orifice.
This theoretical working equation makes two very significant assumptions in addition to those inherent to effusion. First, molecular collisions in the passageway are assumed not to exist. The reason for this assumption is that molecular collisions could cause an escaping molecule to “bounce-back” into the cell. This would, of course, violate the assumption of eq 2.24.10. On a similar note, the length of the passageway is assumed to be infinitely small. This too prevents any bounce-back of escaping molecules that collide with the inside surface of the passageway.

Of course, in practice, it is impossible to experimentally adhere to these required assumptions. So a correction factor, called the Clausing correction factor $W$, is often applied to the working equation as follows:

$$P = \frac{m}{AW} \sqrt{\frac{2\pi RT}{M}}$$

(2.24.11)

where $m = g/t$. The Clausing correction factor $W$ is an empirical parameter based on the orifice (passageway) dimensions. It will be discussed in greater detail in a later section.
Chapter 3. Phase Behavior of Binary, Solid PAH Mixtures: Eutectic and Azeotropic Character

3.1 Introduction

Polycyclic aromatic hydrocarbons (PAHs) are normally found in mixtures of many similarly structured compounds. The goal of the research presented in this chapter is to better understand PAH mixture thermodynamics by studying the phase behavior of binary PAH systems. Anthracene, pyrene, and benzo[a]pyrene consist of three, four, and five fused aromatic rings respectively. They are common PAHs and are common components of PAH mixtures, which have considerable environmental significance.

Melting point studies have been conducted on binary, organic component mixtures and these principally report the temperatures and in some cases, enthalpies of solid to liquid phase transitions, often involving one or two eutectic points. Table 3.1 summarizes reported melting temperatures of binary, aromatic-containing mixtures that form eutectics. Tables 3.2, 3.3, and 3.4 summarize the fusion and interaction energies of other, recently studied binary aromatic-containing mixtures. Interaction energy is that energy associated with interaction of mixture components and it reflects interactions that are non-ideal. In cases where authors did not directly report such values, interaction energies were obtained by subtracting calculated fusion enthalpies from experimentally determined/reported
values (Fu, 2011). In situations where interaction energy is high, ideal mixture behavior should not be expected.

It is worth noting that other groups have previously studied the phase behavior of anthracene + pyrene mixtures, reporting the formation of a eutectic (Szczepanik and Skalmowski, 1963; Szczepanik, 1963). However, these were only melting temperature studies that did not provide the necessary data to fully characterize mixture thermodynamics. Hence, in addition to melting temperature analysis, the present study focused on enthalpies of fusion, microstructures, and vapor pressures of complicated, binary PAH systems. In addition to fusion behavior, many of the results presented here will address the sublimation behavior of the binary mixtures given that such solid-vapor systems are not yet well understood or reported on in the literature.
Table 3.1 Melting temperatures of previously reported binary, organic component mixtures that form one eutectic

<table>
<thead>
<tr>
<th>System</th>
<th>$T_{\text{fus}}$/K</th>
<th>$T_{\text{melt}}$/K</th>
<th>$x_{1e}$</th>
<th>$T_{\text{fus}}$/K</th>
</tr>
</thead>
<tbody>
<tr>
<td>naphthalene (1) + α-naphthylamine (2)$^1$</td>
<td>353.5</td>
<td>323.2</td>
<td>0.36</td>
<td>301.3</td>
</tr>
<tr>
<td>naphthalene (1) + α-naphthol (2)$^1$</td>
<td>353.5</td>
<td>368.2</td>
<td>0.487</td>
<td>327.7</td>
</tr>
<tr>
<td>naphthalene (1) + phenanthrene (2)$^{1,2}$</td>
<td>353.5</td>
<td>373.2</td>
<td>0.558</td>
<td>321.3</td>
</tr>
<tr>
<td>naphthalene (1) + thianaphthene (2)$^{3,4}$</td>
<td>353.5</td>
<td>305.2</td>
<td>0.063</td>
<td>302.4</td>
</tr>
<tr>
<td>naphthalene (1) + diphenyl (2)$^{3,4}$</td>
<td>353.5</td>
<td>343.7</td>
<td>0.442</td>
<td>312.4</td>
</tr>
<tr>
<td>naphthalene (1) + acenaphthene (2)$^{3,4}$</td>
<td>353.5</td>
<td>368.5</td>
<td>0.564</td>
<td>324.6</td>
</tr>
<tr>
<td>naphthalene (1) + fluorene (2)$^{3,4}$</td>
<td>353.5</td>
<td>388.2</td>
<td>0.613</td>
<td>330.2</td>
</tr>
<tr>
<td>naphthalene (1) + fluoranthene (2)$^{3,4}$</td>
<td>353.5</td>
<td>383.2</td>
<td>0.612</td>
<td>331</td>
</tr>
<tr>
<td>naphthalene (1) + pyrene (2)$^{3,4}$</td>
<td>353.5</td>
<td>423.2</td>
<td>0.746</td>
<td>339.2</td>
</tr>
<tr>
<td>naphthalene (1) + chrysene (2)$^{3,4}$</td>
<td>353.5</td>
<td>528.2</td>
<td>0.971</td>
<td>351.4</td>
</tr>
<tr>
<td>biphenyl (1) + fluorene (2)$^{3,4}$</td>
<td>343.7</td>
<td>388.2</td>
<td>0.909</td>
<td>340.8</td>
</tr>
<tr>
<td>biphenyl (1) + acenaphthene (2)$^{3,4}$</td>
<td>343.7</td>
<td>368.5</td>
<td>0.641</td>
<td>319.3</td>
</tr>
<tr>
<td>fluorene (1) + acenaphthene (2)$^{3,4}$</td>
<td>388.15</td>
<td>368.5</td>
<td>0.431</td>
<td>338.6</td>
</tr>
<tr>
<td>phenanthrene (1) + biphenyl (2)$^{3,4}$</td>
<td>373.2</td>
<td>343.7</td>
<td>0.691</td>
<td>324.8</td>
</tr>
<tr>
<td>phenanthrene (1) + acenaphthene (2)$^{3,4}$</td>
<td>373.2</td>
<td>368.5</td>
<td>0.495</td>
<td>327.5</td>
</tr>
<tr>
<td>phenanthrene (1) + pyrene (2)$^{3,4}$</td>
<td>373.2</td>
<td>423.2</td>
<td>0.747</td>
<td>354.7</td>
</tr>
<tr>
<td>anthracene (1) + pyrene (2)$^{3,4}$</td>
<td>489.8</td>
<td>423.2</td>
<td>0.221</td>
<td>404.6</td>
</tr>
<tr>
<td>pyrene (1) + chrysene (2)$^{3,4}$</td>
<td>423.2</td>
<td>528.2</td>
<td>0.855</td>
<td>405.7</td>
</tr>
<tr>
<td>p-dichlorobenzene (1) + p-dibromobenzene (2)$^5$</td>
<td>327.2</td>
<td>362.2</td>
<td>0.8325</td>
<td>315.7</td>
</tr>
<tr>
<td>resorcinol (1) + p-dibromobenzene (2)$^5$</td>
<td>383.2</td>
<td>362.2</td>
<td>0.378</td>
<td>345.95</td>
</tr>
<tr>
<td>benzamide (1) + benzoic acid (2)$^6$</td>
<td>401.2</td>
<td>395.6</td>
<td>0.5122</td>
<td>356.2</td>
</tr>
<tr>
<td>o-chloro benzoic acid (1) + benzoic acid (2)$^7$</td>
<td>414.2</td>
<td>394.6</td>
<td>0.3292</td>
<td>368.2</td>
</tr>
</tbody>
</table>

(1 Rastogi and Rama Varma, 1956; 2 Rastogi and Bassi, 1964; 3 Szczepanik and Skalmowski, 1963; 4 Szczepanik, 1963; 5 Singh et al., 1999; 6 Singh et al., 2008; 7 Das et al., 2009)
Table 3.2 Melting temperatures of previously reported binary organic component mixtures that form two eutectics.

<table>
<thead>
<tr>
<th>System</th>
<th>$T_{fus,1}/K$</th>
<th>$T_{fus,2}/K$</th>
<th>$x_{1,e1}$</th>
<th>$T_{fus,e1}/K$</th>
<th>$x_{1,e2}$</th>
<th>$T_{fus,e2}/K$</th>
</tr>
</thead>
<tbody>
<tr>
<td>p-dimethylaminobenzaldehyde (1) + resorcinol (2)$^8$</td>
<td>348</td>
<td>382.6</td>
<td>0.2695</td>
<td>322.05</td>
<td>0.7209</td>
<td>317.05</td>
</tr>
<tr>
<td>2,4-dinitrophenol (1) + naphthalene (2)$^{7,10}$</td>
<td>353</td>
<td>378</td>
<td>0.3158</td>
<td>358</td>
<td>0.5</td>
<td>367</td>
</tr>
<tr>
<td>p-benzoquinone (1) + pyrene (2)$^{11}$</td>
<td>388</td>
<td>423</td>
<td>0.324</td>
<td>392</td>
<td>0.792</td>
<td>376</td>
</tr>
<tr>
<td>m-dinitrobenzene (1) + pyrene (2)$^{11}$</td>
<td>362</td>
<td>423</td>
<td>0.301</td>
<td>363</td>
<td>0.702</td>
<td>361</td>
</tr>
<tr>
<td>m-nitrobenzoic acid (1) + pyrene (2)$^{11}$</td>
<td>413</td>
<td>423</td>
<td>0.299</td>
<td>403</td>
<td>0.902</td>
<td>413</td>
</tr>
<tr>
<td>m-dinitrobenzene (1) + phenothiazine (2)$^{12}$</td>
<td>362</td>
<td>457</td>
<td>0.302</td>
<td>345</td>
<td>0.699</td>
<td>343</td>
</tr>
<tr>
<td>m-nitrobenzoic acid (1) + phenothiazine (2)$^{12}$</td>
<td>413</td>
<td>457</td>
<td>0.438</td>
<td>400</td>
<td>0.8</td>
<td>390</td>
</tr>
</tbody>
</table>

Table 3.3 Enthalpy of fusion of previously reported binary organic component mixtures that form one eutectic.

<table>
<thead>
<tr>
<th>System</th>
<th>$\Delta_{fus}H_1/J\cdot g^{-1}$</th>
<th>$\Delta_{fus}H_2/J\cdot g^{-1}$</th>
<th>$x_1$</th>
<th>$\Delta_{fus}H_{e1}/J\cdot g^{-1}$</th>
<th>$E_{inter,1}/J\cdot g^{-1}$</th>
<th>$\Delta_{fus}H_{e2}/J\cdot g^{-1}$</th>
<th>$E_{inter,2}/J\cdot g^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>benzamide (1) + benzoic acid (2)$^9$</td>
<td>191.04</td>
<td>152.70</td>
<td>0.5122</td>
<td>144.68</td>
<td>-27.66</td>
<td></td>
<td></td>
</tr>
<tr>
<td>o-chloro benzoic acid (1) + benzoic acid (2)$^7$</td>
<td>175.86</td>
<td>152.70</td>
<td>0.3292</td>
<td>137.44</td>
<td>-22.88</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 3.4 Enthalpy of fusion of previously reported binary organic component mixtures that form two eutectics.

<table>
<thead>
<tr>
<th>System</th>
<th>$\Delta_{fus}H_1/J\cdot g^{-1}$</th>
<th>$\Delta_{fus}H_2/J\cdot g^{-1}$</th>
<th>$x_{1,e1}$</th>
<th>$\Delta_{fus}H_{e1}/J\cdot g^{-1}$</th>
<th>$E_{inter,1}/J\cdot g^{-1}$</th>
<th>$\Delta_{fus}H_{e2}/J\cdot g^{-1}$</th>
<th>$E_{inter,2}/J\cdot g^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>p-dimethylaminobenzaldehyde (1) + resorcinol (2)$^8$</td>
<td>126.01</td>
<td>207.07</td>
<td>0.2695</td>
<td>140.11</td>
<td>-45.12</td>
<td>0.7209</td>
<td>133.12</td>
</tr>
<tr>
<td>p-benzoquinone (1) + pyrene (2)$^{11}$</td>
<td>181.32</td>
<td>86.03</td>
<td>0.324</td>
<td>58.81</td>
<td>-58.09</td>
<td>0.792</td>
<td>141.76</td>
</tr>
<tr>
<td>m-dinitrobenzene (1) + pyrene (2)$^{11}$</td>
<td>143.95</td>
<td>86.03</td>
<td>0.301</td>
<td>55.22</td>
<td>-48.25</td>
<td>0.702</td>
<td>84.14</td>
</tr>
<tr>
<td>m-nitrobenzoic acid (1) + pyrene (2)$^{11}$</td>
<td>95.14</td>
<td>86.03</td>
<td>0.299</td>
<td>79.79</td>
<td>8.96</td>
<td>0.902</td>
<td>83.25</td>
</tr>
<tr>
<td>m-dinitrobenzene (1) + phenothiazine (2)$^{12}$</td>
<td>143.95</td>
<td>142.52</td>
<td>0.302</td>
<td>80.59</td>
<td>-62.37</td>
<td>0.699</td>
<td>90.71</td>
</tr>
<tr>
<td>m-nitrobenzoic acid (1) + phenothiazine (2)$^{12}$</td>
<td>95.14</td>
<td>142.52</td>
<td>0.438</td>
<td>72.36</td>
<td>-49.41</td>
<td>0.800</td>
<td>87.58</td>
</tr>
</tbody>
</table>

(6 Singh et al., 2008; 7 Das et al., 2009; 8 Rai and Varma, 2000; 9 Singh et al., 2001; 10 Singh et al., 2007; 11 Gupta and Singh, 2004; 12 Gupta et al., 2007)
3.2 Experimental

Materials

Anthracene (CAS Reg. No. 120-12-7) and benzo[a]pyrene (CAS Reg. No. 50-32-8) were obtained from Sigma-Aldrich. Pyrene (CAS Reg. No. 129-00-0), fluorene (CAS Reg. No. 86-73-7) and fluoranthene (CAS Reg. No. 206-44-0) were obtained from TCI America. Phenanthrene (CAS Reg. No. 85-01-8) was obtained from Acros Organics. Reported minimum mass fraction purities between 0.95 and 0.99 were verified by gas chromatography/mass spectrometry (GC-MS) analysis. The anthracene contained trace levels of phenanthrene. Analysis of pyrene showed one impurity with ions at mass-to-charge ratios \( m/z \) of 208 and 104. This spectrum could not be identified and further experiments verified that it does not represent anthraquinone (which would not split to an \( m/z \) of 104, but does have a molecular weight of 208 g·mol\(^{-1}\)). The 208 to 104 \( m/z \) split is characteristic of a PAH or long-chain organic that is able to break in half upon ionization. It is equally likely though, that this spectrum indicates phthalate contamination from the sample preparation process. Samples were used with no further purification.

In addition, the melting temperature of each pure compound was measured and results compared favorably to the literature values (Szczepanik and Skalmowski, 1963; Szczepanik, 1963; Stephenson and Malanowski, 1987). The details of the melting temperature analysis are discussed in a later section.
**Mixture Preparation**

PAH mixtures were prepared using a melt and quench-cool technique. The desired quantities of each PAH were measured to ± 0.01 mg, and roughly 40 mg were sealed within a brass vessel. The vessel was then heated to the melting temperature of the component with the highest melting point and agitated, ensuring that components melted and mixed in a liquid state. After a period of 5 min, the vessel was removed from the heat source and immediately immersed in liquid nitrogen, which provided cooling at an estimated 70 to 80 K·s⁻¹ for the first 4 s. The preparation technique was intended to preserve the disorder of the well-mixed liquid during solidification. This heating and quench-cool procedure was repeated four additional times before the solid mixture was removed from the preparation vessel and placed in a glass storage vial. Uniformity of the samples was confirmed by visual examination. This technique was originally developed in order to ensure that “liquid-like” disorder would be preserved in the solids, so they might better model liquid tars. It was subsequently found, though, that the quench cooling technique has relatively little impact on observed results. Similar results can be obtained by simpler melting procedures.

**Melting Temperature and Enthalpy of Fusion**

Melting temperatures and enthalpies of fusion $\Delta_{fus}H$ of mixtures and pure samples were measured using a Thermo Scientific melting temperature analyzer and DuPont differential scanning calorimeter (DSC). In the latter case, hermetically sealed DSC pans were filled with 1 to 3 mg of sample and scanned in both heating
and cooling modes. The rates of heating and cooling were 10 K·min\(^{-1}\) and 2.5 K·min\(^{-1}\) respectively. This procedure produces conveniently integrable peaks on the cooling cycle, increasing the accuracy of the enthalpy of fusion calculation. However, the values of enthalpy and transition temperatures were generally insensitive to changes in heating and cooling rate in the range 2.5 to 20 K·min\(^{-1}\). A melting temperature analyzer was used to visually observe and obtain higher resolution melting temperature measurements. These generally agreed with the DSC onset temperatures in that the melting temperatures from each instrument differed by no more than a few degrees Kelvin, though naturally what is reported from the DSC is a temperature from an endothermic event stretching over several degrees, and hence, these values are less precise than classic melting temperature determination.

Melting behavior was tracked from thaw to liquidus temperatures to ±1 K using the melting temperature analyzer. In following the thaw-melt method (Pounder and Masson, 1934; Rastogi and Rama Varma, 1956), 1 to 2 mg of each sample was placed inside a glass capillary tube and heated at 1 ± 0.5 K·min\(^{-1}\). The thaw temperature is the temperature at which the first droplet of liquid appears in the capillary tube. The liquidus temperature is the maximum temperature at which both solid-crystals and liquid are observed to coexist in the system. Hence, the liquidus temperature is reached when the last crystal melts in the capillary tube. The experimentally measured enthalpies of fusion, thaw temperatures, and liquidus temperatures have been used to build solid-liquid phase diagrams for the binary PAH systems.
Vapor Pressure

The Knudsen effusion technique was used to measure the vapor pressures $P$ of solid PAH mixtures and pure components. This technique allows for vapor pressure measurement of low volatility compounds. Traditional vapor pressure techniques measure pressure directly and would require unacceptably high experimental temperatures that could degrade the PAHs. The Knudsen effusion technique measures sample mass loss from a confining cell through a small orifice and relates it to vapor pressure by

$$P = \frac{m}{AW} \sqrt{\frac{2\pi RT}{M}}$$

(2.24.11)

where $m$ is the mass loss, $t$ is the experimental time, $A$ is the orifice area, $R$ is the universal gas constant, $T$ is the sample temperature, $M$ is the molecular weight, and $W$ is the Clausing correction factor. The Clausing correction factor $W$, gives the probability that an effusing molecule will escape from the cell. It is determined by experimental calibration or calculated empirically by

$$W = \frac{1}{1 + \frac{3l}{8r}}$$

(3.2.1)

where $l$ is the orifice effusion length and $r$ is the orifice radius. Values of $W$ for this study approach unity, ranging between 0.96 and 0.98. Vapor pressure experiments must satisfy fundamental effusion theory, which stipulates that vapor molecules escape a confining cell through orifice passages that are much smaller than their
molecular mean free path. A more detailed development of the Knudsen effusion theory can be found in Chapter 2.

Samples of PAH mixtures were placed inside effusion cells prepared from steel shim stock. The cells were sealed except for a single, circular orifice of diameter $0.60 \pm 0.01$ mm and placed on the arm of a continually recording microbalance contained in a high vacuum chamber. The pressure inside the chamber was reduced to $10^{-4}$ Pa to achieve the required condition of negligible backpressure outside the orifice. A calibrated, type-K thermocouple was used to measure cell temperature to $\pm 0.1$ K and to verify thermal equilibrium in the system. The equilibrium pressure inside the cell is the vapor pressure of the sample, and the leak rate is measured and related to vapor pressure with eq 2.24.11. A schematic of the instrument is given by Figure 3.1. The instrument is called an “intelligent gravimetric analyzer,” purchased from Hiden Isochema (Warrington, England), though significant modifications were made during the experiments of this study. The relative measurement uncertainty within the experimental temperature range is $\delta P/P = 0.045$.

In the case of a mixture, there is obviously a question of what molecular weight must be used for $M$. In this work, the decision was made to use a weighted average of pure component molecular weights. Because the value of molecular weight appears as the square root, there is not particularly great sensitivity to this value. For example, use of the above, assumed value for a binary anthracene (1) + pyrene (2) mixture would result in a maximum difference of 2.6 % in measured
vapor pressure, if we take an extreme composition at $x_1 = 0.90$ at an experimental temperature of 338 K. Such a small difference is seen to be within the overall uncertainties.

Figure 3.1. Schematic of the Knudsen effusion apparatus used to measure vapor pressure of low volatility compounds.

With respect to the values of measured vapor pressures for mixtures, it is important to recognize that what is being examined is a solid sublimation system. The temperatures are always so low that there will be no formation of a liquid
phase. This is important to keep in mind, insofar as the behavior of this system is inherently different than that of a liquid mixture system. If the fundamental condition of thermodynamic equilibrium in the sample cell is fulfilled (as must be considered reasonable), then it is important to recognize that equilibrium must be satisfied for all phases that might be present. What this means is that the vapor pressure of the system cannot exceed the sum of the vapor pressures of the pure components that make up the system, since any component can nucleate its own pure solid phase in the cell, should the vapor pressure of that component in the mixture exceed its pure phase vapor pressure. In other words, the vapor pressure of the system would be bounded on the upper side by the sum of pure component vapor pressures. This is different than in liquid systems, in which mixing would be more favored and the same sort of phase separation would not necessarily be possible.

**X-ray Diffraction**

The crystal structures of some PAHs and their mixtures were qualitatively investigated using powder X-ray diffraction (XRD). Samples were reduced to a fine powder and dusted onto glass slides that were coated with a thin petroleum film. A Siemens X-ray diffractometer (model D5000) was used to measure the diffraction patterns of each sample between 10 and 60 deg.
Gas-Chromatography-Mass Spectrometry

Gas chromatography-mass spectrometry (GC-MS) was used to determine the composition of mixtures before, during, and after vapor pressure experiments. Analytes were dissolved in dichloromethane to an approximate concentration of 100 µg·ml⁻¹ and analyzed by a calibrated Varian combined gas chromatograph (model CP3800) and mass spectrometer (model Saturn 2200). The Varian analytical procedure for EPA Method 8270C was followed (Varian, 2001-2004).

3.3 Results and Discussion: Anthracene + Pyrene Solid Mixtures

Summary of Results

To better characterize the thermodynamic behavior of a binary polycyclic aromatic hydrocarbon mixture, thermochemical and vapor pressure experiments were used to examine the phase behavior of the anthracene (1) + pyrene (2) system. A solid-liquid phase diagram was mapped for the mixture. A eutectic point occurs at 404 K at \( x_1 = 0.22 \). A model based on eutectic phase formation can be used to predict the enthalpy of fusion associated with the mixture (see below). For mixtures that contain \( x_1 < 0.90 \), the enthalpy of fusion is near that of pure pyrene. This and X-ray diffraction results indicate that mixtures of anthracene and pyrene have pyrene-like crystal structures and energetics until the composition nears that of pure anthracene. Solid-vapor equilibrium studies show that mixtures of anthracene and pyrene form solid azeotropes at \( x_1 \) of 0.03 and 0.14. Additionally, mixtures at \( x_1 = \)
0.99 sublime at the vapor pressure of pure anthracene, suggesting that anthracene behavior is not significantly influenced by $x_2 = 0.01$ in the crystal structure.

**Phase Diagram and Enthalpy of Fusion**

The structures of anthracene and pyrene are shown in Figure 3.2. Enthalpies of fusion for all samples were measured using temperature-controlled differential scanning calorimetry. Results from typical DSC scans are given in Figure 3.3. All four scans were conducted in heating-mode between 298 K and 523 K at 10 K·min$^{-1}$. The DSC results here show heat input ($\Phi/W\cdot g^{-1}$) as the system is heated. Peaks in the DSC scan reveal phase changes. The four scans in Figure 3.3 have peaks that represent endothermic, solid to liquid phase transitions. Peaks can be integrated to determine the enthalpy of fusion of the sample with a relative uncertainty of $\delta \Delta_{fus}H/\Delta_{fus}H = 0.07$. Pure anthracene and pyrene melt at 490 K with $\Delta_{fus}H = 156 \pm 11.9 \, \text{J} \cdot \text{g}^{-1}$ and 424 K with $\Delta_{fus}H = 80 \pm 5.6 \, \text{J} \cdot \text{g}^{-1}$ respectively. These results are in fair agreement with those of Domalski and Hearing (1996), who report that pure anthracene and pyrene melt at 489 K with $\Delta_{fus}H = 164.8 \, \text{J} \cdot \text{g}^{-1}$ and 423 K with $\Delta_{fus}H = 85.8 \, \text{J} \cdot \text{g}^{-1}$, respectively.

![Figure 3.2. Structures of anthracene and pyrene taken from NIST chemistry webBook (2011).](image)
Figure 3.3. Differential scanning calorimetry results of pure components and mixtures: solid line, pure anthracene (1); dashed line, pure pyrene (2); dash-dot-dashed line, mixture at $x_1 = 0.22$; dotted line, mixture at $x_1 = 0.90$.

Mixture compositions are given in terms of $x_1$ as it is understood that $x_1 + x_2 = 1$. The DSC results indicate that anthracene (1) + pyrene (2) quench-cooled mixtures in the indicated composition range undergo a phase transition at 404 K, well before either of the pure phases melts. This indicates the existence of a eutectic mixture. In some cases, such as the one shown for a mixture at $x_1 = 0.90$, there appear to be two phase transitions as the sample is heated.
It is important to recall that the results are all for quench-cooled samples. If similar DSC experiments are performed on physical anthracene (1) + pyrene (2) mixtures, the measured values of melting temperature and fusion enthalpy match those of the quench-cooled samples. This suggests that vapors interdiffuse in the vapor-solid system and that a thermodynamically favored eutectic exists for this anthracene + pyrene system, irrespective of initial preparation.

It is worth noting with regard to the results of Figure 3.3 that all evidence of a pyrene solid phase disappears in the presence of the lower temperature eutectic phase peak, irrespective of the magnitude of that latter peak. In other words, it appears as though pure pyrene is not a stable phase in such mixture systems. Figure 3.4 shows the full heating, cooling, and reheating scan of an equimolar anthracene + pyrene mixture. As with the mixture at $x_1 = 0.90$, the equimolar mixture at $x_1 = 0.50$ appears to undergo two endothermic phase transitions upon heating. Then cooling at a rate of 2.5 K·min$^{-1}$ induces crystallization at 426 K of what is most probably an inhomogeneous phase that has limited solubility in the eutectic. This is followed by crystallization of the eutectic phase itself at 390 K. Each of these phase transitions represents the crystallization of a subcooled liquid. When reheated, the phase transitions and associated temperatures match those of the initial heating sequence (Figure 3.4). Additionally, when nucleation of the eutectic phase is prevented by cooling to only 398 K, the eutectic melting peak is no longer present in the reheating step (not shown). These results indicate that the two exothermic transition peaks definitively correspond to those of the two endothermic phase transitions.
Figure 3.4. Differential scanning calorimetry of an equimolar anthracene (1) + pyrene (2) mixture.

In order to more completely explore phase behavior, it was necessary to use a melting temperature analyzer. Although the DSC measures the energy of a phase transition, it is not possible to visually observe the processes. Melting temperatures were measured for all pure components and mixtures and are given in Table 3.5. The melting temperatures were measured in heating mode at $1 \pm 0.5 \text{ K-min}^{-1}$. This relatively slow rate allows for more precise measurement of melting temperatures. The results show that solid, quench-cooled anthracene (1) + pyrene (2) mixtures
have a eutectic point of $404 \pm 1 \, \text{K}$ at $x_1 = 0.22 \pm 2 \cdot 10^{-4}$. For all other compositions, only a portion of the crystals melts at the eutectic temperature. Consequently, both solid and liquid coexist until the liquidus temperature is reached. Thus, Figure 3.5 represents a phase diagram for the anthracene (1) + pyrene (2) system in which only solid phases exist below the thaw curve and only a liquid phase exists above the liquidus curve. The areas between these curves show the equilibrium coexistence of both solid and liquid phases. The point at which the liquidus curve meets the thaw temperature is the anthracene + pyrene eutectic point. Similar results have been previously reported by both Kravchenko (1953) and Szczepanik and Skalmowski (1963) who report a eutectic point of $403.15 \, \text{K}$ and $404.6 \, \text{K}$ at $x_1 = 0.209$ and 0.221, respectively.
Figure 3.5. Phase diagram and $\Delta_{\text{fus}}H$ of the anthracene (1) + pyrene (2) system: -○-, thaw curve; -□-, liquidus curve; ▲, $\Delta_{\text{fus}}H_{\text{eutectic peak}}$; dash-dot-dashed line, estimated $\Delta_{\text{fus}}H_{\text{eutectic peak}}$ from eq 3.3.3 and 3.3.6; ..△.., $\Delta_{\text{fus}}H_{\text{tot}}$, with error bars representing uncertainty.
Table 3.5. Measured melting temperatures and enthalpies of fusion of the anthracene (1) + pyrene (2) system.

<table>
<thead>
<tr>
<th>$x_1$</th>
<th>$T_{\text{fus, thaw}}$/K</th>
<th>$T_{\text{fus, liquidus}}$/K</th>
<th>$\Delta_{\text{fus}}H_\text{i}$/ J·g$^{-1}$</th>
<th>$\Delta_{\text{fus}}H_\text{tot}$/ J·g$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.00 ± 0</td>
<td>424 ± 1</td>
<td>424 ± 1</td>
<td>0 ± 0</td>
<td>80 ± 5.6</td>
</tr>
<tr>
<td>0.10 ± 1·10$^{-4}$</td>
<td>404 ± 1</td>
<td>419 ± 1</td>
<td>47 ± 3.3</td>
<td>83 ± 5.8</td>
</tr>
<tr>
<td>0.12 ± 1·10$^{-4}$</td>
<td>404 ± 1</td>
<td>418 ± 1</td>
<td>73 ± 5.1</td>
<td>73 ± 5.1</td>
</tr>
<tr>
<td>0.15 ± 2·10$^{-4}$</td>
<td>404 ± 1</td>
<td>415 ± 1</td>
<td>83 ± 5.8</td>
<td>83 ± 5.8</td>
</tr>
<tr>
<td>0.18 ± 2·10$^{-4}$</td>
<td>404 ± 1</td>
<td>413 ± 1</td>
<td>89 ± 6.2</td>
<td>89 ± 6.2</td>
</tr>
<tr>
<td>0.20 ± 2·10$^{-4}$</td>
<td>404 ± 1</td>
<td>409 ± 1</td>
<td>89 ± 6.2</td>
<td>89 ± 6.2</td>
</tr>
<tr>
<td>0.22 ± 2·10$^{-4}$</td>
<td>404 ± 1</td>
<td>406 ± 1</td>
<td>92 ± 6.4</td>
<td>92 ± 6.4</td>
</tr>
<tr>
<td>0.24 ± 2·10$^{-4}$</td>
<td>404 ± 1</td>
<td>409 ± 1</td>
<td>88 ± 6.1</td>
<td>88 ± 6.2</td>
</tr>
<tr>
<td>0.26 ± 3·10$^{-4}$</td>
<td>404 ± 1</td>
<td>413 ± 1</td>
<td>87 ± 6.1</td>
<td>87 ± 6.1</td>
</tr>
<tr>
<td>0.28 ± 3·10$^{-4}$</td>
<td>404 ± 1</td>
<td>418 ± 1</td>
<td>82 ± 5.7</td>
<td>82 ± 5.7</td>
</tr>
<tr>
<td>0.30 ± 3·10$^{-4}$</td>
<td>404 ± 1</td>
<td>422 ± 1</td>
<td>86 ± 6.0</td>
<td>86 ± 6.0</td>
</tr>
<tr>
<td>0.50 ± 5·10$^{-4}$</td>
<td>404 ± 1</td>
<td>453 ± 1</td>
<td>54 ± 3.8</td>
<td>98 ± 6.8</td>
</tr>
<tr>
<td>0.75 ± 8·10$^{-4}$</td>
<td>404 ± 1</td>
<td>475 ± 1</td>
<td>21 ± 1.5</td>
<td>101 ± 7.1</td>
</tr>
<tr>
<td>0.90 ± 9·10$^{-4}$</td>
<td>404 ± 1</td>
<td>485 ± 1</td>
<td>9 ± 0.6</td>
<td>106 ± 7.4</td>
</tr>
<tr>
<td>1.00 ± 0</td>
<td>490 ± 1</td>
<td>490 ± 1</td>
<td>0 ± 0</td>
<td>156 ± 10.9</td>
</tr>
</tbody>
</table>

In addition to the melting temperatures, the results from the thermal analyses are given in Table 3.5 and shown in Figure 3.5. The $\Delta_{\text{fus}}H$ observed at the eutectic temperature of 404 K characterizes the necessary heat input for the initial melting to occur. The total $\Delta_{\text{fus}}H$ is a summation of both endothermic phase transition peaks observed in the DSC scan. It is worth noting that the total $\Delta_{\text{fus}}H$ is very similar to that of pure pyrene over a wide range of compositions and that the $\Delta_{\text{fus}}H$ for both pure pyrene and the eutectic mixture are very similar. What this means is that when the mixture contains only a modest amount of anthracene, energetically it behaves quite similarly to pure pyrene, and this persists until the mixture is nearly pure anthracene. There is a slight increase in fusion enthalpy when the mixtures are enriched in anthracene beyond the eutectic composition, but the shift is only modest as compared with the increase of fusion enthalpy to that of pure anthracene. This indicates that the ability of anthracene to reach a lower energy
crystalline configuration is significantly impeded by the presence of relatively small amounts of pyrene.

In Figure 3.5, the data for $\Delta_{\text{fus}}H$ at the eutectic temperature clearly establishes that the eutectic is a thermodynamically preferred phase, whose formation is limited by the system stoichiometry. At low concentrations of anthracene, eutectic formation is limited by the availability of anthracene. Since the actual eutectic composition occurs near $x_1 = 0.22$, at low anthracene concentrations, addition of $N_1$ moles anthracene produces $(N_1 + (78/22) \cdot N_1 = 4.55 \cdot N_1)$ moles of eutectic. This means that as an approximation for small additions of anthracene,

$$\frac{d\Delta H_{\text{eutectic peak}}}{dN_1} = 4.55 \cdot \Delta H_e$$

(3.3.1)

in which the $\Delta H_e$ represents the molar enthalpy of fusion of the pure eutectic phase. If the addition of anthracene is done while keeping the total moles in the system roughly constant, then since $d(N_1/N_{\text{tot}}) = dx_1$ it is possible to see that

$$\frac{d\Delta H_{\text{eutectic peak}}}{dx_1} = 4.55 \cdot \Delta H_{e,\text{max}}$$

(3.3.2)

where $\Delta H_{e,\text{max}}$ is now the maximum enthalpy of fusion at the eutectic point.

Integration gives as a result (for the relevant range of anthracene-limited eutectic formation)

$$\Delta H_{\text{eutectic peak}} = 4.55 \cdot 90 \ J \cdot g^{-1} \cdot x_1 = 410 \cdot x_1 \ J \cdot g^{-1}$$

(3.3.3)
This is valid only for \( x_1 < 0.22 \). So for example at \( x_1 = 0.10 \), the predicted enthalpy for the 404 K peak is 41 J⋅g\(^{-1}\), whereas the measured value is just slightly greater than this.

Beyond the eutectic composition, \( x_1 > 0.22 \), the concentration of pyrene is assumed to limit the ability to form the eutectic phase. Again, for the eutectic, it is true that \( \left( \frac{x_{1,e}}{x_{2,e}} \right) = 0.22/0.78 = 0.282 \). The fraction of moles involved in forming the eutectic can be expressed as \( (\underline{x_e} = x_{1,e} + x_{2,e}) \), but since pyrene is assumed to be the limiting component, it is possible to say that \( (\underline{x_e} = x_{2,e}) \), i.e., all of the pyrene is in the eutectic phase. It is true that \( (x_1 + x_2 = 1) \), which means

\[
x_e = x_{1,e} + (1 - x_1) = 0.282 \cdot x_{2,e} + (1 - x_1) = 1.282 \cdot (1 - x_1)
\]

(3.3.4)

This in turn means that for \( x_1 > 0.22 \)

\[
\frac{d\Delta H_{\text{eutectic peak}}}{dx_1} = -1.282 \cdot \Delta H_{e,\text{max}}
\]

(3.3.5)

Upon integration, this yields

\[
\Delta H_{\text{eutectic peak}} = 90 \; J \cdot g^{-1} - 1.282 \cdot 90 \; J \cdot g^{-1} \cdot (x_1 - 0.22) = 90 \; J \cdot g^{-1} - 115 \cdot (x_1 - 0.22) \; J \cdot g^{-1}
\]

(3.3.6)

So for example, at \( x_1 = 0.50 \), the enthalpy of fusion at 404 K is predicted to be about 58 J⋅g\(^{-1}\). This is in reasonable agreement with the observed value.

The agreement between the values obtained from this simple modeling of system behavior and experiment are shown in Figure 3.5 and strongly support the
conclusion that formation of a eutectic phase at $x_1 = 0.22$ is thermodynamically favored. What this means is that the enthalpy of fusion per gram of the non-eutectic phase is increasing proportionally with anthracene fraction, since overall, the enthalpy of fusion of the whole mixture does not vary much with composition. The enthalpy of fusion of the non-eutectic anthracene-rich phase is not the same as that of pure anthracene, meaning that there must be some contribution of pyrene to this phase until the mixture approaches truly pure anthracene.

**X-Ray Diffraction**

Powder X-ray diffraction studies were conducted to study the crystal structures of anthracene (1) + pyrene (2) mixtures in comparison to those of the pure components. The results are qualitative. The peak intensity from one spectrum to another has no significance and was related only to the quantity of sample used (mixtures were used more sparingly).

Peak positions from the mixture results can be compared to those of the pure component X-ray diffraction patterns. Figure 3.6 shows that the crystal structure of the eutectic mixture is similar to that of pyrene because peaks at 10.6, 11.6, 14.9, 16.3, 18.2, 23.3, 24.7 and 28.0 deg are all retained in the mixture diffraction pattern. This is consistent with the DSC result that implies that the $\Delta_{\text{fus}}H$ of the eutectic is very close to that of pure pyrene. This indicates that the crystal structures of the eutectic mixture and pure pyrene are similar. Likewise, Figure 3.6 shows that the crystal structure of a mixture at $x_1 = 0.90$ is comparable to that of pure anthracene.
This suggests that the crystal structure of anthracene is approached at low levels of pyrene.

Figure 3.6. X-ray diffraction patterns of pure components and mixtures: A, pure anthracene (1); B, pure pyrene (2); C, anthracene-rich mixture at $x_1 = 0.90$; D, eutectic mixture $x_1 = 0.22$.

Figure 3.7 is an enlargement of the X-ray pattern from Figure 3.6 between 10 and 12 deg. When reviewed at this magnification, it is possible to see the minor differences in the peaks for pyrene and the eutectic. In this case, the peak from the eutectic mixture at 10.6 deg has lost the doublet from the pure pyrene peak.
Additionally, the peaks near 11.6 deg do not align perfectly. The eutectic mixture retains much of the crystal structure of pure pyrene, indicating that the eutectic composition is a pyrene-like mixture that does not completely preserve the pure component characteristics. Again, this is consistent with the results of the thermal analysis.

Figure 3.7. Magnified portion of X-ray diffraction pattern from Figure 3.6 that shows the modified-pyrene peaks in the eutectic anthracene (1) + pyrene (2) mixture: B, pure pyrene (2); D, eutectic mixture $x_1 = 0.22$. 
Vapor Pressure

Knudsen effusion experiments were conducted by measuring the vapor pressure of various initial quench-cooled mixtures and pure components. The measured vapor pressure of pure anthracene $\ln P_1 / \text{Pa} = 32.211 - 11683 \cdot T / \text{K}^{-1}$ (300 to 373 K), and pyrene $\ln P_2 / \text{Pa} = 31.735 - 11679 \cdot T / \text{K}^{-1}$ (315 to 378 K), compare favorably to literature values (Goldfarb and Suuberg, 2008). Based on the notion that anthracene and pyrene were individual organic compounds, it was originally hypothesized that mixtures of the two components would behave ideally and sublime according to a weighted average of pure component vapor pressures, i.e., Raoult’s law would be followed. Figure 3.8 shows that this did not hold true. Continuous vapor pressure measurements were performed on samples of known initial composition. Instead of approaching the ideal mixture values, the vapor pressures of the anthracene (1) + pyrene (2) mixtures initially behaved as a sum of the two pure species vapor pressures. Again, this summation represents the maximum possible pressure in the effusion cell because the vapor pressure cannot exceed that of the pure, equilibrated species. These data could be interpreted as indicating that mixtures of anthracene and pyrene are phase-separated systems in which the pure species do not interact. However, the aforementioned phase diagram and X-ray data show that the species are interacting in a complicated, non-ideal way.
Vapor pressure measurements were continuously performed on a sample of known initial composition. These experiments required that the composition of the mixture be known throughout the sequence. Thus, samples were occasionally removed from the effusion cells, dissolved in dichloromethane, and analyzed by GC-MS. Reported mole fractions are accurate to ± 0.01. Figure 3.9 shows the results of two experiments that examined vapor pressure as a function of mass loss of an
initially eutectic mixture. Both experiments initially tracked vapor pressure at 318.2 K to the point at which the vapor pressure stabilized. It needs to be kept in mind that upon vaporization, unless both components vaporize at exactly the same rate, composition, and with that, vapor pressure, will continuously change. With reference to Figure 3.8, it is seen that anthracene is the more volatile pure component (despite its higher melting temperature compared with pyrene). As anthracene is then preferentially lost in the experiment of Figure 3.9, the vapor pressure would drop, unless the two components behave as separate pure phases.

The decreasing vapor pressure shown in Figure 3.9 establishes that for the purposes of vapor pressure, there is interaction between components. Interestingly, a subsequent, stable vapor pressure was then achieved after loss of about 13% by mass of the initial mixture. The overlapping vapor pressure data in the low temperature (318.2 K) region of Figure 3.9 represent two separate samples and demonstrate the degree of reproducibility of this experimental method.
At this point, the temperature was increased to 333.2 K and 338.2 K for the remainder of the experiments of Figure 3.9. As a result of the increase in temperature, measured vapor pressure increases, as expected. The dashed and dotted lines of Figure 3.9 show theoretical maximum vapor pressures that would exist for independent anthracene (1) and pyrene (2) phases.

GC-MS analysis showed that the mole fraction of anthracene in the solid was reduced from an initial value of $x_1 = 0.22$ to $x_1 = 0.14$ during the transient at 318.2 K.
Once this stable composition was reached, both the vapor pressure and the composition remained unchanged for the remainder of the experiment. This indicates that mixtures of anthracene and pyrene form a solid-azeotrope at $x_1 = 0.14$. It is important to bear in mind the distinction between the eutectic mixture and the azeotrope. The eutectic mixture exhibits a minimum melting temperature at $x_1 = 0.22$. The azeotrope is a constant subliming mixture at $x_1 = 0.14$. There is no particular reason that the eutectic and azeotrope should occur at the same composition (Section 3.5).

It is now possible to extract the data from Figure 3.9 to characterize the behavior of the azeotrope as a function of temperature (Figure 3.10). The maximum possible vapor pressure and Raoult’s law prediction for a mixture at $x_1 = 0.14$ have been plotted along with the measured azeotrope data. Although the azeotrope happens to give a vapor pressure close to the Raoult’s law value for that mixture composition, the observed behavior does not represent ideal thermodynamic mixture behavior. If the system were behaving ideally, the composition of the mixture would change throughout the experiment causing both the experimental vapor pressure and reference curves to shift accordingly. This does not occur with the azeotrope, which sublimes at constant composition.
Figure 3.10. Vapor pressure of the solid azeotrope at $x_1 = 0.14$: -•-, $P_{\text{measured}}$; dotted line, $P_{\text{max}}$; dash-dot-dashed line, Raoult’s law prediction for $x_1 = 0.14$.

The results for the case of an anthracene-rich mixture initially at $x_1 = 0.90$, are shown in Figures 3.11 and 3.12. The mixture also forms a solid azeotrope at $x_1 = 0.99$. This suggests the existence of an inhomogeneous mixture that must partially sublime before the solid azeotrope is reached. The vapor pressure measurements shown in Figure 3.12 were taken after the azeotrope concentration was achieved in the experiments of Figure 3.11. The vapor pressure of the azeotrope at $x_1 = 0.99$ is close to that of pure anthracene, suggesting that the vapor pressure is insensitive to
the existence of $x_2 = 0.01$ in the crystal structure. This is consistent with the X-ray patterns (Figure 3.6) and the phase diagram (Figure 3.5) showing that the anthracene-rich mixture has a crystal structure, liquidus temperature, and enthalpy of fusion approaching that of pure anthracene. In other words, the behavior of the anthracene (1) + pyrene (2) system approaches that of pure anthracene when the pyrene impurity level reaches $x_2 = 0.01$. To call this an azeotrope such as that at $x_1 = 0.14$ is perhaps misleading. In fact, it is suggested that instead, this low level of pyrene impurity can be retained in the anthracene crystallographic structure without any significant impact on measured thermodynamic properties.
Figure 3.11. Vapor pressure and composition of an anthracene-rich mixture versus sample mass loss: solid line, $P_{\text{measured}}$; dotted line, $P_{1, 338.2 \, \text{K}}$; dashed line, $P_{1, 333.2 \, \text{K}}$; dash-dot-dashed line, $P_{\text{max}, 318.2 \, \text{K}}$; dashed-dotted line, $P_{1, 318.2 \, \text{K}}$; -•-, measured $x_1$ of solid mixture.
Figure 3.12. Vapor pressure of the solid azeotrope at \( x_1 = 0.99 \): -•-, \( P_{\text{measured}} \); dotted line, \( P_{\text{max}} \); dash-dot-dashed line, \( P_1 \).

The results for the case of a pyrene-rich mixture, initially at \( x_1 = 0.10 \), are given in Figures 3.13 and 3.14. The mixture forms a solid azeotrope at \( x_1 = 0.03 \). As with the eutectic composition and anthracene-rich mixtures, this final mixture only reaches a stable vapor pressure when the azeotrope concentration is obtained. This again implies the existence of an inhomogeneous mixture that gradually gives way to the azeotrope behavior. Note that the Raoult’s law vapor pressure predictions for the mixture at \( x_1 = 0.03 \) are not given in Figures 3.13 or 3.14 because they are
essentially that of pure pyrene. The reference curves of Figures 3.13 and 3.14 show that the pyrene-rich azeotrope at \( x_1 = 0.03 \) has a unique vapor pressure close to that of the azeotrope at \( x_1 = 0.14 \). This result suggests that the anthracene (1) + pyrene (2) system is capable of forming multiple azeotropes. Although binary polyazeotropy is rare, it has been reported in the literature (Christensen and Olson, 1992; Aucejo et al., 1997). This, then, is in sharp contrast to the behavior of the anthracene-rich mixture, in which pure phase behavior was approached. Here, sublimation of the mixture occurs at constant composition, significantly removed from pure pyrene behavior, for substantial extents of mass loss. The measured vapor pressures for the three solid azeotropes are tabulated and given in Table 3.6. It is interesting to note that the commercial supply impurities of both anthracene and pyrene were at the respective azeotrope type limits.
Figure 3.13. Vapor pressure and composition of a pyrene-rich mixture versus sample mass loss: solid line, $P_{\text{measured}}$; large-dashed line, $P_2, 338.2$ K; dashed-dotted line, $P_{318.2}$ K of azeotrope at $x_1 = 0.14$; dash-dot-dashed line, $P_{\text{max}, 318.2}$ K; small-dashed line, $P_2, 318.2$ K; dotted line, $P_{338.2}$ K of azeotrope at $x_1 = 0.14$; - - measured $x_1$ of solid mixture.
Figure 3.14. Vapor pressure of the solid azeotrope at $x_1 = 0.03$: -•-, $P_{\text{measured}}$; dotted line, $P_{\text{max}}$; dashed line, $P$ of azeotrope at $x_1 = 0.14$; dash-dot-dashed line, $P_2$. 
### Table 3.6 Measured vapor pressures of the three solid anthracene (1) + pyrene (2) azeotropes.

<table>
<thead>
<tr>
<th>Azeotrope $x_1 = 0.03$</th>
<th>Azeotrope $x_1 = 0.14$</th>
<th>Azeotrope $x_1 = 0.99$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$T/K$</td>
<td>$P/Pa$</td>
<td>$T/K$</td>
</tr>
<tr>
<td>318.1</td>
<td>0.0087</td>
<td>318.1</td>
</tr>
<tr>
<td>333.1</td>
<td>0.0474</td>
<td>333.1</td>
</tr>
<tr>
<td>338.1</td>
<td>0.0773</td>
<td>338.1</td>
</tr>
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</table>

### 3.4 Results and Discussion: Anthracene + Benzo[a]pyrene Solid Mixtures

#### Summary of Results

Similar thermochemical and vapor pressure experiments were used to examine the phase behavior of the anthracene (1) + benzo[a]pyrene (2) system. A solid-liquid phase diagram was mapped for the mixture. A eutectic point occurs at $x_1 = 0.26$. The eutectic mixture is an amorphous solid that lacks organized crystal structure and melts between 414 and 420 K. For mixtures that contain $0.10 < x_1 < 0.90$, the enthalpy of fusion is dominated by that of the eutectic. Solid-vapor equilibrium studies show that mixtures of anthracene and benzo[a]pyrene at $x_1 < 0.10$ sublime at the vapor pressure of pure benzo[a]pyrene. These results suggest
that the solid-vapor equilibrium of benzo[a]pyrene is not significantly influenced by moderate levels of anthracene in the crystal structure.

**Phase Diagram and Enthalpy of Fusion**

Results from typical DSC scans are given in Figure 3.15. All four scans were conducted in heating-mode at 10 K·min⁻¹. The full heating, cooling, and reheating scan is given for pure benzo[a]pyrene. The anthracene scan has been shown to be in fair agreement Domalski and Hearing (1996) who report that pure anthracene melts at 489 K with $\Delta_{\text{fus}}H = 164.8$ J·g⁻¹. In the case of pure benzo[a]pyrene, two phase transitions were observed in the initial heating sequence. It was determined that the first peak in the scan is not that of a melting endotherm. Rather, it is attributable to a crystal transition and is previously reported by Casellato et al. (1973). The second peak in the benzo[a]pyrene scan at 449 K corresponds to the true solid to liquid phase transition and indicates a $\Delta_{\text{fus}}H = 44.6$ J·g⁻¹. As the liquid benzo[a]pyrene sample is subsequently cooled and reheated, a single subcooled fusion exotherm and single melting endotherm are repeatedly observed. This indicates that the initial crystal structure is not recovered during fusion and is likely a result of synthesis and purification. The commonly reported fusion enthalpy of benzo[a]pyrene contains both the crystal transition and melting endotherms (Casellato et al., 1973; Acree, 1991). Since all mixture samples were melted and quench cooled prior to analysis, this study reports the fusion enthalpy of pure benzo[a]pyrene to be $44.6 \pm 3.1$ J·g⁻¹, corresponding only to the true melting behavior in the DSC scan. It is worth noting
that the enthalpy of crystallization from the subcooled fusion exotherm matches the reported enthalpy of fusion within the experimental uncertainty.

Figure 3.15. Differential scanning calorimetry results of pure components and mixtures: solid line, pure benzo(a)pyrene (2); dashed line, pure anthracene (1); dash-dot-dashed line, mixture at $x_1 = 0.30$; dotted line, mixture at $x_1 = 0.70$.

Mixture compositions are again given in terms of $x_1$ as anthracene mole fraction and it is understood that $x_1 + x_2 = 1$. The DSC results indicate that anthracene (1) + benzo[a]pyrene (2) quench-cooled mixtures in the indicated composition range undergo a phase transition between 414 and 420 K, well before
either of the pure phases melts. This indicates the existence of a eutectic mixture. In some cases, such as the one shown for a mixture at $x_1 = 0.70$, there appear to be two phase transitions as the sample is heated. These results are similar to the anthracene + pyrene results reported in section 3.3.

As with the anthracene + pyrene mixtures, vapors interdiffuse in the vapor-solid system and a thermodynamically favored eutectic exists for this anthracene + benzo[a]pyrene system, irrespective of initial preparation (i.e., these results were not sensitive to quench cooling).

It is worth noting with regard to the results of Figure 3.15 that since all evidence of an anthracene and benzo[a]pyrene solid phase disappear in the presence of the lower temperature eutectic phase peak, neither pure anthracene nor benzo[a]pyrene are stable phases in such mixture systems. Figure 3.16 shows the full DSC scan of an anthracene + benzo[a]pyrene mixture at $x_1 = 0.70$. As previously discussed, the mixture at $x_1 = 0.70$ undergoes two endothermic phase transitions upon heating. Then cooling at a rate of 2.5 K·min$^{-1}$ induces crystallization at 440 K of what is most probably an inhomogeneous phase that has limited solubility in the eutectic. This is followed by crystallization of the eutectic phase itself at 411 K. As was the case for the anthracene + pyrene mixtures, each of these phase transitions represents the crystallization of a subcooled liquid. When reheated, the phase transitions and associated temperatures match those of the initial heating sequence (Figure 3.16). Additionally, when nucleation of the eutectic phase is prevented by cooling to only 423 K, the eutectic melting peak is no longer present in the reheating
step (not shown). These results indicate that the two exothermic transition peaks definitively correspond to those of the two endothermic phase transitions.

Figure 3.16. Differential scanning calorimetry of an anthracene (1) + benzo[a]pyrene (2) mixture at $x_2 = 0.70$.

To visually observe the phase transitions, a melting temperature analyzer was used to measure the melting temperatures of all pure components and mixtures. The results are given in Table 3.7. The process is analogous to that discussed in Section 3.3. The results show that solid, quench-cooled anthracene (1)
+ benzo[a]pyrene (2) mixtures form a eutectic phase that melts between 414 and 420 ± 1 K at $x_1 = 0.26 ± 2 \cdot 10^{-4}$. For all other compositions, only a portion of the crystals melts in the eutectic temperature range. Consequently, both solid and liquid coexist until the liquidus temperature is reached. Thus, Figure 3.17 represents a phase diagram for the anthracene (1) + benzo[a]pyrene (2) system in which only solid phases exist below the thaw curve and only a liquid phase exists above the liquidus curve. The areas between these curves show the equilibrium coexistence of both solid and liquid phases. The point at which the liquidus curve meets the eutectic temperature range is the anthracene + benzo[a]pyrene eutectic point. Since the eutectic mixture does not melt at a singular temperature, defining this as a eutectic point is confusing and requires further explanation. So it is suggested here that mixtures of anthracene and benzo[a]pyrene form a single, amorphous, solid eutectic phase at $x_1 = 0.26$ that lacks any organized crystal structure and which melts throughout the 414 to 420 K temperature range. This region of phase transition, represented by the shaded region of Figure 3.17, is not rate dependant and is observed in both the DSC and melting temperature analyzer for all combinations of anthracene + benzo[a]pyrene, providing assurance that this region represents the melting temperature range of a single, amorphous, solid phase. Further evidence supporting this conclusion will be presented in a later X-ray diffraction section.
Table 3.7. Measured melting temperatures and enthalpies of fusion of the anthracene (1) + benzo[a]pyrene (2) system.

<table>
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<tr>
<th>(x_1)</th>
<th>(T_{\text{fus,mel}}/\text{K})</th>
<th>(T_{\text{fus,liquidus}}/\text{K})</th>
<th>(\Delta_{\text{fus}}H / \text{J} \cdot \text{g}^{-1})</th>
<th>(\Delta_{\text{fus}}H_{\text{tot}} / \text{J} \cdot \text{g}^{-1})</th>
</tr>
</thead>
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<td>0.00 ± 0</td>
<td>449 ± 1</td>
<td>449 ± 1</td>
<td>0 ± 0</td>
<td>44.6 ± 3.1</td>
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<tr>
<td>0.10 ± 1 \cdot 10^{-4}</td>
<td>414 ± 1</td>
<td>438 ± 1</td>
<td>21.1 ± 1.5</td>
<td>33.0 ± 2.3</td>
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<td>0.20 ± 1 \cdot 10^{-4}</td>
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<td>425 ± 1</td>
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<td>56.9 ± 4.0</td>
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<td>0.22 ± 2 \cdot 10^{-4}</td>
<td>414 ± 1</td>
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<td>55.0 ± 3.9</td>
<td>60.0 ± 4.2</td>
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<td>414 ± 1</td>
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<td>0.26 ± 3 \cdot 10^{-4}</td>
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<td>46.6 ± 3.3</td>
</tr>
<tr>
<td>0.42 ± 4 \cdot 10^{-4}</td>
<td>414 ± 1</td>
<td>433 ± 1</td>
<td>47.4 ± 3.3</td>
<td>61.9 ± 4.3</td>
</tr>
<tr>
<td>0.50 ± 5 \cdot 10^{-4}</td>
<td>414 ± 1</td>
<td>440 ± 1</td>
<td>40.4 ± 2.8</td>
<td>68.0 ± 4.8</td>
</tr>
<tr>
<td>0.70 ± 8 \cdot 10^{-4}</td>
<td>414 ± 1</td>
<td>468 ± 1</td>
<td>21.2 ± 1.5</td>
<td>79.4 ± 5.6</td>
</tr>
<tr>
<td>0.90 ± 9 \cdot 10^{-4}</td>
<td>414 ± 1</td>
<td>486 ± 1</td>
<td>5.37 ± 0.4</td>
<td>103 ± 7.2</td>
</tr>
<tr>
<td>1.00 ± 0</td>
<td>490 ± 1</td>
<td>490 ± 1</td>
<td>0 ± 0</td>
<td>156 ± 10.9</td>
</tr>
</tbody>
</table>
Figure 3.17. Phase diagram and $\Delta_{\text{fus}}H$ of the anthracene (1) + benzo[a]pyrene (2) system: large-dashed line, thaw curve; -□-, liquidus curve; ▲, $\Delta_{\text{fus}}H_{\text{eutectic peak}}$; dash-dot-dashed line, estimated $\Delta_{\text{fus}}H_{\text{eutectic peak}}$ from eq 3.4.1 and 3.4.2; ..△.., $\Delta_{\text{fus}}H_{\text{tot}}$, with error bars representing uncertainty; shaded region, eutectic melting range.

The results from the thermal analyses are listed in Table 3.7 and shown in Figure 3.17. As was the case for the anthracene + pyrene mixtures, the total $\Delta_{\text{fus}}H$ of the new anthracene + benzo[a]pyrene mixtures is very similar to that of the eutectic mixture over a wide range of compositions. So, in this case, when the mixture contains only modest amounts of anthracene and benzo[a]pyrene, the energetics of the eutectic phase are favored and characterize the mixture system. It is not until the mixtures are enriched in either anthracene or benzo[a]pyrene beyond the
eutectic composition that the fusion enthalpy shifts towards that of the pure
components. This indicates that the ability of anthracene to reach a lower energy
crystalline configuration is significantly impeded by the presence of relatively small
amounts of not only pyrene (section 3.3), but now benzo[a]pyrene and potentially
other similarly structured PAHs.

In Figure 3.17, the data for $\Delta_{\text{fus}}H$ at the eutectic temperature clearly
establishes that the eutectic is a thermodynamically preferred phase, whose
formation is limited by the system stoichiometry. At low concentrations of
anthracene, eutectic formation is limited by the availability of anthracene. Since the
actual eutectic composition occurs near $x_1 = 0.26$, at low anthracene concentrations,
addition of $N_1$ moles anthracene produces $(N_1 + (74/26) \cdot N_1 = 3.85 \cdot N_1)$ moles of
eutectic. Now recall and apply the mathematics given in the previous section to
predict the enthalpy of fusion for the relevant range of anthracene-limited eutectic
formation as follows:

$$\Delta H_{\text{eutectic peak}} = 3.85 \cdot 60.7 \, \text{J} \cdot \text{g}^{-1} \cdot x_1 = 234 \cdot x_1 \, \text{J} \cdot \text{g}^{-1}$$

(3.4.1)

This is valid only for $x_1 < 0.26$. So for example at $x_1 = 0.10$, the predicted enthalpy for
the eutectic peak is 23.4 J·g⁻¹, whereas the measured value is just slightly lower than
this.

Beyond the eutectic composition, $x_1 > 0.26$, the concentration of
benzo[a]pyrene is assumed to limit the ability to form the eutectic phase. Again, for
the eutectic, it is true that $(x_{1,e}/x_{2,e} = 0.26/0.74 = 0.351)$ and the predicted enthalpy of
fusion for this range of benzo[a]pyrene-limited eutectic formation is given by

$$\Delta H_{\text{eutectic peak}} = 60.7 \text{ J} \cdot \text{g}^{-1} - 1.351 \cdot 60.7 \text{ J} \cdot \text{g}^{-1} \cdot (x_1 - 0.26) = 60.7 \text{ J} \cdot \text{g}^{-1} - 82 \cdot (x_1 - 0.26) \text{ J} \cdot \text{g}^{-1}$$

(3.4.2)

So for example, at $x_1 = 0.50$, the enthalpy of fusion at 414 K is predicted to be about 41 J·g⁻¹. This is in agreement with the observed value.

The agreement between the values obtained from this simple modeling of system behavior and experiment is shown in Figure 3.17 and strongly support the conclusion that formation of a eutectic phase at $x_1 = 0.26$ is thermodynamically favored. This result is analogous to that of the anthracene + pyrene mixture and hence similar conclusions can be drawn. Here, the enthalpy of fusion per gram of the non-eutectic phase is increasing proportionally with anthracene fraction, since overall, the enthalpy of fusion of the whole mixture does not vary much with composition. The enthalpy of fusion of the non-eutectic anthracene-rich phase is not the same as that of pure anthracene, meaning that there must be some contribution of benzo[a]pyrene to this phase until the mixture approaches truly pure anthracene.

**X-ray Diffraction**

Powder X-ray diffraction studies were conducted to study the crystal structures of anthracene (1) + benzo[a]pyrene (2) mixtures in comparison to those of the pure components. Details of the procedure are identical to those provided in the previous two sections.

Peak positions from the mixture results can be compared to those of the pure component X-ray diffraction patterns. Figure 3.18 shows that the eutectic mixture
lacks any organized crystal structure because the few peaks that exist in the X-ray pattern are not well defined and do not rise much above the baseline. Additionally there is no real similarity between the eutectic mixture scan and those of the pure components. This result is consistent with the DSC and melting point studies that imply that the mixtures form a single, amorphous solid phase at the eutectic composition.

**Figure 3.18.** X-ray diffraction patterns of pure components and mixtures: D, pure anthracene (1); C, pure benzo(a)pyrene (2); B, eutectic mixture; A, benzo[a]pyrene rich mixture at $x_1 = 0.10$. 
Figure 3.18 also shows that the crystal structure of a mixture at $x_1 = 0.10$ is comparable to that of pure benzo[a]pyrene because peaks at 16.8, 23.4, 23.8 and 26.4 deg are all retained in the mixture diffraction pattern. This suggests that the crystal structure of benzo[a]pyrene is approached at low levels of anthracene. When X-ray patterns are reviewed at higher magnification, it is possible to see the minor differences in the peaks for a benzo[a]pyrene-rich mixture and pure benzo[a]pyrene. This means that although the mixture retains much of the crystal structure of pure benzo[a]pyrene, the pure component characteristics are not completely preserved in the mixture. Again, this is consistent with the results of the thermal analysis that suggest that the energetics of the pure components are only approached when mixtures are highly enriched in either anthracene or benzo[a]pyrene.

**Vapor Pressure**

Knudsen effusion experiments were conducted by measuring the vapor pressure of various initial quench-cooled mixtures and pure components. The measured vapor pressure of pure anthracene $\ln P_1 / \text{Pa} = 32.211 - 11683 \cdot T / \text{K}^{-1}$ (300 to 373 K), and benzo[a]pyrene $\ln P_2 / \text{Pa} = 32.802 - 13971 \cdot T / \text{K}^{-1}$ (358 to 428 K), compare favorably to literature values (Goldfarb and Suuberg, 2008). Continuous vapor pressure measurements were performed on samples of known initial composition (Figures 3.19 and 3.20). Instead of approaching the ideal mixture values, the vapor pressures of the anthracene (1) + benzo[a]pyrene (2) mixtures initially behaved as a sum of the two pure species vapor pressures. This is the
maximum possible vapor pressure and, due to the relatively low vapor pressure of benzo[a]pyrene, it is essentially that of pure anthracene. As was the case with the anthracene + pyrene mixtures, these data could be interpreted as indicating that anthracene and benzo[a]pyrene do not interact in the solid mixture. However, the aforementioned phase diagram and X-ray data show that the species are interacting in a complicated, non-ideal way.

Figure 3.19. Vapor pressure measurements of an anthracene (1) + benzo[a]pyrene (2) mixture initially at $x_1=0.30$. 

Figure 3.20. Vapor pressure measurements of anthracene (1) + benzo[a]pyrene (2) mixtures with varied initial composition: solid line, \( P_{\text{max}} \approx P_1 \); dashed line, \( P_2 \); \( P_{\text{Mix} x_{1,\text{initial}}} = 0.30 \); \( P_{\text{Mix} x_{1,\text{initial}}} = 0.10 \); \( P_{1 + 2} \) at \( x_{1,\text{initial}} = 0.30 \); \( P_{1 + 2} \) at \( x_{1,\text{initial}} = 0.10 \); \( P_{1 + 2} \) at \( x_{1,\text{initial}} = 0.70 \).

As the measurements of Figures 3.19 and 3.20 progress towards higher temperature, the vapor pressures decrease and this establishes that for the purposes of vapor pressure, there is interaction between components. The decreasing vapor pressure in Figure 3.20 is path dependent, based on mass loss and is not meant to represent the equilibrium vapor pressure of the mixture. This region of transient vapor pressure is shown only for an initially eutectic mixture, but is observed for all anthracene (1) + benzo[a]pyrene (2) mixture compositions.
Interestingly, a subsequent, stable vapor pressure was ultimately achieved and is shown for an assortment of mixtures with varied initial composition. This stable vapor pressure approaches that of pure benzo[a]pyrene even though the measurements are for an anthracene + benzo[a]pyrene mixture system.

These experiments lent themselves to composition analysis throughout the sequence. Reported mole fractions are given in Table 3.8 and are accurate to ± 0.01. GC-MS analysis showed that the vapor pressure of the system approached that of pure benzo[a]pyrene as the mole fraction of anthracene in the solid was reduced from any given initial value to $x_1 \approx 0.10$. Once this stable vapor pressure was reached, it remained unchanged for the remainder of the experiments. Interestingly, the mixture compositions changed only gradually throughout the final stage of these experiments in which the mole fraction of anthracene never decreased below $x_1 \approx 0.03$. The vapor pressure of anthracene is roughly three orders of magnitude greater than that of benzo[a]pyrene in this temperature range. Hence, if the system were behaving ideally, the composition of the mixture would change significantly and the experimental vapor pressure would shift accordingly. This non ideal behavior indicates that mixtures of anthracene and benzo[a]pyrene at $x_1 < 0.10$ act similarly to a solid-azeotrope. It must be kept in mind that this system does not represent true azeotropy because the mixture concentration does, in fact, change slightly during sublimation. It is suggested instead, that this low a level of anthracene impurity can be retained in the benzo[a]pyrene crystallographic structure without any significant impact on measured solid-vapor equilibrium. It is important to bear in mind the distinction between the eutectic mixture and an azeotrope. The eutectic
mixture exhibits a minimum melting temperature at $x_1 = 0.26$. The pseudo
azeotrope is a nearly constant subliming mixture at $x_1 < 0.10$. There is no particular
reason that a eutectic and an azeotrope should occur at the same composition.

**Table 3.8. Composition of anthracene (1) + benzo[a]pyrene (2) solid mixtures, measured during vapor pressure experiments by GC-MS**

<table>
<thead>
<tr>
<th>$x_{1,\text{initial}}$</th>
<th>$x_{2,\text{initial}}$</th>
<th>mass loss (%)</th>
<th>$x_{1,\text{solid}}$</th>
<th>$x_{2,\text{solid}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1</td>
<td>0.9</td>
<td>14</td>
<td>0.049</td>
<td>0.951</td>
</tr>
<tr>
<td>0.1</td>
<td>0.9</td>
<td>44</td>
<td>0.030</td>
<td>0.970</td>
</tr>
<tr>
<td>0.1</td>
<td>0.9</td>
<td>80</td>
<td>0.032</td>
<td>0.968</td>
</tr>
<tr>
<td>0.3</td>
<td>0.7</td>
<td>15</td>
<td>0.102</td>
<td>0.899</td>
</tr>
<tr>
<td>0.3</td>
<td>0.7</td>
<td>18</td>
<td>0.104</td>
<td>0.897</td>
</tr>
<tr>
<td>0.3</td>
<td>0.7</td>
<td>50</td>
<td>0.040</td>
<td>0.961</td>
</tr>
<tr>
<td>0.5</td>
<td>0.5</td>
<td>23</td>
<td>0.168</td>
<td>0.832</td>
</tr>
<tr>
<td>0.5</td>
<td>0.5</td>
<td>37</td>
<td>0.068</td>
<td>0.932</td>
</tr>
<tr>
<td>0.5</td>
<td>0.5</td>
<td>45</td>
<td>0.049</td>
<td>0.951</td>
</tr>
<tr>
<td>0.7</td>
<td>0.3</td>
<td>56</td>
<td>0.048</td>
<td>0.952</td>
</tr>
<tr>
<td>0.7</td>
<td>0.3</td>
<td>74</td>
<td>0.051</td>
<td>0.949</td>
</tr>
</tbody>
</table>

**3.5 Concluding Remarks**

The anthracene + pyrene and anthracene + benzo[a]pyrene mixture systems
are complicated and non-ideal. The solid-liquid equilibrium studies shows that
binary mixtures of (anthracene + pyrene) and (anthracene +benzo[a]pyrene) have
minimum melting temperatures, i.e., eutectic points. In the case of anthracene +
pyrene mixture system, the eutectic point at 404 K occurs at $x_1 = 0.22$. The
anthracene + benzo[a]pyrene eutectic phase is formed at $x_1 = 0.26$ and melts in the
range 414 to 420 K. Additionally, for a wide range of composition, the crystal
structure and energetics of these two binary systems are controlled by that of the eutectic mixture. The eutectic behavior is a solid-liquid equilibrium phenomenon and should not be confused with the (pseudo) azeotropy observed at solid-vapor equilibrium.

Mixtures of anthracene and pyrene exhibit two pyrene-rich, stable azeotropes. In contrast, at high anthracene compositions, the vapor pressure above the solid equilibrates that of pure anthracene, indicating that anthracene can accommodate low levels of pyrene in its crystal structure. Furthermore, the observed solid-vapor equilibrium behavior of the binary anthracene + benzo[a]pyrene system indicates only that benzo[a]pyrene can accommodate low levels of anthracene in its crystal structure and not that the mixture is behaving as a true azeotrope.

It is hypothesized that the behavior observed in these binary mixture systems might be described by formation of clusters. A schematic of this model is given in Figure 3.21.
Figure 3.21. A qualitative schematic of the cluster formation of an anthracene + pyrene solid mixture.

The observed experimental results for solid/liquid and solid/vapor systems indicate that binary PAH mixtures may form cluster-like entities of constant, preferred molar ratio at equilibrium. If these clusters are bound only weakly to one another, then long-range crystal order would not be established and the clusters would define the
sublimation behavior. This, of course, would partially explain the depressed melting temperatures (eutectic formation) and constant-molar ratio sublimation (azeotrope behavior) observed in the binary anthracene + pyrene and anthracene + benzo[a]pyrene systems.

It was mentioned in passing (above) that there was no particular reason that the eutectic and azeotropic phases had to occur at the same composition. This may require more explanation. Based on the descriptions and definitions of azeotropy and eutectic formation provided in chapters 2 and 3, it should be clear that both processes are very different and occur under very different conditions. Eutectic behavior is a solid/liquid equilibrium phenomenon that occurs at a given experimental $T$ and $P$. The ratio at which the eutectic point occurs of course as always depends on the system finding a minimum free energy $\Delta G$ at the experimental $T$ and $P$. Azeotropy is (in the context of systems in this thesis) a solid/vapor equilibrium process that is observed under a much different set of $T$ and $P$ conditions than the solid/liquid equilibrium. There is no reason to expect that the free energy conditions for this different set of conditions would yield the same composition for the azeotrope as that for the eutectic. In other words, just because the given systems have reached some minimum energy state does not mean that these exist at the same composition, or that a system that shows eutectic behavior will necessarily show azeotrope behavior.

From a more macroscopic viewpoint, these results begin to suggest that solid PAH mixtures (and potentially other systems of large, organic compounds) with a
finite number of components may be surprisingly non-ideal. In other words, similar systems may exhibit deviations from Raoult’s law, solid azeotropy, depressed melting temperatures, and accommodation of low-concentration compounds. This is not what one would expect from a “like dissolves like” theory, and though these results are not meant to be projected on all binary mixtures, they should be taken as a fair warning that non-ideality may exist in other similar mixtures.
Chapter 4 Thermodynamics of Multicomponent PAH Mixtures and Development of Tarlike Behavior

4.1 Introduction

Multicomponent mixtures of polycyclic aromatic hydrocarbons (PAHs) are among the main components in various types of tars. There is surprisingly little in the way of reliable phase behavior information on PAH mixtures in the literature, considering the commercial and environmental importance of such multicomponent mixtures. This laboratory has been engaged in studying the phase behavior of binary mixtures of PAHs and related compounds for some time (Chapter 3), and we (Oja and Suuberg, 1998a) and other laboratories (Peters et al., 1993; 1997; 1999; 2000; Brown et al., 1999; Lee et al., 2007; Birak and Miller, 2009; Burks and Harmon, 2001) have studied some aspects of tar mixtures. Furthermore, solid/liquid equilibrium of systems containing tar components (i.e., PAHs) has been examined by melting temperature analysis that reports the formation of eutectic phases, but, as mentioned in Chapter 3, does not fully characterize the mixture thermodynamics (Szczepanik and Skalmowski, 1963; Szczepanik, 1963). The picture that has emerged is that the two component mixtures are generally non-ideal in every respect, but other results have suggested that the multicomponent mixtures might approach ideal behavior.

Thus this study begins to address the question of what determines the difference between the non-ideal room temperature solid phase mixtures and the
usual sorts of room temperature, viscous “tar” liquids that have been claimed to exhibit ideal mixture behavior. There are many aspects that are related to this question. Some earlier workers have, for example, been concerned with the water solubility of PAH mixtures, motivated by an interest in dissolution of tars in water (Peters et al., 1993; 1997; 1999; Brown et al., 1999; Lee et al., 2007). Here, the choice is to instead focus on the solid to liquid and solid to vapor transitions of PAHs with no other components present. The experimental methods employed are those that have been discussed in Chapter 3 in connection with the earlier studies of binary PAH mixtures (Rice et al., 2010a; 2010b; Fu et al., 2010).

**Summary of Results**

This study explores the solid/liquid phase behavior of mixtures of polycyclic aromatic hydrocarbons (PAHs), exploring the transition from non-ideal solid mixtures to a relatively ideal liquid behavior characteristic of “tars”. PAH mixtures have been studied using differential scanning calorimetry, melting point analysis and Knudsen effusion. Ternary mixtures of anthracene, pyrene and fluoranthene show behavior that is consistent with other binary PAH mixtures; that is, the initially solid mixture exhibits a significant melting point depression, relative to the pure components, and in a certain range of composition, solid azeotrope behavior on vaporization. As the number of distinct PAH species is increased (by adding in benzo[a]pyrene, phenanthrene, fluorene and chrysene) this behavior gradually gives way to liquid phase character even at room temperature, and the vaporization behavior approaches that crudely predictable from ideal mixture theory.
4.2 Ternary Solid Azeotropy of Anthracene, Pyrene, and Fluoranthene.

The previous chapter examined the phase behavior of binary PAH mixtures, reporting the formation of eutectic points, solid azeotropy, and non-ideal phase equilibrium. In establishing a better understanding of PAH systems that usually contain multiple components, the next logical step was to study the behavior of a ternary PAH system. Various experimental data for an equimolar, three-component system of anthracene (1) + pyrene (2) + fluoranthene (3) are given in Figures 4.1 – 4.3. The results are quite similar to those of the binary anthracene (1) + pyrene (2) system in that the ternary system exhibits solid azeotropy, depressed melting temperature, and multiple phases associated with complicated binary phase behavior.

Figure 4.1 shows the continuously measured vapor pressure as a function of mass loss of an initially equimolar 1 + 2 + 3 system held first at 318.15 K and subsequently at 328.15 K. In the case of a thermodynamically ideal mixture that follows Raoult’s law, except for the unlikely situation of equal pure component vapor pressures, the mixture will become progressively enriched in the less volatile components and the total mixture vapor pressure (eq 2.13.8) will continuously decrease as the mixture loses mass through vaporization or sublimation.

\[ P = \sum x_i P_{i_{\text{sat}}} \]  

(2.13.8)
In eq 2.13.8, $P$ is the total system vapor pressure, $x_i$ is the condensed-phase mole fraction, and $P_{i\text{sat}}$ is the vapor pressure of pure species $i$ at a given system temperature.

![Graph showing vapor pressure of an initially equimolar anthracene + pyrene + fluoranthene mixture.](image)

Figure 4.1. Vapor pressure of an initially equimolar anthracene + pyrene + fluoranthene mixture.

Vapor pressure results for the ternary mixture shown in Figure 4.1 do not indicate ideal mixture behavior, since the vapor pressure of the mixture is relatively constant for the first 65% of sample mass loss by sublimation. This is analogous to liquid azeotropic behavior, which in this instance involves a subliming solid, as
opposed to the more usual liquid azeotropic phase. Following the loss of 65% of
initial sample mass, a different behavior is seen, consistent with the existence of a
second phase that exhibits more usual mixture behavior of declining vapor pressure
with mass loss. Further evidence for the existence of this second phase will be
presented below. Continued sublimation of this second mixture phase involves a
progressive decrease in vapor pressure, although a brief period of relatively stable
vapor pressure is seen when the phase composition approaches that of pure pyrene.
It should also be kept in mind that both phases initially present in the mixture are
subliming in parallel, but that the higher vapor pressure azeotropic phase initially
dominitates the observed behavior.

Samples from the vapor pressure experiments of Figure 4.1 were
occasionally removed from the effusion cells, dissolved in dichloromethane, and
analyzed by GC-MS. Reported mole fractions are accurate to ± 0.01. Accounting for
the approximately 65% of solid in the azeotropic phase, the GC-MS data allowed
calculation of a ternary azeotrope composition of $x_1 = 0.38$, $x_2 = 0.42$, and $x_3 = 0.20$.
The result suggests a 2:2:1 molar ratio of anthracene:pyrene:fluoranthene in this
phase.

It was also possible to extract from data such as those of Figure 4.1, vapor
pressures for the azeotrope as function of temperature. These are shown in Figure
4.2. The pure component and maximum possible vapor pressures (representing the
summed contributions of the three pure phases) have been plotted along with the
measured azeotrope data for comparison.
Figure 4.2. Vapor pressure of the solid azeotrope ($P_{AZEOTROPE}$) at $x_1 = 0.38$, $x_2 = 0.42$, and $x_3 = 0.20$. The vapor pressures of each pure component are given for reference. The maximum possible vapor pressure ($P_{MAXIMUM}$) is the sum of the pure component vapor pressures.

Based upon the integrated form of the Clausius-Clapeyron equation given below, the enthalpy of sublimation for each compound can be determined. This of course depends on the assumptions that enthalpy of sublimation is independent of temperature in the given range and that the vapor is an ideal gas. These
assumptions are quite plausible given the limited temperature range, low system pressure, and moderate temperature.

\[
\ln \frac{P^{\text{vap}}}{P^{\text{ref}}} = -\frac{\Delta_{\text{sub}} H}{RT} + \frac{\Delta_{\text{sub}} S}{R}
\]  

(2.16.3)

The sublimation enthalpies (Table 4.1) obtained from the slopes of the curves in Figure 4.2 are virtually identical, indicating that the cohesive energy density in the azeotropic mixture is not very different than that of the pure components themselves. On the other hand, the entropy of sublimation (given in Table 4.1, as calculated from \( \Delta_{\text{sub}} S = \Delta_{\text{sub}} H / T \) at \( T = 298 \) K) shows that the entropy change from the solid phase to the vapor phase is greater for the azeotropic mixture state than for the pure components. This indicates a more ordered state for the azeotropic mixture, bearing in mind that the pure components are crystalline solids.

In addition to literature values previously obtained and reported in this laboratory (Goldfarb and Suuberg, 2008; Oja and Suuberg 1998b), the pure component enthalpies and entropies of sublimation that were measured and used in this recent study are also provided in Table 4.1. The results from this study are in fair agreement with the literature. However, there is reason to suspect that the previously reported enthalpy of sublimation of phenanthrene was slightly high due to sample impurities; a purer sample was now used.

The vapor pressure of compounds with a relatively high vapor pressure, i.e., phenanthrene and fluorene, must be measured in a low temperature range where sample mass loss from the effusion cell does not exceed allowable experimental
design. For these reasons, the vapor pressure of fluorene and the higher purity phenanthrene (97%) were now measured at lower temperatures with a more precise microbalance, and the new values are improvements to the previously reported results.

Roux et al. (2008) have summarized the thermodynamics of all of the pure compounds of interest in this study. In general the values reported in our study agree with the summarized literature. Note that our sublimation enthalpies often fall below those recommended by Roux et al. for 298 K, but it should be noted that our experimental results were generally measured at higher than ambient temperatures, and that the enthalpies decrease with increasing temperature.
Table 4.1. Enthalpies and entropies of sublimation of pure PAHs, mixtures, and real coal tars.

<table>
<thead>
<tr>
<th>Description</th>
<th>MW</th>
<th>( \Delta_{\text{sub}}H ^{\text{This Lab}} )</th>
<th>( \Delta_{\text{sub}}S ^{\text{This Lab}} )</th>
<th>( \Delta_{\text{sub}}H ^{\text{Published}} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure Components</td>
<td></td>
<td>(kJ·mol(^{-1}))</td>
<td>(J·mol(^{-1})K(^{-1}))</td>
<td>(kJ·mol(^{-1}))</td>
</tr>
<tr>
<td>Anthracene (1)</td>
<td>178.23</td>
<td>97.1 ± 1.1 (300-373 K)</td>
<td>326 ± 3.7</td>
<td>98.5 ± 3.3(^1) (288-323 K)</td>
</tr>
<tr>
<td>Pyrene (2)</td>
<td>202.25</td>
<td>97.1 ± 1.2 (333-375 K)</td>
<td>326 ± 3.7</td>
<td>97.8 ± 3.3(^1) (322-381 K)</td>
</tr>
<tr>
<td>Fluoranthene (3)</td>
<td>202.25</td>
<td>94.2 ± 0.9 (308-338 K)</td>
<td>316 ± 3.0</td>
<td>96.9 ± 2.8(^1) (327-359 K)</td>
</tr>
<tr>
<td>Benzo(a)pyrene (4)</td>
<td>252.31</td>
<td>116.2 ± 7.5 (398-430 K)</td>
<td>390 ± 25</td>
<td>113.3 ± 3.1(^1) (392-424 K)</td>
</tr>
<tr>
<td>Phenanthrene (5)</td>
<td>178.23</td>
<td>88.5 ± 1.0 (296-308 K)</td>
<td>297 ± 3.4</td>
<td>95.0 ± 4.4(^2) (303-333 K)</td>
</tr>
<tr>
<td>Fluorene (6)</td>
<td>166.22</td>
<td>82.6 ± 2.5 (296-317 K)</td>
<td>277 ± 8.3</td>
<td>87.1 ± 3.8(^2) (298-324 K)</td>
</tr>
<tr>
<td>PAH Mixtures – This Study</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3 comp. Mixture (1-3 azeotrope)</td>
<td>194.2</td>
<td>97.8 ± 6.0 (308-328 K)</td>
<td>328 ± 20</td>
<td>N/A</td>
</tr>
<tr>
<td>5 comp. Mixture (1-5 equimolar)</td>
<td>202.6</td>
<td>89.6 ± 3.1 (308-323 K)</td>
<td>301 ± 10</td>
<td>N/A</td>
</tr>
<tr>
<td>6 comp. Mixture (1-6 equimolar)</td>
<td>196.6</td>
<td>84.2 ± 3.0 (278-288 K)</td>
<td>283 ± 10</td>
<td>N/A</td>
</tr>
<tr>
<td>Real Coal Tars</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pittsburgh No. 8 Coal Tar</td>
<td>230</td>
<td>143.7 (360-400 K)</td>
<td>328</td>
<td>N/A</td>
</tr>
<tr>
<td>(Oja and Suuberg, 1998a)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Upper Freeport Coal Tar</td>
<td>215</td>
<td>106.5 (360-400 K)</td>
<td>357</td>
<td>N/A</td>
</tr>
<tr>
<td>(Oja and Suuberg, 1998a)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Wyodak Coal Tar</td>
<td>240</td>
<td>143.7 (360-400 K)</td>
<td>482</td>
<td>N/A</td>
</tr>
<tr>
<td>(Oja and Suuberg, 1998a)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\(^1\) Goldfarb and Suuberg, 2008; \(^2\) Oja and Suuberg, 1998b

Figure 4.3 displays the DSC heating, cooling, and reheating scans of the ternary 1 + 2 + 3 mixture and of pure pyrene. Heating and cooling scans were conducted between 298 and 523 K at 10 K·min\(^{-1}\) and 2.5 K·min\(^{-1}\), respectively. Peaks in the scans represent phase transitions and can be integrated to determine the enthalpy of fusion of the sample with a relative uncertainty of \( \delta \Delta_{\text{fus}}H / \Delta_{\text{fus}}H = 0.07 \).
Focusing first on the behavior of a typical pure compound (pyrene), the reproducible peak that occurs during the heating scan represents an endothermic solid to liquid phase transition at 426 K with $\Delta_{\text{fus}}H = 80 \pm 5.6 \text{ J} \cdot \text{g}^{-1}$. The exothermic peak that occurs at 402 K during the cooling scan represents the crystallization of pyrene from a subcooled state, as is typically observed in such experiments. As discussed in Chapter 3, this and other pure compound DSC scans have been noted to be in good agreement with literature values (Domalski and Hearing, 1996).

The DSC scan in Figure 4.3 for the ternary $1 + 2 + 3$ mixture of Figure 4.1 shows that the initial mixture is comprised of two distinct, solid phases. The first melts with a sharp, endothermic peak at 379 K with $\Delta_{\text{fus}}H = 47 \pm 3.3 \text{ J} \cdot \text{g}^{-1}$ (this is the enthalpy per mass of total mixture). The poorly defined peak associated with the second mixture phase is observed between 398 and 432 K and it may be approximately integrated to show a solid to liquid enthalpy $\Delta_{\text{fus}}H$ between 20 and 30 J·g$^{-1}$. This behavior is likely a result of both true melting and dissolution of the second, solid phase into the first, melted phase. Information from the cooling scan confirms that this solid system actually forms two distinct phases.
Figure 4.3. Differential scanning calorimetry results of pyrene and an equimolar ternary PAH mixture.

The exothermic peaks in the cooling scan for the ternary mixture occur at 402 K and 374 K with $\Delta_{\text{fus}}H = 26.4 \text{ J.g}^{-1}$ and 48.7 J.g$^{-1}$, respectively. These crystallization peaks correspond to the fusion peaks noted above and are consistent with the two-phase behavior implied by the vapor pressure data. The enthalpy associated with the azeotrope represents about 66% of total fusion enthalpy, consistent with the conclusion from the vapor pressure data that the azeotropic phase represents 65% of the total mixture mass, though there is no particular
reason to a priori believe that the enthalpies of fusion of the two phases should, on a mass basis, be equal. Also it is worth noting that since the enthalpy of fusion of the larger, lower temperature crystallization peak (that due to what is believed to be the phase that gives rise to the azeotrope behavior on sublimation) represents about 65% of the total mixture mass, the actual azeotrope phase crystallization/fusion enthalpy may be estimated to be approximately 75 J·g⁻¹ for that phase alone, and the same value emerges for the other phase that is present. In other words, the enthalpies of these phase changes are comparable, and not very much different than the fusion enthalpies of pure components that make up these phases. Moreover, the azeotrope phase must then have a higher entropy of fusion than the second mixture phase.

It is also worth noting here that melting point analysis was used to substantiate the DSC results found above and to verify that the endothermic peaks in the DSC scan do not represent solid crystal transitions of pure phases (Casellato et al., 1973). Results from the melting point analysis show that the equimolar 1 + 2 + 3 mixture has a thaw point at 377 ± 1 K and liquidus point at 433 ± 1 K. This is consistent with the DSC scans for this mixture. Hence, it is clear that there exist only two true mixture phases in this system.
4.3 Quaternary System of Anthracene, Pyrene, Fluoranthene, and Benzo[a]pyrene.

Benzo[a]pyrene was then added to the previous components to create an equimolar 4-component mixture of anthracene (1) + pyrene (2) + fluoranthene (3) + benzo[a]pyrene (4). The pure phase vapor pressure of benzo[a]pyrene is considerably lower than that of the other mixture components and it has exhibited complicated phase behavior when mixed with anthracene to form the binary 1 + 4 system in Chapter 3.

Figure 4.4 shows the full DSC scan of the 4-component mixture. In contrast to the binary and ternary mixtures, addition of benzo[a]pyrene as a fourth component has allowed the mixture to form a single phase. This is evidenced by single, well-defined, broad endothermic and exothermic peaks in the DSC scan. A separate melting point analysis (not shown) illustrates that the mixture melts in the range of 353 to 369 K, further indicating that the single phase, solid mixture has formed.
A notable trend has begun to appear at this point in the study, in which the enthalpies of fusion and melting temperatures, listed in Table 4.2, appear to be decreasing with the number of components added to the mixture. The 4-component mixture is approaching a liquid, that is, tar behavior in which $\Delta_{\text{fus}}H = 0$ and discrete melting is not observed. In other words, addition of benzo[a]pyrene has limited the energetically favorable interaction of the pure species. It is important to clarify that the 4-component mixture has not yet reached the liquid state and is only
approaching liquid behavior. Also note that the enthalpies of fusion are much lower than those associated with sublimation.

In reference to the enthalpies reported in Table 4.2, it should be noted that the available equipment limits the accuracy of this DSC technique and the comparatively larger reported uncertainties here compared with other literature result from the inherent uncertainty in peak integration. Except for pure benzo[a]pyrene, which has a complicated DSC signature, the enthalpies of fusion of pure components reported in Table 4.2 are in fair agreement with those recommended in the literature. In the case of benzo[a]pyrene, two peaks (not shown) are initially observed in the DSC scan (Rice et al., 2010b; Casellato et al., 1973). Again, the first peak is not associated with melting. Rather, it is attributed to a crystal transition associated with preparation and is only observed when heating a sample for the first time. It has been shown in this laboratory (discussion in Chapter 3) and in others that the benzo[a]pyrene transition peak is not recovered when reheating a previously melted sample (Rice et al., 2010b; Casellato et al., 1973). Since the mixtures from this study are melted during preparation, the lower value of 11.3 kJ·mol⁻¹ is appropriate.
Table 4.2. Melting temperatures and fusion enthalpies of pure PAHs and multicomponent PAH mixtures.

<table>
<thead>
<tr>
<th>Description</th>
<th>$T_{\text{onset}}$</th>
<th>$T_{\text{melt}}$</th>
<th>$T_{\text{melt}}$</th>
<th>$\Delta_{\text{fus}}H$ This Laboratory</th>
<th>$\Delta_{\text{fus}}H$ Recommended&lt;sup&gt;3&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Pure Components</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Anthracene (1)</td>
<td>487.0</td>
<td>489</td>
<td>DSC/Visual</td>
<td>27.8 ± 1.9</td>
<td>29.4 ± 0.1</td>
</tr>
<tr>
<td>Pyrene (2)</td>
<td>422.0</td>
<td>423</td>
<td>DSC/Visual</td>
<td>16.2 ± 1.1</td>
<td>17.36 ± 0.04</td>
</tr>
<tr>
<td>Fluoranthene (3)</td>
<td>382.5</td>
<td>384</td>
<td>DSC/Visual</td>
<td>18.2 ± 1.3</td>
<td>18.73 ± 0.02</td>
</tr>
<tr>
<td>Benzo(a)pyrene (4)</td>
<td>442.2</td>
<td>449</td>
<td>DSC/Visual</td>
<td>11.3 ± 0.8</td>
<td>17.3 ± 0.6</td>
</tr>
<tr>
<td>Phenanthrene (5)</td>
<td>371.1</td>
<td>372</td>
<td>DSC/Visual</td>
<td>16.3 ± 1.1</td>
<td>16.46 ± 0.04</td>
</tr>
<tr>
<td>Fluorene (6)</td>
<td>386.7</td>
<td>388</td>
<td>DSC/Visual</td>
<td>19.4 ± 1.4</td>
<td>19.58 ± 0.06</td>
</tr>
<tr>
<td>Chrysene (7)</td>
<td>525.3</td>
<td>526</td>
<td>DSC/Visual</td>
<td>23.3 ± 1.6</td>
<td>26.2 ± 0.2</td>
</tr>
<tr>
<td><strong>Binary Mixtures</strong></td>
<td></td>
<td>$T_{\text{thaw}}$</td>
<td>$T_{\text{liquidus}}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1 + 2 at $x_1 = 0.10$</td>
<td>404</td>
<td>419</td>
<td>Visual</td>
<td>16.6 ± 1.2</td>
<td>N/A</td>
</tr>
<tr>
<td>1 + 2 at $x_1 = 0.50$</td>
<td>404</td>
<td>453</td>
<td>Visual</td>
<td>18.6 ± 1.3</td>
<td>N/A</td>
</tr>
<tr>
<td>1 + 2 at $x_1 = 0.90$</td>
<td>404</td>
<td>485</td>
<td>Visual</td>
<td>19.2 ± 1.3</td>
<td>N/A</td>
</tr>
<tr>
<td>1 + 4 at $x_1 = 0.10$</td>
<td>414</td>
<td>438</td>
<td>Visual</td>
<td>8.1 ± 0.6</td>
<td>N/A</td>
</tr>
<tr>
<td>1 + 4 at $x_1 = 0.50$</td>
<td>414</td>
<td>440</td>
<td>Visual</td>
<td>14.6 ± 1.0</td>
<td>N/A</td>
</tr>
<tr>
<td>1 + 4 at $x_1 = 0.90$</td>
<td>414</td>
<td>486</td>
<td>Visual</td>
<td>19.0 ± 1.3</td>
<td>N/A</td>
</tr>
<tr>
<td><strong>Ternary Mixture</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1 + 2 + 3 (equimolar)</td>
<td>377</td>
<td>433</td>
<td>Visual</td>
<td>14.6 ± 1.0</td>
<td>N/A</td>
</tr>
<tr>
<td><strong>Quaternary Mixture</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1 – 4 (equimolar)</td>
<td>353</td>
<td>369</td>
<td>Visual</td>
<td>6.9 ± 0.5</td>
<td>N/A</td>
</tr>
<tr>
<td><strong>Five Component Mixture</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1 – 5 (equimolar)</td>
<td>342</td>
<td>358</td>
<td>DSC</td>
<td>6.3 ± 0.4</td>
<td>N/A</td>
</tr>
<tr>
<td><strong>Six Component Mixtures</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1 – 6 (equimolar)</td>
<td>321</td>
<td>348</td>
<td>DSC</td>
<td>4.5 ± 0.3</td>
<td>N/A</td>
</tr>
<tr>
<td>1 – 5 + 7 (equimolar)</td>
<td>333</td>
<td>353</td>
<td>DSC</td>
<td>5.8 ± 0.4</td>
<td>N/A</td>
</tr>
</tbody>
</table>

<sup>3</sup> Roux et al., 2008
Although still very complicated, the solid-vapor equilibrium study for the 4-component system demonstrates a trend towards liquid mixture behavior. Figure 4.5 shows the continuously measured vapor pressure of the solid mixture for the first 21% of sample mass loss, first at $T = 318$ K and then at $T = 333$ K. There is a brief period of vapor pressure stability between 5 and 10% mass loss. The system composition in this region of constant sublimation pressure was found to be $x_1 = 0.21, x_2 = 0.24, x_3 = 0.26, \text{ and } x_4 = 0.29$. Although this behavior might initially appear similar to the previously discussed solid azeotropy, the brevity of the segment and sudden decrease in pressure at 10% mass loss indicate otherwise. It should be understood that the system composition is not yet significantly changed during the first 10% of sample mass loss and consequently, the rate of sublimation appears steady. It needs to be remembered that the DSC indicated existence of a single phase.

In the experiment of Figure 4.5, the vapor pressure of the system decreases with increasing mass loss beyond 10% mass loss, as the more volatile components decrease in concentration. This behavior resembles more ideal mixture behavior, but does not yet follow ideal, Raoult’s law thermodynamics. For instance, at 21% mass loss and 333 K, the experimentally measured vapor pressure is $P = 0.026$ Pa. However, composition here was determined to be $x_1 = 0.14, x_2 = 0.26, x_3 = 0.26, \text{ and } x_4 = 0.34$ and the calculated Raoult’s law vapor pressure for a mixture at this composition is $P = 0.039$ Pa. This means that the system vapor pressure is slightly below that predicted by Raoult’s law.
Figure 4.5. Vapor pressure of an initially equimolar anthracene + pyrene + fluoranthene + benzo[q]pyrene mixture versus sample mass loss. Raoult’s law is calculated for measured concentrations noted in the text.

As the vapor pressure decreases, the mass loss rate from the effusion cell can become so low that impractically long times are needed to measure the vapor pressures. This can be addressed in many cases by simply increasing the temperature of the experiment. However, since this 4-component mixture has a low melting temperature of 355 K, this fact limited the ability to study vapor pressures in the sublimation regime that was of main interest here to below this temperature.
Figure 4.6 shows the complex behavior that can be observed when phase changes are permitted to occur in these types of sublimation/vaporization experiments.

![Graph of vapor pressure vs. time](image)

Figure 4.6. Vapor pressure of an initially equimolar anthracene + pyrene + fluoranthene + benzo[\(a\)]pyrene mixture versus time during a continuous temperature ramp and subsequent period of temperature stability.

Figure 4.6 shows the continuously measured vapor pressure of the 4-component equimolar mixture as temperature is increased from 318 to 368 K at 0.3 K·min\(^{-1}\). In region A of Figure 4.6, the mixture vapor pressure increases with temperature, reaches a maximum, and begins to decrease as the more volatile constituents are exhausted. This is consistent with the behavior from Figure 4.5.
When, in region B of Figure 4.6, the temperature of the mixture reaches 355 K, the mixture melts. This causes an increase in vapor pressure as the process changes from solid sublimation to liquid vaporization. The liquid then undergoes the expected decline in vapor pressure consistent with composition change associated with loss of more volatile components.

Upon reaching region C of Figure 4.6, the mixture becomes concentrated in benzo[a]pyrene, and it appears that a solid phase crystallizes. As the remaining liquid is vaporized from the system, the vapor pressure of a solid, benzo[a]pyrene rich mixture begins to dominate and is shown in region D. The concentration of this stable phase is $x_1 = 0, x_2 = 0.07, x_3 = 0.07,$ and $x_4 = 0.86.$ DSC results (not shown) indicate that this new phase begins to melt at $T_{fus} = 388$ K and this corroborates the conclusion that the mixture must have crystallized in region C of Figure 4.6. This observation of relatively stable vapor pressure in region D does not necessarily represent true azeotropy. Rather, it is suggested that solid phase structure is defined by the majority benzo[a]pyrene component, and this defines the system’s behavior. In other words benzo[a]pyrene can accommodate moderate pyrene and fluoranthene impurities within its crystal structure without significant concentration or enthalpy variation.

It is believed that the trends described here are general, in that the ternary mixture has been observed to behave much like the binary systems earlier studied (Rice et al., 2010a; 2010b; Fu et al., 2010); azeotrope behavior is observed, and multiple phases exist. With the ternary system and 4-component systems examined
here, there is a continuation of the decrease in melting temperature and enthalpy of fusion from the binary mixtures and pure components.

4.4 Five and Six Component PAH Mixtures.

The five-component system includes all components 1 + 2 + 3 + 4 in addition to phenanthrene (5). The pair of six component mixtures consists of 1 + 2 + 3 + 4 + 5 and either fluorene (6), or chrysene (7). All mixtures are again initially equimolar.

Figure 4.7 shows DSC scans for the five and six component mixtures between 310 and 420 K. As the number of components in the mixture increases, the peaks begin to lose definition and the baseline appears to lack stability, in part because the scale has been expanded to show the relatively smaller heat effects. The fusion enthalpies continue to approach the liquid limit of $\Delta_{fus}H = 0$ with addition of each new component (Table 4.2).
Figure 4.7. Differential scanning calorimetry results of one, 5-component and two, 6-component, PAH mixtures.

All of these five and six component mixtures have become black in color and inhomogeneous, meaning that solid inclusions are observed amongst a tacky and glass-like semisolid – in short, the mixture is already visually indistinguishable from a tar in appearance. Hence, melting point analysis can no longer be used to discern either a thaw or a liquidus point because visual differentiation between true melting, dissolution, or change in viscosity is not possible. This is in stark contrast to
the mixtures with fewer components, and to the pure PAHs, which are generally white or yellow, homogenous, solid, crystalline powders.

The reason for such color change from the white and yellow few-component mixtures to the black tarlike mixtures is not necessarily obvious. The observed color of a compound is directly linked to regions of molecules that absorb and/or reflect visible light, i.e., photons, at varying wavelengths. These regions are referred to as chromophores. It is important to recall that each PAH molecule has certain, well-defined bonds. Hence, each molecular structure is defined by a basic electronic structure that will not change due to presence in a mixture (unless chemical reactions have occurred). Thus PAHs, which do not change in structure upon mixing, are able to absorb a fuller range light from the visible spectrum as a result of charge transfer phenomena. In other words, mixtures of PAHs form charge transfer complexes that behave as systems instead of distinct molecular entities because the pi complexes of such systems could interact to permit absorption of photons that the pure species molecules cannot.

Solid/liquid/vapor equilibrium (i.e., vapor pressure) results for five and six component mixtures are provided in Figure 4.8. In the case of the six component mixture, it was that containing components 1 through 6. These data are plotted in Clausius-Clapeyron form, but the experiments were carried out using a different procedure than in the case of the experiments reported above. In this instance, system temperature was held constant only long enough to allow equilibration and measurement of 30 minutes of mass loss data, before raising the temperature to the
next higher value. Thus each data point represents the result of an isothermal measurement.

Figure 4.8. Vapor pressure of initially equimolar 5 & 6-component PAH mixtures, with Raoult’s Law ($P_{RL}$) estimates for both equimolar and GC-MS measured mole fractions. The transitional region of $P_{6-COMPONENT}$ maps the loss of more volatile components and is experimentally path dependent. It does not represent the equilibrium vapor pressure of an equimolar mixture.
Beginning with the 6-component mixture at low temperatures (i.e., high 1000/T), the results closely follow the predicted Raoult’s law behavior for the initial composition. In other words, the system has approached ideal solution behavior. Because of how these experiments were performed, the mixture gradually lost the more volatile components in preference to the less volatile, and the vapor pressures dropped as temperatures were increased (1000/T decreases). A new limit was achieved at high temperatures, which was suggestive of a constant vapor pressure system. The GC-MS analysis of the mixture recovered after these experiments indicated that the mixture still contained fluorene, the most volatile compound, at \( x_6 = 0.07 \), so it was still a 6-component mixture. The solid line in Figure 4.8 shows what Raoult’s law would predict for a 5-component mixture of the measured composition, if the presence of fluorene were disregarded. There is not necessarily any physical significance to the relatively good fit, but the Raoult’s law prediction for the actual measured mixture composition (including fluorene) is considerably higher, as shown in Figure 4.8. It is not known whether the 6-component system approached some azeotrope behavior (given the constancy of vapor pressure as temperature was raised to high values) or if there was some other complex phase behavior involved in giving the observed results. What is important to note is that the earlier reported and assumed ideal mixture behavior of multicomponent PAH systems was observed with this 6-component mixture until it approached a 5-component system in composition.

The experiments of the initially equimolar 5-component mixture give a vapor pressure that is near that predicted from Raoult’s law for that composition, but also
close to the final limit for the initially 6-component mixture (if the presence of fluorene in that latter mixture is ignored). It is presently unclear why this is the case.

The final compositions of the 6-component mixture is $x_1 = 0.08, x_2 = 0.23, x_3 = 0.23, x_4 = 0.24, x_5 = 0.15, x_6 = 0.07$ and for the 5-component mixture $x_1 = 0.17, x_2 = 0.22, x_3 = 0.18, x_4 = 0.23, x_5 = 0.20$. This means that the 6-component mixture transitioned to something relatively close to the 5-component mixture. The question of whether these mixtures transition towards some new azeotrope has not been explored in detail. It should be noted that the Raoult’s Law predicted vapor pressure for the initially equimolar 5-component mixture (dot-dash line in Figure 4.8) is indistinguishable from that for the final GC-MS measured composition of the 5-component mixture (not shown). Essentially, if plotted together, the lines would overlap.

Enthalpies and entropies of sublimation for these mixtures and for actual coal tar fractions (Oja and Suuberg, 1998a) are given in Table 4.1. The results presented here are consistent with those previously reported for real coal tars (Oja and Suuberg, 1998a), though the enthalpies are a bit lower for the present mixtures than for the coal tars. The coal tars have significant heteroatomic (oxygen and nitrogen) contents, particularly in the case of Wyodak and Pittsburgh coal tars and it is known that heteroatomic substituted PAHs can have higher enthalpies of sublimation compared with their parent PAHs (Goldfarb and Suuberg, 2010). In addition, it should be noted that the present mixtures are also of somewhat lower molecular weight than the reported averages for the lowest molecular weight fractions of the coal tars, and this would also lead to the enthalpies of vaporization...
being higher for the latter materials. Hence, the Upper Freeport tar fraction is closest to the presently studied materials and it is not surprising that it approaches most closely the presently obtained values.

4.5 Concluding Remarks

These results show that the thermodynamic behavior of multicomponent low molecular weight PAH mixtures is determined by the number of components in the mixture. Tarlike visual appearance begins to manifest itself when the number of components exceeds 5. The approach to tarlike behavior in such systems is supported by the gradual transition from distinct solid melting behavior to a much more ill defined “melting” behavior in 5 and 6-component mixtures. The near-ambient vapor pressure and phase behavior of 3-component systems show a continuation of non-ideal solid mixture behavior that also characterizes binary PAH mixtures. As the number of mixture components increases, the non-ideal solid mixture behavior of 2 and 3-component systems gives way to the commonly assumed ideal mixture behavior, and is clearly seen in a 6-component mixture examined here. The present results also warn of complicated phase behavior that can be encountered as components are lost to evaporation. In some instances, the phase behavior has been observed to approach that of a system with fewer components, in which small amounts of a lower molecular weight component appear to no longer significantly influence the vapor pressure behavior of the
mixture. The vapor pressure behavior of the tar-model system examined here is consistent with that observed for real coal tar systems.
Chapter 5. Aqueous Solubility of Binary and Multicomponent, Tarlike PAH Mixtures

5.1 Introduction

The frequent role of PAH mixtures as subsurface contaminants has been heavily covered in previous chapters of this thesis. PAH-containing tars and non-aqueous phase liquids (NAPLs) are of concern during various environmental remediation operations, and the purpose of this thesis is to better characterize the phase and partitioning behavior (and associated thermodynamics) of PAH mixtures that might be found in natural settings. In doing so, one must consider that PAH mixtures sometimes exist in places where contact with water is to be expected. This was not yet considered or discussed in the previous chapters, which cover solid/liquid and solid/vapor systems that contain only PAHs.

Tars (generally solid) and NAPLs (liquid) were produced in large quantities by former MGPs and may still exist in the environment due to disposal and/or storage practices and uncontrolled releases. Additionally tars and NAPLs may exist naturally as contaminants from processing of fossil fuels, e.g., crude oil, coal, gasoline, and diesel fuel. In both cases, water is likely to be present in the environmental system of interest, and this will have some effect on the phase and partitioning behavior of NAPL and tar components. In other words, the fate and transport of these chemicals and the stability of the source material may be affected by the presence of water.
The topic at hand is complicated by, amongst other things, three very important factors. The first consideration is that, despite similar molecular structures, PAHs vary in their pure component solubilities, spanning many orders of magnitude (May et al., 1978). This is not surprising, in light of the variations in pure component vapor pressures observed in chapters 3 and 4. That is, a wide range of thermodynamic behavior has been observed and is expected to extend to other properties.

The second relevant consideration is that PAHs commonly exist as complicated mixtures of PAHs and other components, and these mixtures may be found as (semi)-solids (tars) or liquids (NAPLs) in natural settings. Furthermore, it is not always clear whether these mixtures are real solutions or, rather, non-interacting, phase separated systems. With this, and the variation of pure component solubilities (noted above), comes potentially complicated aqueous partitioning behavior.

The third important factor is that the nature of a particular site can vary greatly from place to place and this will likely affect the way PAHs move in the environment. For example PAH-rich tars and NAPLs may be located (1) in soil below the groundwater table, (2) in moist soil above the groundwater table, (3) in sediment, (4) in aquifers, or (5) in other bodies of water. Of course, combinations of these site characteristics may also exist in areas where PAHs are present.

The factors discussed in the previous three paragraphs are related to the fact that mass transfer of PAHs to water is possible and potentially governed by very
complicated thermodynamics. Furthermore, as tars and NAPLS age in an aqueous environment, their composition may change with time due to chemical reactions or the dissolution and removal of the more soluble and/or available fractions. In fact, it has been shown that mass transfer to the aqueous phase can cause shifts in NAPL composition on the time scale of years or even decades (Knightes and Peters, 1996; Brown et al., 1999; Peters et al., 1999). It has already been noted, both in this study and in others, that mixtures of PAHs form eutectic mixtures and that their depressed melting temperatures can lead to near ambient liquid behavior particularly as the number of components in a mixture increases. Recall that pure PAHs, and some simple mixtures thereof, are solid at room temperature. So, as the more soluble components of a NAPL are lost to an aqueous phase over time, the mixture might become enriched in less soluble components, and these fractions may solidify if they reach a concentration that is higher than their solubility in the NAPL. The point here is that environmental PAHs might show complicated dissolution behavior and kinetics.

The ability to understand PAH mixture dissolution is important for many environmental (risk reduction, risk assessment, and remediation) and commercial (petroleum industry) applications. For example, the long-term, aqueous solubility of an MGP tar or NAPL may define its impact on an ecosystem, its risk to human health, and also the viability of remediation techniques. Hence, this topic has been examined and summarized both theoretically and experimentally, particularly by Lane and Loehr (1992; 1995), Birak and Miller (2009), and Peters and coworkers (1993; 1997; 1999; 2000). Though some work has been done on binary and ternary
mixtures, a larger part of these earlier studies examines the aqueous phase partitioning and long-term stability of tars or mixtures of several components intended to mimic tars.

The study in this thesis was motivated by the gaps in understanding for few-component PAH mixtures, such as the ones previously examined in Chapters 3 and 4. Since tarlike behavior has been observed in some of these mixtures and because it is understood that NAPLs and tars may evolve to a limited number of components, this study is aimed at understanding the aqueous phase solubility of these transitional multicomponent mixtures, not containing the wide range of compounds that characterize authentic tars. We have been interested in determining whether these mixtures partition into water as individual, phase separated species or following some solution behavior. Solution theory is quite different for liquids than for solids (as will be discussed below), and this raises the question as to which predictive model might be best.

**Predictive Models**

Lane and Loehr examined three approaches to predict the aqueous solubility of PAHs from complex mixtures of dense NAPLs, soil, and water (1995). It should be kept in mind that these systems contain many more components than the mixtures studied in this thesis. The results from Lane and Loehr’s study were compared to experimentally determined reference values for each mixture. Lane and Loehr determined these reference values by mixing 7 contaminated soil samples with water for 24 hours. After equilibration, the mixtures were centrifuged
and the aqueous phases were directly sampled and analyzed (for PAHs) by high performance liquid chromatography (HPLC).

Lane and Loehr’s first approach correlated the aqueous phase concentration of PAHs in water-miscible organic cosolvent systems (1995). Methanol or 2-propanol were mixed with contaminated soil and water, and this enhanced the water solubility of the PAHs. After equilibration and centrifugation steps, the mixed water/alcohol solvent phase was directly sampled and analyzed (for PAHs) by HPLC. Lane and Loehr report that the following relationship can be used to describe the enhanced solubility of PAHs in a cosolvent system:

\[
\log S_i^m = \log S_i^w + \sigma f_c
\]  

(5.1.1)

Here \( S_i^m \) is the solubility of species \( i \) in the mixed solvent phase, \( S_i^w \) is the solubility of \( i \) in pure water, \( \sigma \) is the cosolvency power, and \( f_c \) is the fraction of organic solvent in the mixed solvent phase. Lane and Loehr made use of this relationship by plotting experimentally determined values of \( S_i^m \) against \( f_c \) on log axes. Linear regression curves were fit to the data and the aqueous solubility \( S_i^w \) of each PAH was estimated as being the y-intercept of these curves.

Lane and Loehr’s second approach described PAH solubility from DNAPL + soil mixtures using the following version of Raoult’s law (1995):

\[
C_i^w = x_i^t S_{SCL}
\]  

(5.1.2)

Here \( x_i^t \) is the mole fraction of species \( i \) in the tar phase and \( S_{SCL} \) is the subcooled liquid solubility. The subcooled liquid solubility is used here because pure PAHs are
solid at ambient conditions. Lane and Loehr make use of the following semiempirical relationship to calculate the subcooled liquid solubility of each species (Yalkowsky and Valvani, 1980):

$$\log S_{scl} = \log S_i + 0.01(MP - 25) \quad (5.1.3)$$

Here $S_i$ is the solubility of pure crystalline $i$ and $MP$ is the melting point of species $i$ in deg. C

Lane and Loehr’s final method will not be discussed in detail because it makes use of soil-water partition coefficients, and the presence of soil is considered later in this study. Furthermore this final method did not reliably predict the aqueous dissolution of PAHs from the studied systems (1995).

Table 5.1. A sample of Lane and Loehr’s results, which compare predicted PAH aqueous solubilities to actual measured values (1995).

<table>
<thead>
<tr>
<th>Compound</th>
<th>Technique</th>
<th>Site 1</th>
<th>Site 3</th>
<th>Site 5</th>
<th>Site 7</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fluorene</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Actual</td>
<td></td>
<td>0.02</td>
<td>0.31</td>
<td>0.156</td>
<td>ND</td>
</tr>
<tr>
<td>Predicted</td>
<td>Cosolvent</td>
<td>0.022</td>
<td>0.33</td>
<td>0.135</td>
<td>NA</td>
</tr>
<tr>
<td>Predicted</td>
<td>Raoult's law</td>
<td>0.186</td>
<td>0.169</td>
<td>0.287</td>
<td>0.011</td>
</tr>
<tr>
<td>Anthracene</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Actual</td>
<td></td>
<td>0.009</td>
<td>0.03</td>
<td>0.016</td>
<td>ND</td>
</tr>
<tr>
<td>Predicted</td>
<td>Cosolvent</td>
<td>0.01</td>
<td>0.029</td>
<td>0.013</td>
<td>NA</td>
</tr>
<tr>
<td>Predicted</td>
<td>Raoult's law</td>
<td>0.076</td>
<td>0.042</td>
<td>0.052</td>
<td>0.003</td>
</tr>
<tr>
<td>Phenanthrene</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Actual</td>
<td></td>
<td>0.012</td>
<td>ND</td>
<td>0.078</td>
<td>0.01</td>
</tr>
<tr>
<td>Predicted</td>
<td>Cosolvent</td>
<td>0.013</td>
<td>0.114</td>
<td>0.066</td>
<td>0.009</td>
</tr>
<tr>
<td>Predicted</td>
<td>Raoult's law</td>
<td>0.012</td>
<td>0.147</td>
<td>0.238</td>
<td>0.02</td>
</tr>
<tr>
<td>Pyrene</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Actual</td>
<td></td>
<td>0.015</td>
<td>0.05</td>
<td>0.017</td>
<td>0.01</td>
</tr>
<tr>
<td>Predicted</td>
<td>Cosolvent</td>
<td>0.015</td>
<td>0.03</td>
<td>0.013</td>
<td>0.008</td>
</tr>
<tr>
<td>Predicted</td>
<td>Raoult's law</td>
<td>0.012</td>
<td>0.024</td>
<td>0.053</td>
<td>0.006</td>
</tr>
</tbody>
</table>
A sample of Lane and Loehr’s results are given and Table 5.1. The full data set indicates that the cosolvent-partitioning model provided accurate prediction of aqueous PAH concentrations. Though this approach produced the most reliable results, it is difficult to implement as a universal tool because it requires that experiments be conducted on a case-by-case basis. In other words, the cosolvent approach is not necessarily general and no conclusion exists that extends it to other PAH-containing mixtures.

Out of the 39 solubility values predicted using Lane and Loehr’s Raoult’s law approach, 33 were within an order of magnitude of the actual reference values (1995). Nevertheless there were several cases where variation between the predicted and measured values was significant. Lane and Loehr attribute these differences to erroneous mixture characterization, non-ideal behavior of mixture components, and/or absence of a distinct NAPL phase. All of these factors could invalidate the Raoult’s law prediction.

Birak and Miller did not conduct PAH solubility experiments themselves, but they summarize the results of others for the purpose of developing prediction approaches (2009). They report that some researchers have used partition coefficients to describe the equilibrium partitioning of PAHs from NAPLs. The relevant partition coefficient between a NAPL and water is defined as

\[
K_{nwj} = \frac{C^n_j}{C^a_{ei}}
\]  

(5.1.4)
where $C_i^n$ is the concentration of species $i$ in the NAPL and $C_{ei}^w$ is the equilibrium concentration of species $i$ in the water (Lee et al., 1992; Endo and Schmidt, 2006). Using a common approach, the octanol-water partition coefficient (a ratio of component concentration in the octanol and water phases $K_{ow_i} = C_i^o / C_i^w$) has been related to $K_{nw}$ of coal tar-water systems using the following regression developed from a survey of literature data (Endo and Schmidt, 2006).

$$\log K_{nw_i} = 1.16 \log K_{ow_i} - 0.19$$

(5.1.5)

Of course, this method of prediction only applies to PAHs with characterized and reported octanol-water partition coefficients. Hence, it is somewhat limited. Furthermore, it was determined that this method provides unreasonably high solubility predictions for few-component PAH mixtures, and so it will not be considered further.

Birak and Miller also consider the previously discussed Raoult’s law method and suggest that, in some non-ideal cases, the addition of an activity coefficient $\gamma_i^n$ should be applied as follows:

$$C_i^n = \gamma_i^n x_i^n S_{SCL}$$

(5.1.6)

Furthermore, they introduce another method to predict the subcooled liquid solubility $S_{SCL}$ by way of fugacity ratio. Peters and coworkers developed this theory (2000). It will be discussed in detail below:
Thermodynamic theory states that the chemical potential, or its surrogate fugacity, of a single species must be equal for all phases present in an equilibrated system. This concept is central to solid-liquid phase equilibrium analyses and consequently, it defines the framework for the development of many solubility models. For example, when applied to environmentally relevant PAH mixtures, conclusions can be drawn regarding the possible coexistence of phases and also about the aqueous solubility of such multicomponent systems.

The equality of species $i$ fugacities between hypothetical phases $\alpha$, $\beta$, etc., can be written generically as

$$
\hat{f}_i^\alpha = \hat{f}_i^\beta = ... = \hat{f}_i^\pi
$$

(5.1.7)

where $\hat{f}_i$ is the fugacity of species $i$ in the different solution phases. These values can be represented by the following expression, which defines activity coefficients in terms of fugacities:

$$
\gamma_i = \frac{\hat{f}_i}{x_i f_i}
$$

(5.1.8)

Here, $x_i$ is the mole fraction of species $i$ in solution and $f_i$ is the fugacity of pure species $i$. Upon rearrangement and substitution, eq 5.1.7 can be written as follows:

$$
x_i^{\alpha} \gamma_i^{\alpha} f_i^{\alpha} = x_i^{\beta} \gamma_i^{\beta} f_i^{\beta} = ... = x_i^{\pi} \gamma_i^{\pi} f_i^{\pi}
$$

(5.1.9)

To describe the behavior of a NAPL, Peters et al. considered a multicomponent, multiphase (solid and liquid) system of PAHs (2000). Such a system is described (at equilibrium) by rewriting eq 5.1.9 as follows:
Here, superscripts N and S symbolize the NAPL and solid phases, respectively with the assumption that only these two phases need to be considered (i.e., that there are not multiple solid or NAPL phases nor water present). Many NAPL components are actually solid in their pure state under the system conditions, so $f_i^L$ is a hypothetical fugacity of pure species $i$ in some subcooled liquid state, used for defining the liquid phase activity coefficients (Peters et al., 2000).

Algebraic rearrangement of eq 5.1.10 gives a definition for the mole fraction of species $i$ in the NAPL phase $x_i^N$:

$$x_i^N = x_i^S \gamma_i^S f_i^S \gamma_i^N f_i^L = x_i^S \gamma_i^S \left( \frac{f_i^S}{f_i^L} \right)$$

(5.1.11)

Clearly, the equilibrium solubility of solute $i$ in the NAPL depends on a ratio of fugacities $f_i^S/f_i^L$. This ratio is known as the solid-liquid fugacity ratio. It accounts for the energy associated with a solid to liquid phase transition at a given system temperature. Of course, the fugacity ratio will be unity for any pure species that is a liquid at the system conditions.

Eq 5.1.11 shows that, in addition to the fugacity ratio, the solubility of solute $i$ in the NAPL depends on composition and on measures of solution ideality in both the solid and liquid phases. Peters et al. (2000) have collected and defined these terms as the “nonideality factor” where,
Nonideality factor $= \frac{x_i^S y_i^S}{y_i^N}$ (5.1.12)

Eq 5.1.11 can be simplified by imposing two assumptions. Consider first that the NAPL is an ideal solution. In such cases molecules are similar in structure and molecular interactions have a negligible effect on the behavior of the mixture, i.e., $\Delta H_{\text{mix}}=0$. In such cases, the activity coefficient for species $i$ in the NAPL phase is unity, $y_i^N \approx 1$. This assumption is often used for NAPLs that are composed mainly of PAHs because molecular size and structure are quite similar and molecular interactions can sometimes be ignored. Nonetheless, making this assumption requires careful analysis of the system at hand and it may not be appropriate for many NAPL or tar systems, as the results in earlier chapters have clearly indicated.

Next consider that if the concentration of species $i$ in the NAPL phase exceeds that component’s equilibrium solubility, a solid phase will precipitate from the liquid solution. Peters et al. assume that these solids will precipitate as pure species, rather than as solid solutions, and the entire numerator of eq 5.1.12 will become unity, $x_i^S y_i^S = 1$ (2000). Clearly, this is not necessarily true in general, but it is useful to consider the consequences.

These two assumptions give rise to the following form of eq 5.1.11:

$$x_i^N = \left( \frac{f_i^S}{f_i^L} \right)$$ (5.1.13)

Therefore, if both assumptions are imposed, the equilibrium concentration of species $i$ in the NAPL reduces to just the solid-liquid fugacity ratio. This result is of
importance to those interested in behavior of NAPLs in subsurface media because it removes all dependence on concentration and molecular interaction and reduces to a very simple relationship. Of course, it entirely disregards the possibility of nucleation of other phases.

Consider now that the NAPL system described above is in equilibrium with water. Such a system has been considered by Peters and coworkers as describing the gradual evolution of a NAPL phase from which groundwater extracts some components over time (2000). Despite low pure-PAH species aqueous solubility, these mixtures have the potential to dissolve to some extent into the surrounding groundwater. The fugacity of components in the newly considered aqueous phase must be equivalent to those of the previously discussed liquid and solid PAH phases. This could be described by a relationship similar to that of eq 5.1.10 so that

\[ x_i^A \gamma_i^A f_i^A = x_i^N \gamma_i^N f_i^L \]  

(eq 5.1.14)

Eq 5.1.14 can be rearranged to separate the aqueous phase concentration of species \( i \) from the other variables:

\[ x_i^A = \frac{x_i^N \gamma_i^N}{\gamma_i^A} \frac{f_i^L}{f_i^A} = \frac{x_i^N \gamma_i^N}{\gamma_i^A} \]  

(eq 5.1.15)

The equality in eq 5.1.11 can be used to eliminate \( x_i^N \) from eq 5.1.15:

\[ x_i^A = \frac{x_i^S \gamma_i^S f_i^S f_i^L}{\gamma_i^A f_i^L} = \frac{1}{\gamma_i^A} \frac{f_i^S}{f_i^L} \]  

(eq 5.1.16)
This shows that the aqueous phase concentration of each component is inversely proportional to the actual aqueous phase activity coefficient of species \( i (\gamma_i^A) \). If the molecular interactions of species \( i \) in the aqueous phase are small, it is assumed that the actual aqueous phase activity coefficient \( (\gamma_i^A) \) of species \( i \) is equivalent to the activity coefficient of species \( i \) in equilibrium with a pure solute \( (\gamma_i^A^*) \) (Peters et al., 2000; Banerjee, 1984). So then,

\[
\gamma_i^A \approx \gamma_i^A^* = \frac{1}{x_i^A^*} \left( \frac{f^S}{f^L} \right)_i
\]  

(5.1.17)

Here, \( x_i^A^* \) is the aqueous solubility of pure species \( i \). This definition can be substituted into eq 5.1.15, to thereby express the solubility of any NAPL component.

\[
x_i^A = x_i^N \gamma_i^N x_i^A^* \left( \frac{f^L}{f^S} \right)_i
\]  

(5.1.18)

Consider again that the aqueous phase is dilute. Consequently, its total volume is assumed to be unaffected by the presence of dissolved components. Under such conditions, aqueous phase mole fractions are proportional to mass concentrations and eq 5.1.18 becomes,

\[
C_i^A = x_i^N \gamma_i^N S_i^S \left( \frac{f^L}{f^S} \right)_i \quad \text{FOR LIQUID NAPL (Peters et al., 2000)}
\]  

(5.1.19)

Here, \( C_i^A \) (mass/volume) is the predicted aqueous phase concentration of species \( i \) in equilibrium with a liquid PAH mixture and \( S_i^S \) is the aqueous solubility of pure solid \( i \)
(mass/volume). Combination of the terms $S_i^S\left(f_i^L / f_i^S\right)$ gives an expression for the **subcooled liquid solubility** (described above).

To this point, the NAPL phase has been discussed as a liquid mixture only. Now consider that if the components in the NAPL were to exist as solids (as might be the case in a dense NAPL or a tar), the species-specific fugacity ratios would be unity and eq 5.1.19 would take the following form:

$$C_i^A = x_i^N \gamma_i^N S_i^S$$ \hspace{1cm} \text{FOR SOLID SOLUTION (Peters et al., 2000)} \hspace{1cm} (5.1.20)

This solid solution model simplifies to the Raoult’s law relationship under ideal conditions, i.e., $\gamma_i^N = 1$.

The relationships given by eqs 5.1.19 and 5.1.20 illustrate that the aqueous solubility of a NAPL or tar components might depend on the relative quantity of that species in the bulk material and on either pure solubility or subcooled liquid solubility. Thus, components of PAH mixtures may dissolve into water much differently than pure PAH species.

Mukherji, Peters, and Weber studied the aqueous solubility of PAHs from synthetic tars or dense non-aqueous phase liquids (DNAPLs) and used the experimental data and eq 5.1.19 to calculate component activity coefficients (1997). The NAPL compositions and experimental results are given in Table 5.2 and Figure 5.1, respectively.
Table 5.2. Composition of laboratory-made DNAPL mixtures, used in the experiments of Mukherji et al., 1997.

<table>
<thead>
<tr>
<th>components</th>
<th>DNAPL-I</th>
<th>DNAPL-II</th>
<th>DNAPL-III</th>
<th>DNAPL-IV</th>
</tr>
</thead>
<tbody>
<tr>
<td>toluene</td>
<td>0.05</td>
<td>0.05</td>
<td>0.04</td>
<td>0.03</td>
</tr>
<tr>
<td>naphthalene</td>
<td>0.00</td>
<td>0.05</td>
<td>0.10</td>
<td>0.25</td>
</tr>
<tr>
<td>1-methylnaphthalene</td>
<td>0.29</td>
<td>0.28</td>
<td>0.26</td>
<td>0.22</td>
</tr>
<tr>
<td>2- ethynaphthalene</td>
<td>0.14</td>
<td>0.13</td>
<td>0.13</td>
<td>0.11</td>
</tr>
<tr>
<td>acenaphthene</td>
<td>0.15</td>
<td>0.14</td>
<td>0.14</td>
<td>0.11</td>
</tr>
<tr>
<td>fluorene</td>
<td>0.07</td>
<td>0.07</td>
<td>0.06</td>
<td>0.05</td>
</tr>
<tr>
<td>phenanthrene</td>
<td>0.13</td>
<td>0.12</td>
<td>0.12</td>
<td>0.10</td>
</tr>
<tr>
<td>fluoranthene</td>
<td>0.12</td>
<td>0.11</td>
<td>0.10</td>
<td>0.09</td>
</tr>
<tr>
<td>pyrene</td>
<td>0.05</td>
<td>0.05</td>
<td>0.05</td>
<td>0.04</td>
</tr>
</tbody>
</table>

Based upon the results shown in Figure 5.1, Mukherji and coworkers concluded that the activity coefficients of DNAPL components approached the Raoult's law prediction of unity and that despite positive and negative deviation in the results, eq 5.1.19 “holds for these DNAPL mixtures” (1997). The authors attribute deviation from $\gamma = 1$ to uncertainty in the fugacity ratio and to lack of any experimental provision to control temperature, which was allowed to vary between 293 and 298 K. It has been shown in this laboratory (see below) and others that temperature control is extremely important during PAH solubility experiments. Furthermore, the error noted above is also associated with the uncertainty in pure component solubilities reported in the literature.
In a separate but similar study, Peters et al. report aqueous concentrations of NAPL components from water/NAPL phase equilibrium experiments (1997). Results from the study are given in Table 5.3 and are compared to values predicted by eq 5.1.19. Based upon the results from the previously noted study, the activity coefficients (in eq 5.1.19) are assumed to be unity. The solubilities obtained in the study were found to be in fair agreement with those predicted by eq 5.1.19. In fact, it is reported that eq 5.1.19 "provides a reliable means of predicting aqueous concentrations in multicomponent NAPL/water systems" if the assumption of ideality ($\gamma = 1$) was imposed (1997). Despite this conclusion, there exists deviation between the measured and predicted concentrations (Table 5.3), especially for the
higher molecular weight PAHs. As was done in the previous study, the authors attributed this error to uncertainties in pure component solubilities and in fugacity ratios.

**Table 5.3** Measured and estimated aqueous concentrations of NAPL components in the NAPL/water phase equilibrium experiments of Peters et al., 1997.

- Toluene
- Naphthalene
- 1-Methylnaphthalene
- 2-Methylnaphthalene
- Acenaphthene
- Fluorene
- Phenanthrene
- Fluoranthene
- Pyrene

These results, amongst other similar reports, are the basis for the study reported here. Though ideal NAPL theory has been shown to fairly well predict the solubilities of liquid mixtures of PAHs, the results are not so clear for semi-solid tars that exhibit some liquid-like character. Though it was hypothesized that the behavior reported by Peters and coworkers might not be well followed (considering the solid character of the mixtures used here), uncertainty remained surrounding the ability of the more solid mixtures to dissolve as solid solutions (eq 5.1.20) or as phase separated systems.
5.2 Experimental

Materials

Compounds used in the solubility experiments of this chapter are analogous to those described in Section 3.2.

Mixture Preparation

Mixtures were prepared by two methods and results were highly sensitive to the procedure (see below). Since well-defined experimental protocols do not exist for these types of solubility experiments, both procedures and their associated experimental results will be described and examined.

Method 1 – Solvent Evaporation Technique: Based upon the work previously reported by Peters et al. (1997) and on differential scanning calorimetry conducted in this laboratory (see below), it was hypothesized that a solvent evaporation technique could be used to coat solid solutions of binary and multicomponent PAH mixtures onto the inner surfaces of 500 mL Erlenmeyer flasks. From there, these materials would be dissolved into water, for measurements of solubility.

Peters et al. prepared some NAPL mixtures (above) using a similar technique to the one described here (1997). Furthermore, other investigators interested in dissolving a known quantity of hydrophobic material in water commonly use this type of procedure. For example, studies that aim at characterizing the partition coefficients of hydrophobic contaminants from aqueous solution to passive
samplers (these samplers are generally solid plastics immersed in the solutions) sometimes involve coating the compounds of interest onto the walls of a glass container before filling the container with water and placing the passive sampler inside.

Recall that in Chapter 3 DSC results indicated that binary mixtures exhibited depressed melting temperatures, i.e. mixture solution behavior. Simple melt and slow cooling mixtures were not used in the experiments of Chapters 3 or 4 because there was some concern about inducing mixture heterogeneity (i.e., pure phases might nucleate during solidification). However, based on these results that showed little effect of preparation method, and the precedent of the experimental procedures of Peters et al. (1997), it was initially thought that a solvent evaporation technique could be used for preparing the mixtures for the solubility experiments of this chapter.

The solvent evaporation technique is shown (for a typical binary mixture of anthracene + pyrene) in steps 1 and 2 of the schematic of Figure 5.2.
1. Anthracene and pyrene are added to a DCM solution within a 500 mL Erlenmeyer flask. The mole ratio of components is selected, with a slight excess above the solubility limit.

2. The flask is placed in a rotary evaporator. As the DCM is vaporized, the PAHs are left in a smooth coating on the walls.

3. 500 mL of water is added to the flask. The flask is then kept in a temperature controlled orbital shaker for two weeks at 25°C and 125 cycles per min.

4. If flakes are visible, the solution is filtered through a fritted glass filter. The PAHs in water solution are then extracted using DCM, and their concentration is determined using GC/MS analysis.

Figure 5.2. Schematic of the solvent evaporation technique and subsequent method to dissolve and measure PAH concentrations in aqueous solution at equilibrium.
In step 1, desired quantities of each PAH were measured (on a microbalance to ± 0.01 mg) and placed within a Pyrex glass 500 ml Erlenmeyer flask. Then roughly 100 mL of an organic solvent was used to dissolve the PAHs into a liquid solution. Initially methylene chloride (DCM) was used as a solvent, but it was subsequently determined by visual analysis that dissolution in hexane provided better results.

The evaporation step (step 2 of Figure 5.2) involved placing the solvent/PAH-containing flask on a rotary evaporator and heating to about 313 K. This provided fast evaporation of the solvent and sometimes produced a smooth coating of solid, PAH solution on the walls of the flask. Unfortunately, in cases where more than a milligram of PAH mixture was used, the coating was not always smooth and there was concern that the solid particles could flake off into the added water (see below). By itself, this would not be a problem, but the water content of the flasks did need to be filtered out prior to analysis, so that only the PAH that was truly in solution would be measured in the subsequent step.

**Method 2 – Quench Cooling Technique:** As will be discussed in the following section, initial results suggested that solvent evaporation did not appear to produce solid solutions of anthracene + pyrene in the flask. It was deemed necessary to resort to the previously discussed quench-cooling techniques to provide true mixtures, for the solubility experiments.

The quench cooling procedure used for preparing samples for solubility experiments is that described in Chapter 3. Following this preparation, the desired quantities of binary or multicomponent quench-cooled mixtures were placed inside
500 ml Erlenmeyer flasks. These mixtures ranged from crystalline powders (binary mixtures) to semi-solid flakes (multi-component mixtures). In order to promote mass transport into the aqueous phase, the solids were not confined in any secondary containment, i.e., they would float freely in the added water.

Aqueous Dissolution

Flasks that were either coated with (method 1) or that contained (method 2) quench cooled PAH mixtures, were filled with 500 ml of nanopure water, sealed with a glass plug, and placed inside an incubating shaker (Step 3 of Figure 5.2). The solutions were equilibrated at 298 K and agitated at 125 cycles per minute for up to 2 weeks. Although the dissolution kinetics were not formally investigated, it was determined that the results from 4 day experiments were no different than those from 2 week experiments, and accordingly, many of the later samples were equilibrated for only 4 days.

Flasks were removed after equilibration from the incubating shaker and the water was visually inspected for suspended solids. In cases where the solvent evaporative preparation technique (method 1) was used, solids were observed in flasks that contained greater than 1 mg of solid mixture. Hence, it was decided that particles (not necessarily seen by eye) might exist in all systems prepared by method 1 and so all water was subsequently filtered using a Pyrex glass fritted filter.

Of course, all the water in equilibrium with the quench-cooled samples prepared by method 2 required filtering. Recall that in the case of method 2, all of the mixture was suspended in the water, that is, none of the mixture was coated on
the walls. It is worth mentioning that centrifugation was investigated as a possible solid-PAH separation technique, but the particles were too buoyant and this method proved to be ineffective.

Temperature is an important factor during both the equilibration and filtration steps. As was observed in some early experimental results (reported below), when the solution temperature is allowed to drop, from say $T = 298 \text{ K}$ to $T = 293 \text{ K}$, dissolved PAHs could precipitate from solution to preserve equilibrium. In other words, solubility is a function of temperature and as a solution cools, the equilibrium solubility of each PAH decreases, causing them to precipitate in the flask. Hence, the water/PAH system must be kept at the desired equilibration temperature during the filtration step and temperature cannot be allowed to decrease until measured and filtered volumes of PAH-containing water are placed in flasks for liquid-liquid extraction (see below). In much of this study, the laboratory temperature was held at $298 \pm 1 \text{ K}$ to prevent sample cooling during the handling, i.e., filtration steps of this procedure.

250 ml aliquots of PAH-containing water were measured, filtered, and placed inside 250 ml Pyrex glass extraction flasks. Since each dissolution flask initially contained 500 ml of water, this method provided replicate samples, the results from which verified reproducibility of the experimental technique, i.e., filtration, extraction, drying, dilution, and GC-MS analysis (see below). 15 ml of DCM (organic solvent) was then added to the extraction flasks and the flasks were subsequently shaken. This procedure is a liquid-liquid separation technique used to extract
hydrophobic solutes from an aqueous phase to an organic solvent phase. The overarching purpose is to concentrate the solutes (PAHs) in a small volume of organic solvent so that they can be measured by available analytical techniques (e.g., gas chromatography).

Once shaken, the extraction flasks were held still for a few minutes to allow the water and DCM to separate into respective layers. This is shown in Figure 5.3. The DCM was then removed through a valve at the bottom of the extraction flask and into 40 ml glass vials. This extraction procedure was repeated two more times, each with 10 ml of DCM.
Extracted DCM/PAH solutions were then dried completely using a turbo evaporation system. Left behind in 40 ml glass vials was a visible, albeit difficult to see, layer of solid PAH. These solid PAHs were dissolved in a carefully measured volume of DCM (usually 5 mL) that was then transferred by glass pipette to amber
gas-chromatography vials. The vials were sealed with a Teflon lined cap to reduce evaporation of DCM. Vials were stored in a refrigerator at 277 K.

**Gas-Chromatography-Mass Spectrometry**

Gas chromatography-mass spectrometry (GC-MS) was used to determine the concentration of PAHs in the DCM/PAH aliquot (described above). The concentration, or aqueous solubility, of the PAHs can be determined, as shown below for a typical 5 μg of PAH in 1 ml DCM, extracted from the full 250 ml of water taken from the extraction flask fluid.

\[
\left( \frac{5 \, \mu g \, PAH}{1 \, ml \, DCM} \right) \cdot \left( \frac{5 \, ml \, DCM}{250 \, ml \, water} \right) = 0.1 \, mg \, PAH/L \, water
\]

Analytes were actually diluted in dichloromethane to an approximate concentration of 5 μg ml⁻¹ and analyzed by a calibrated PerkinElmer Clarus 680 combined gas chromatograph and mass spectrometer. The analytical procedure for EPA Method 8270C was followed.

**A Note About the Required Quantities of PAHs**

The desired quantities of each PAH to be added to the dissolution flask were not trivial to determine. Since it was initially unclear whether the PAH mixtures would behave as true solid solutions or as phase separated PAH species, it was necessary to use at least enough of each PAH to ensure that the reported solubility of each pure component was indeed a saturated solution value for a given mixture. Therefore, in order to avoid running short of a dissolving PAH prior to equilibrium,
each mixture had to contain at least enough of each component to reach this hypothetical maximum. Of course, each pure PAH has a reported solubility in water and this value represents the maximum aqueous phase concentration (of that species) allowed in the aqueous system, as higher aqueous concentrations would lead to precipitation of a pure phase.

The above became somewhat problematic in cases where mixtures were enriched in one component (e.g. a binary mixture with $x_1=0.90$ and $x_2=0.10$). As discussed above, both components had to exist in the system at a quantity slightly in excess of what could potentially dissolve if components were to behave as phase separated species. Therefore, to retain the intended mixture mole fractions, large quantities of PAHs sometimes had to be used. This simple picture is further complicated in situations in which multiple phases of differing stoichiometry exist. In that case, one phase could be depleted. This possibility was not considered further here.

So for example, at least 0.325 mg of pyrene was required in a mixture with a desired pyrene mole fraction of 0.10. Since, in this case, pyrene is the lesser component, the remaining 90 mol% of mixture is accounted for with an added 2.93 mg of anthracene. As noted above, such a large quantity of material was difficult to deal with. The quantities of anthracene and pyrene listed in Table 5.4 represent the minimum required masses of each component and shaded numbers represent the lesser component. Similar calculations were carried out for all mixtures of this
study. Of course, the comfortable operating range of the available analytical equipment (GC-MS described above) also dictated the quantities used.

**Table 5.4.** Minimum quantities of anthracene and pyrene needed for a 500 ml aqueous solubility experiment. Shaded numbers represent limiting components.

<table>
<thead>
<tr>
<th>Mole Fraction</th>
<th>Required Anth. (mg)</th>
<th>Mole Fraction</th>
<th>Required Pyrene (mg)</th>
<th>Total Mass (mg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Anthracene</td>
<td>Pyrene</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.00</td>
<td>0.33</td>
<td>0</td>
<td>0.00</td>
<td>0.33</td>
</tr>
<tr>
<td>0.90</td>
<td>1.15</td>
<td>0.1</td>
<td>0.11</td>
<td>1.26</td>
</tr>
<tr>
<td>0.78</td>
<td>0.45</td>
<td>0.22</td>
<td>0.11</td>
<td>0.57</td>
</tr>
<tr>
<td>0.50</td>
<td>0.33</td>
<td>0.5</td>
<td>0.29</td>
<td>0.61</td>
</tr>
<tr>
<td>0.10</td>
<td>0.33</td>
<td>0.9</td>
<td>2.93</td>
<td>3.25</td>
</tr>
<tr>
<td>0.00</td>
<td>0.00</td>
<td>1</td>
<td>0.11</td>
<td>0.11</td>
</tr>
</tbody>
</table>

5.3 Results and Discussion

*Binary, Anthracene + Pyrene Solid Mixtures Prepared by Solvent Evaporation Technique*

Binary mixtures of anthracene + pyrene and respective pure components were prepared by the solvent evaporation technique (method 1) described above. They were then allowed to equilibrate with 500 ml of nanopure water at 298 K for two weeks and samples were analyzed by calibrated GC-MS as described above. Results are shown in Figure 5.4 for the full range of mole fractions, including that of the pure components.
First considering the final concentrations of the pure components, it was immediately apparent that the measured concentrations fell below those reported in the literature for anthracene (0.045 mg/L) and pyrene (0.13 mg/L) at 298 K (May et al., 1978). Subsequent investigation of the experimental technique showed that losses from the liquid-liquid extraction and turbo evaporation steps were within a few percent and could not account for the nearly 30% lower equilibrium values initially seen here. These losses were eventually attributed to accidental cooling of the solution from 298 K to 293 K (laboratory temperature) during the filtration step. As the mixtures cooled, a new solubility limit was achieved and the dissolved PAHs precipitated from the aqueous phase. The results given in Figure 5.4 support this hypothesis, where the measured solubilities of pyrene and anthracene are perfectly in line with pure component solubilities at 293 K.

As a result, the results from these binary mixtures (prepared by solvent evaporation method 1) appear to be unaffected by mixture composition, and as a result of the unintended cooling step, it is not known if the absence of a trend with composition is real. If the solid mixtures were truly solid solutions and behaving as such, the aqueous phase solubilities might have followed the weighted solid solution curves shown in Figure 5.4 for 298 K. For a significant range of mole fractions, it is clear that the solubility of the PAHs should have been below the observed values and hence, solid PAHs would not have precipitated upon cooling to 293 K.
Thus, it is believed that the observed results do not agree with the literature, which suggests that the aqueous solubility of the mixture components are affected by their existence in a mixture. Furthermore, it was shown in earlier solid/liquid and solid/vapor studies (Chapters 3 and 4) that the binary (and multicomponent) mixtures interact in a complicated and sometimes non-ideal way. Therefore, it is believed that the solvent evaporation technique produced a phase-separated system.
of anthracene and pyrene. This could have allowed the PAHs to partition into the aqueous phase independently of one another. Based on these results, it was decided that quench-cooled PAH mixtures (method 2) should be used for all subsequent solubility experiments.

**Binary Quench-Cooled PAH Mixtures**

Figures 5.5, 5.6, and 5.7 show the equilibrium solubility of components in separate equimolar, binary, quench-cooled PAH mixtures. The solubilities of the pure components and also those calculated by ideal solid solution theory (eq 5.1.20) are given for reference and comparison. These samples were carefully kept at 298 K during the equilibration and filtration steps to avoid the precipitation that was observed in the previous section.

The most striking observation is that the measured concentrations of all mixture components are significantly less than those reported for the respective pure compounds. Hence, the solubility of each component is affected by its presence in the quench-cooled mixtures. Recall that this was not observed in solvent evaporated mixtures of Figure 5.4.
In the case of an equimolar anthracene + fluoranthene mixture (Figure 5.5), the measured solubility of each pure component is about 0.015 mg/L and 0.05 mg/L, respectively. The final anthracene concentration is roughly half of what is expected from ideal mixture theory (eq 5.1.20). The predicted fluoranthene concentration is 0.13 mg/L and this too is about double the measured value.
In the case of an equimolar anthracene + benzo(a)pyrene mixture (Figure 5.6), the measured solubility of anthracene is again about 0.01 mg/L and this is roughly 50% less than what is expected by ideal mixture theory (eq 5.1.20). Though benzo(a)pyrene was detected in the aqueous phase, the level was too low for quantitation using the available equipment. Nevertheless, the concentration is below that predicted by ideal mixture theory, which would have produced a quantifiable concentration.
A study was then conducted to investigate the solubility of quench-cooled anthracene + pyrene mixtures that varied in composition over the full range of mole fractions. Results are given in Figure 5.7. The equimolar mixture exhibits solubility that is well predicted by ideal solid solution theory. An interesting trend appears in this data set. It seems as though mixtures enriched in a component above 50 mol% exhibit slightly lower than expected solubility. Similarly, mixtures that exist at
concentrations below 50 mol% seem to equilibrate at concentrations slightly above that predicted by ideal solution theory. The measured solubilities from Figure 5.7 are also reported as a line plot in Figure 5.8. The measured concentrations (of each component) exhibit no clear trend with respect to mole fraction.

Figure 5.8. Aqueous solubility of quench-cooled anthracene + pyrene solid mixtures.

Though there is variability in the results, there is also a minimum solubility value at 22 mol% anthracene, which happens to be the eutectic phase composition. This may suggest complicated mixture composition dependence, which was not examined further in this study.
Multicomponent Quench-Cooled PAH Mixtures

Three equimolar, multi-component PAH mixtures were examined in this part of the study. The results are not significantly different than those reported for the binary mixtures.

In the case of a quaternary mixture of anthracene + pyrene + fluoranthene + benzo(a)pyrene shown in Figure 5.9, the former three components exist in the aqueous phase at about 0.01 mg/L. This value is near that predicted for anthracene, but much lower than that predicted for pyrene and fluoranthene. As was the case in all experiments of this study, benzo(a)pyrene was detected in the sample, but was at a concentration too low to be quantified by the available GC-MS.
Figure 5.9. Aqueous solubility of an equimolar, quench-cooled mixture of anthracene + pyrene + fluoranthene+ benzo(a)pyrene.

In the experiments of Figures 5.10 and 5.11, for five and six component PAH mixtures, respectively, the solubilities of most components range between about 0.01 and 0.05 mg/L. This is not much different (though admittedly a bit higher than in the quaternary mixture) from what has been reported above for fewer component mixtures. What becomes apparent though, is that as the number of components increases, the predicted solubility (eq 5.1.20) of each component decreases. Thus, these higher component mixtures appear to more closely follow
the predicted values. This is obviously not true for phenanthrene whose relatively high pure component solubility far exceeds the compound’s solubility from the multi-component mixtures.

![Figure 5.10](image.png)

Figure 5.10. Aqueous solubility of an equimolar, quench-cooled mixture of anthracene + pyrene + fluoranthene + benzo(a)pyrene + phenanthrene.

It is not clear whether the solubilities of the components in the multicomponent mixtures have reached some limit that keeps the solubility of each
component similar for a range of mixtures studied or if ideal mixture behavior is actually approached as the number of compounds in these mixtures increases.

Figure 5.11. Aqueous solubility of an equimolar, quench-cooled mixture of anthracene + pyrene + fluoranthene + benzo(a)pyrene + phenanthrene + chrysene.

The results from Figures 5.5 – 5.11 are tabulated in Table 5.5. Predicted aqueous solubilities based on both solid solution theory and on Peters’ NAPL solution model are given (Table 5.5) for comparison. It is important to recall that the
five and six component mixtures studied here exhibit solid/vapor and solid/liquid behavior that approaches tarlike behavior. And though there is no clear trend in the data shown here, these mixtures do not obey the NAPL models proposed by Peters et al. (eq 5.1.19). In fact, the values predicted by eq 5.1.19 are 1 to 2 orders of magnitude greater than the measured values. In contrast, the aqueous partitioning behavior of these mixtures is better predicted by ideal solid solution theory (eq 5.1.20), which provides estimates that are more often within the same order of magnitude of the measured values.

Table 5.5. Summary of predicted and experimentally measured component solubilities from few-component PAH mixtures. Pure component solubilities are also given for comparison (May et al., 1978).

<table>
<thead>
<tr>
<th>Equimolar Mixture Components</th>
<th>SOLUBILITY (mg/L)</th>
<th>²/f² 298 K</th>
<th>Pure Comp (Lit)</th>
<th>Measured Mixture</th>
<th>Solid Soln. Model</th>
<th>NAPL Soln. Model</th>
</tr>
</thead>
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<tr>
<td>Anthracene</td>
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<td>0.0098</td>
<td>0.045</td>
<td>0.025</td>
<td>0.023</td>
<td>2.296</td>
</tr>
<tr>
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<td>0.13</td>
<td>0.071</td>
<td>0.065</td>
<td>0.607</td>
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<td>0.045</td>
<td>0.01</td>
<td>0.023</td>
<td>2.296</td>
</tr>
<tr>
<td>Benzo[a]pyrene delegates</td>
<td></td>
<td>0.03</td>
<td>0.004</td>
<td>&lt;DL</td>
<td>0.002</td>
<td>0.067</td>
</tr>
<tr>
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<td>0.045</td>
<td>0.016</td>
<td>0.023</td>
<td>2.296</td>
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<tr>
<td>Fluoranthene</td>
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<td>0.213</td>
<td>0.26</td>
<td>0.054</td>
<td>0.130</td>
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<td>&lt;DL</td>
<td>0.001</td>
<td>0.033</td>
</tr>
<tr>
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<td>0.244</td>
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<td>Benzo[a]pyrene delegates</td>
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<td>0.004</td>
<td>&lt;DL</td>
<td>0.001</td>
<td>0.027</td>
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<tr>
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<td>1.1</td>
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<td>0.022</td>
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<td>&lt;DL</td>
<td>0.0003</td>
<td>0.034</td>
</tr>
</tbody>
</table>
5.4 Concluding Remarks

The solubility of binary and multicomponent mixtures can be roughly predicted by ideal solid solution theory. For the equimolar binary mixtures, some experimental evidence suggests that the solubility of each component may be less than what is predicted, but other data show that the solubilities of anthracene + pyrene solid mixtures fall both above and below the predicted values, and that there might be a complicated mixture composition dependence. There is no clear trend in the data and it is presently not clear why there is such variability in the experimental results. As more PAHs are added to create tarlike mixtures, the solubility seems to better fit the values predicted by eq 5.1.20, though there is still significant failure to predict actual values.

There is a fair amount of unexplained variability in these results, and hence, they can serve only as a preliminary indication of behavior. Further work is needed to better describe the trends here. Nevertheless, these results do suggest that as PAH mixtures become enriched in components to a point at which only a discrete number of compounds exist in the mixture, solubility is roughly predicted by ideal solid solution theory. Though there was no reason to initially hypothesize that the multicomponent, tarlike mixtures in this study would follow the theory reported by Peters et al. for NAPLs, the behavior observed here is quite different from what one would expect if that model was used (2000). Of course, this conclusion is significant for those dealing with such mixtures in natural settings.
Chapter 6. Sorption Behavior of PAHs to Natural Particles

6.1 Introduction

The sorption behavior onto soil of organic compounds, specifically PAHs, is an important factor involved in the fate and transport of chemicals in the subsurface environment. A variety of questions arise when considering such complicated environmental systems, and hence, a significant amount of research has been devoted to this topic.

Subsurface soils and sediments are highly heterogeneous. They are composed of both inorganic and organic matter at various stages of decomposition, each with unique chemical composition. Soil chemistry is determined by many factors such as pH, cation exchange capacity, bacterial growth, available metals, moisture content, etc. In addition to complicated chemistry, the particle size and porosity of different soil fractions vary significantly and these are directly linked to the surface area available for chemical sorption. It is widely understood that hydrophobic compounds, including PAHs, preferentially adhere to soil organic matter (Luthy et al., 1997). Initially this may seem convenient for sorption characterization, but analyses become complicated because both soil organic matter and PAH sorbates can be highly complex.
Organic and inorganic carbon (OC & IC) make up the total carbon (TC) content in a soil system. The inorganic fractions are mainly found as carbonates, i.e., salts of carbonic acid.

As mentioned above, organic matter is complex and is largely responsible for sorption of organic compounds in soil systems. It is worth briefly clarifying the common definitions associated with this topic. Organic carbon (OC) is a part of the soil organic matter (OM). In other words, the organic compounds associated with soils and sediments are not entirely composed of carbon. Traditionally, soil OM is quantified by combustion analysis where the difference in mass of a soil sample (pre- to post-combustion) is the OM content. It is important not to confuse this result with the OC content. Estimated ratios are commonly used to convert from OM to OC, but there can be significant uncertainty associated with the approximation (Tiessen and Moir, 1993).

Figure 6.1. A typical breakdown of organic matter in soil: taken from the University of Minnesota Extension www.extension.umn.edu.
Organic matter (and also organic carbon) can be divided into subsets (Figure 6.1) including active organic matter, humus, and elemental carbon. Active organic matter, not to be confused with activated carbon, is associated with comparatively young organic material. It results from the recent, partial decomposition of dead organisms, such as animals, plants, fungus, and bacteria. Active organic matter is rich in the soil nutrients required to sustain living organisms.

In contrast, the soil humus is a group of slowly degrading organic compounds, often referred to as “stable” or “resistant” organic matter. Like the active organic matter, the humic fractions come from dead organic materials; however, they do not degrade at rates significant enough to provide nutrients to the soils. The humus is older than the active organic matter. Humic and fulvic acids (HA and FA) are important components of the humus. They are acid mixtures associated with the stable organic matter and are understood to be responsible for much of the sorption capacity of organic carbon. Chemical structures of typical HA and FA are given in Figure 6.2.

Finally, elemental carbon is often associated with anthropogenic activity and consists of graphite, charcoal, and generally inappropriately, coal is included in this list. Despite the fact that charcoal and coal are derived from dead organic material, they are sometimes separated from the aforementioned (active and humic) subsets based upon their high carbon content, high degree of degradation, and high solid-state porosity. They too act as sorbents for organic sorbates, but the adsorption here
likely results from porosity and surface area rather than direct chemical interaction with chemical components, such as in the case of interaction with HA.

Figure 6.2. Chemical structures of typical humic and fulvic acids (Morrill et al., 1982).

Significant research has been conducted in an effort to characterize the ways in which the aforementioned parameters affect sorption processes in soils. Dzombak and Luthy (1984) and Delle Site (2001) summarize much of the work in substantial literature reviews. Though these reviews are quite thorough, it is worthwhile to highlight and to summarize conclusions of recent workers in this field. The remainder of this introductory section will serve as a brief summary of
relevant literature, meant only to acquaint the reader with recent issues, experimental design, and findings.

Dzombak and Luthy (1984) summarized the predictions of adsorption properties of soils for a wide range of PAHs by combining both limited adsorption data and known molecular characteristics. The authors acknowledged the importance of this topic and the deficiency of data in this field. Some important conclusions were brought to light in their analysis. Firstly, the Freundlich adsorption model (below) was discussed as a potentially useful tool for describing PAH adsorption.

\[ C_{is} = K_{if} C_{iw}^{n_i} \]  \hspace{1cm} (2.21.1)

Here \( C_{is} \) is the concentration of sorbed species \( i \), \( C_{iw} \) is the aqueous phase concentration of species \( i \), \( K_{if} \) is the Freundlich adsorption constant (know by other names, e.g., Freundlich constant capacity factor), and \( n_i \) is the Freundlich exponent.

Dzombak and Luthy (1984) also discussed how adsorption relates to transport by a retardation factor for organic component movement in soil and reported that both pure species and those associated with mixtures will travel at a rate defined by a correlation,

\[ v / v_c = 1 + \rho \left[ (1 - \varepsilon) / \varepsilon \right] K_{if} \]  \hspace{1cm} (6.1.1)

Here \( v \) is the average linear velocity of bulk fluid (i.e., water), \( v_c \) is the velocity of the \( C/C_o=0.5 \) (half relative solute concentration breakthrough) point, \( \rho \) is the density of the porous medium, and \( \varepsilon \) is the total effective porosity. \( K_{if} \) is a Freundlich
adsorption constant related to the Freundlich isotherm described above. It is an empirical measure of sorption strength, specific to the sorbate and sorbent. The entire term on the right hand side of eq 6.1.1 is called the retardation factor.

Lambert et al. (1965) concluded that the sorption process for dissolved aqueous organics in soil is similar to that into an organic solvent, meaning that a water/soil system can be compared to a water/immiscible solvent system. Furthermore, Karickoff and coworkers (1979; 1980) showed that organic carbon plays a role in sorption and defined the adsorption constant for organic carbon $K_{iOC}$ with respect to the concentration of total species-specific sorbate concentration associated with natural organic carbon ($C_{iOC}$) and the concentration of a given solute in the aqueous phase ($C_{iw}$).

$$K_{iOC} = \frac{C_{iOC}}{C_{iw}}$$  \hspace{1cm} (6.1.2)

Means and coworkers (1979; 1980a; 1980b) showed (experimentally) that $K_{iOC}$ and $K_{iOW}$ can be linearly correlated. $K_{iOW}$ is the oil/water partition coefficient of the organic species of interest, where $C_{iO}$ and $C_{iw}$ are species-specific solute concentrations in the octanol and aqueous phase, respectively.

$$K_{iOW} = \frac{C_{iO}}{C_{iw}}$$  \hspace{1cm} (6.1.3)

They reported experimentally determined $K_{iOW}$ values, and a number of linear correlations between $K_{iOC}$ and $K_{iOW}$ are given. From this, Dzombak and Luthy (1984) concluded that significant retardation occurs in groundwater with sediments that
contain moderate OC content. Proposed relationships between adsorption and soil OC content, between $K_{iow}$ and adsorption, and between $K_{iow}$ and molecular structure were offered, e.g., Figure 6.3, a correlation between adsorption coefficient $K$ and $K_{iow}$ for lower molecular weight PAHs (Dzombak and Luthy, 1984). It is concluded that there is great need for careful characterization of soil organic matter and its interactions with PAHs.

![Figure 6.3. Correlations between adsorption coefficient and octanol-water partition coefficient (Dzombak and Luthy, 1984).](image)

**Sorption by Activated Carbon, Soot, and Coal Fly Ash**

Some studies have addressed the question of sorption of organics by activated carbon, soot, and coal fly ash. Walters and Luthy (1984) used batch shake testing of 11 PAHs in water (saturated solutions) to test the adsorption onto activated carbon at 298 K and concluded that the Langmuir equation (eq 2.23.3)
best represents the data. They report Henry’s Law adsorption constants ($K_h$) from 2,390 (mg/g)/(mg/L) to 326,000 (mg/g)/(mg/L) for naphthalene and chrysene, respectively. The Henry’s law adsorption isotherm describes equilibrium solute concentrations ($q_e$) by $q_e = K_h C_e$, but is limited to low equilibrium aqueous concentrations ($C_e$). They also report maximum adsorption capacities $q^o$, which were calculated from the Langmuir equation for much higher solute concentrations. Results are summarized in Table 6.1. The authors conclude that adsorption of PAHs from water onto activated carbon is much stronger than that to soil, sediments, and other organic matter. Of course, such a table is not of particular general utility, since the values of $q^o$ would depend upon the surface area of the carbons and their surface properties.

Table 6.1. Henry’s law adsorption constants and adsorption capacities for 11 PAH/activated carbon systems (Walters and Luthy, 1984)

<table>
<thead>
<tr>
<th>Compound</th>
<th>$k_h$ (mg/g)/(mg/L)</th>
<th>$q^o$ mg/g</th>
</tr>
</thead>
<tbody>
<tr>
<td>naphthalene</td>
<td>2300</td>
<td>580</td>
</tr>
<tr>
<td>acenaphthylene</td>
<td>5270</td>
<td>500</td>
</tr>
<tr>
<td>acenaphthene</td>
<td>16800</td>
<td>465</td>
</tr>
<tr>
<td>fluorene</td>
<td>5640</td>
<td>440</td>
</tr>
<tr>
<td>phenanthrene</td>
<td>$\geq$13000</td>
<td>231</td>
</tr>
<tr>
<td>anthracene</td>
<td>6140</td>
<td>23.1</td>
</tr>
<tr>
<td>fluoranthene</td>
<td>$\geq$59000</td>
<td>104</td>
</tr>
<tr>
<td>pyrene</td>
<td>30500</td>
<td>82.8</td>
</tr>
<tr>
<td>triphenylene</td>
<td>$\geq$5900</td>
<td>36.8</td>
</tr>
<tr>
<td>benz[a]anthracene</td>
<td>$\geq$20400</td>
<td>14.7</td>
</tr>
<tr>
<td>chrysene</td>
<td>$\geq$136000</td>
<td>38.4</td>
</tr>
</tbody>
</table>
Low and Batley (1988) utilized a column apparatus and liquid chromatography to study the adsorption of anthracene, chrysene, and dibenz[a,c]anthracene on nine fly ash samples. The PAHs were dissolved in organic solvent, passed through a packed column of ash. They reported that the Freundlich isotherm best described the results (Figure 6.4).

Figure 6.4. Sorption of PAHs to fly ash: Comparison of Henry (‐), Langmuir I (‐‐‐‐), Langmuir II (‐‐), Freundlich (‐‐‐‐‐‐), and Weber-Matthews (‐‐‐‐‐‐‐) isotherms to experimental points (•) (Low and Batley, 1988).

It is again reported here that residual carbon controls the adsorption processes, though the authors warned that other adsorption processes might need
to be considered. Of course the choice of organic solvent for these experiments means that the results are not necessarily going to be simple to interpret, as the solvent interactions with carbon and PAH will be complex.

Banerjee et al. (1995) reported findings from batch and dynamic studies of fly ash sorption, in which partitioning of alcohols, aromatics, and ketones from aqueous solution was observed (this study did not include any PAHs). The organic compounds studied preferentially partitioned to fly ash, and carbon content is again reported as the main factor controlling total uptake. Furthermore, correlations between the Freundlich sorption capacity parameter $K_{if}$ and molar volume, parachor, $K_{iow}$ (Figure 6.5), and electronic polarizability were reported. Parachor is a property defined by molecular structure, i.e., surface tension, molecular weight, and density. Banerjee et al. (1995) concluded that weak induction forces of London or dispersion type account for the adsorption of organic compounds to fly ash.
Figure 6.5. Correlations between fly ash sorption capacity and octanol-water partition coefficient (Banerjee, 1995).

Gustafsson et al. (1997) proposed and validated an “extended, soot partitioning inclusive, distribution model” to better describe the carbon-normalized partition coefficient. In other words, they expanded the existing hydrophobic partition models to include adsorption onto a soot phase. They did so considering field data, which showed that soot affects the partitioning of PAHs in environmental media. The experimental portion of the study involved the removal of the non-soot organic carbon and inorganic carbonates from two Maine sediments before PAH uptakes were measured.

**Sorption Energetics**

Some researchers have been interested in the energetics associated with PAH sorption processes. The more cleanly interpretable studies are those involving just
soil and PAH, with no water present. Maguire et al. (1995) studied the interaction of PAHs and soil fractions using a differential scanning calorimeter. PAHs were mixed with soil fractions and sealed inside DSC pans. A small hole was drilled in each DSC pan to allow vaporized PAHs to escape the system. Differential scanning calorimetry scans (e.g., Figure 6.6) showed that fluorene, naphthalene, and anthracene preferentially dissolved into soil fractions such as humin, humic acid, and fulvic acid. Peaks (or lack thereof) in the DSC scans indicate that the PAHs are miscible in the organic fractions and that they exist at temperatures above their pure phase boiling point temperatures. The implication here is that chemicals that preferentially absorb into soil fractions may be very difficult to remove by thermal treatment because they don’t necessarily vaporize at their normal boiling point temperature. Maguire et al. (1995) concluded that temperatures of thermal desorption may need to be raised well above the boiling point in order to completely remove PAH contaminants from the soil fractions. Of course, as the DSC results show, it might be difficult to clearly establish when the PAH actually evaporates, since if it is not in a pure phase, it is unlikely to give a clean evaporation peak. Hence, it is unclear how quantitatively reliable these results might be.
Figure 6.6. DSC thermograms for pure PAHs (a), PAHs + HA (b), and PAHs + FA (c) (Maguire et al., 1995).

Nicholl et al. (2004) used thermal programmed desorption-mass spectrometry (TPD) to determine the release energies of a 16 component PAH mixture coated on glass beads, sand, and kaolin. Desorption parameters were calculated using the Polanyi-Wigner equation, which can be used to model the kinetics of thermal desorption from a surface.

\[
\frac{d\theta}{dT} = -v(\theta)\theta e^{-E(\theta)/RT}
\]  
(6.1.4)
Here \( v \) is the pre-exponential factor, \( E \) is desorption activation energy, \( \theta \) is the adsorbate coverage, and \( n \) is the desorption order. Based on the results (an example of which is provided Figure 6.7), it was determined that this model was not necessarily adequate for calculations of \( E \) from TPD thermograms. The authors did not provide an alternative to the Polanyi-Wigner equation. Of course, the values near those seen to offer a reasonable hope of fitting the data are close to values for sublimation from mixed PAH systems examined in this thesis.

![Figure 6.7. Polanyi-Wigner model results (1, 2, and 3) fit to an experimentally determined TPD thermogram for glass beads, showing similar error values (Nicholl et al., 2004).](image)

Figure 6.7. Polanyi-Wigner model results (1, 2, and 3) fit to an experimentally determined TPD thermogram for glass beads, showing similar error values (Nicholl et al., 2004).
Slow Sorption Processes

Pignatello and Xing (1996) recognized that sorption of organic chemicals to natural particles could be very slow, and these authors expressed concern that many previous studies had not determined sorption at true equilibrium. They hypothesized that particular slow, rate-limiting steps exist in the sorption processes (both adsorption and desorption). They provided two mechanistic explanations for this behavior and suggested that these are synergistic. The Organic Matter Diffusion (OMD) model associates rate-limited adsorption and desorption with slow diffusion through natural organic matter solids. This mechanism is of relevance in either the dry or wet soil state. The Sorption-Retarded Pore Diffusion model associates the rate-limiting step with retarded, chromatographic-like molecular diffusion in pore water, in which organics locally adsorb to pore walls as they diffuse. This model of course would not apply in dry soil studies, though the possibility of pore transport limitations needs to be considered in any case.

Sorption and Desorption Studies

Many researchers have used batch studies in which aqueous PAH solutions are mixed with natural particles to study sorption processes. In most cases the PAH/water solutions are mixed with methanol (low concentration) to enhance the aqueous solubility of the PAHs. Xia and Ball (1999; 2000) studied the sorption of PAHs and chlorinated benzenes on subsurface sediments. PAHs were dissolved in methanol before agitating with soil and synthetic groundwater for 7 days at room temperature. The authors recognize the work of Pignatello et al. (1996) by
acknowledging that their system may have reached only “apparent” equilibrium. They introduce the following Polanyi-Manes modeling approach, which is based on the adsorption potential ($\Phi$) between the sorbate and soil surface:

$$\log(q_c') = \log(Q_o') + a'(\phi/V_s')^b'$$

(6.1.5)

where

$$\phi = RT \ln(S_w/C_e)$$

(6.1.6)

Here, $S_w$ and $C_e$ are the solubility and the equilibrium concentration of solute, respectively. $q_c'$ is the adsorbed solute volume per unit mass sorbent, $Q_o'$ is the adsorption volume capacity at saturation, $a'$ and $b'$ are fitting parameters, and $V_s$ is the bulk molar volume of the adsorbate at $T$ of adsorption. At low concentrations, adsorption was well described by Langmuir and Polanyi-type isotherms (Figure 6.8). In contrast, the same figure shows that at high concentration, the PAHs adsorbed at greater than expected levels.
The authors proposed that pore filling within micropores contributed to the observed process. The Polanyi isotherms, which fail at high concentration, fit well at low concentration and may indicate pore filling of PAHs into spaces that have low affinity for water.

Xing (2001) combined naphthalene and phenanthrene with six humic acids in the presence of water to characterize the sorption behavior of PAHs with this important soil component. They reported exponents for the Freundlich isotherm between 0.87 and 0.95 for naphthalene and 0.86 and 0.92 for phenanthrene (e.g., Figure 6.9). The values increased with increasing aromaticity of the humic acids (not shown here).
Conte et al. (2001) conducted a study in which exogenous humic acid and a PAH mixture (100 µl of standard reference material 1647C) was added to soil. PAH sorption increased with the increasing quantities of organic carbon (HA). It is also interesting to note that oxidation of soil organic matter (with hydrogen peroxide) prior to PAH/HA addition reduced sorption capacity. Results indicated that increasing levels of humified organic-matter in soils retard transport of PAHs, consistent with earlier discussed results.

Accardi-Dey and Gschwend (2002; 2003) present findings for dissolved pyrene in an aqueous system. They report that absorption into organic carbon fractions and adsorption onto combustion-derived black carbon fractions occur in
parallel in cases where both sorbents are available. They recommend that sorption models consider the possibility of combined mechanisms.

Zhou et al. (2004) studied the effects of particle size and CaCl$_2$ content on phenanthrene adsorption. Phenanthrene was dissolved in water and methanol before mixing with the sorbent in a batch system. It was reported that the increased total organic carbon content of finer particles led to increasing sorption capacities with decreasing particle size for both soils and sediments studied. It is also not surprising that since the sediment used had 10-20 times more dissolved organic carbon than the soil (depending on particle size), its sorption capacities were found to be much higher than for soil.

An et al. (2005) observed the effect of a surfactant HDTMA bromide on the sorption behavior of naphthalene and phenanthrene in loess soil. Their procedure was similar to others mentioned above, in which water, methanol, PAH, soil, and in this case, surfactant are mixed in a flask and sorption is observed. The surfactant did in fact increase the rate of sorption in all cases by at least a factor of three, indicating that an agent that can enhance the stability of PAH in an aqueous phase promotes its movement onto surfaces.

Huang et al. (2008) showed similar results for the adsorption and desorption behavior of phenanthrene to/from organo-mineral aggregates of Northeast China. The isotherms for all studies could be matched to the Freundlich model. The batch experiments showed increased sorption of PAHs with decreased particle size, as the adsorption capacities were greater for silt and clay than for sand. Additionally, there
was positive correlation between the organic carbon normalized partition coefficients \( K_{\text{OC}} \) and both nonpolar and aromatic carbon. Values of \( K_{\text{OC}} \) were calculated by dividing the Freundlich adsorption coefficients \( K_{\text{IF}} \) from organic carbon fractions \( f_{\text{OC}} \). It is proposed that phenanthrene undergoes a \( \pi-\pi \) interaction with the organic matter.

Teixeira et al. (2010) studied the adsorption of pyrene on two Brazilian soils and showed that the soil with higher clay content had a higher sorption capacity. They attributed their results to filling intermolecular space in clays. However, it is also known (see above) that clay contains relatively high levels of organic matter and this may also be responsible for the increased sorption levels.

The work of some groups has been motivated by interest in desorption of PAHs and organic compounds from environmental media. Hawthorne and Grabanski (2000) collected vapor phase PAHs from two PAH-contaminated sediments on a polyurethane foam (PUF) plug. Sediment-filled glass flasks were placed in sunlight for 100 days. A second sample set (of the same two sediments) was shaken in water in the laboratory for 50 days. Total PAH evaporation from the sunlit sediments reached between 10% and 90% for up to 3-ring compounds. Trace levels of the 5-ring PAHs were found on the PUF plugs. Total PAH removals of 51% and 28% were reported for each sunlit sample. Evaporative losses for the sediments in water (which also contained PAH-degrading bacteria) were 23% and 8%. These results suggest that evaporation of PAHs contributes to decreasing levels of PAHs in soils and sediments and that this process works in conjunction with biological
treatment. Those monitoring biological activity of PAH impacted sediments should also account for evaporation losses of PAHs.

Jonker et al. (2005) measured the slow desorption of PAHs from pure charcoal, coal, and soot using a mild supercritical fluid extraction method. This process was meant to mimic desorption processes in water. The impetus for this study was the recognition that conventional lab methods failed to accurately measure desorption kinetics of PAHs from soil and sediment. Very low quantities of PAHs were removed from the samples during this study, showing that desorption of coal and combustion-derived PAH can be much slower than those observed in sediments not containing these components. These results imply that there may be reduced risk of PAH availability in systems that contain soot and carbonaceous materials. This was the basis of a study in this laboratory in which the residual carbon content in coal fly ash was used to bind PAHs found in sediments (Burgess et al., 2009)

A study by Hong et al. (2003) confirms that PAHs will preferentially absorb to lampblack-containing parts of soil. Again, lampblack is a fine carbonaceous material like soot. It is a solid byproduct, which results from the incomplete gasification of crude oil at high temperatures in gas making operations. Analysis showed that between 81 and 100% of PAHs in lampblack-containing soils were associated with the lampblack fractions. The authors also noted that an aromatic oil phase might also be present on the lampblack particles that contain high PAH concentrations.
A column study by García-Herruzo et al. (2000) was used to characterize the impact of humidity on the removal of hexane, benzene, toluene, and p-xylene from sandy soil. The conditions of this inverse gas chromatographic system were meant to mimic those of soil vapor extraction. The experimental setup consisted of a packed column, through which humid air and gas-phase volatile organic compounds (VOCs) were passed. The concentration of VOC in the exiting gas was continuously measured with a flame ionization detector. The results for all contaminants showed that VOC retention coefficients decreased with increasing humidity. It was concluded that the presence of water reduces the number of adsorption sites available for the organic compounds. A model that correlates retention coefficients to subsurface humidity was proposed.

A study by Pignatello et al. (2006) measured the sorption of humic and fulvic acids on environmental black carbon. The researchers here were addressing the effects of the natural organic substances on surface properties and sorption capacities of wood charcoal. The acids are restricted to adsorbing to the external surfaces of the black carbon in that they block pores. In some cases HA and FA can act as competitive adsorbates. Rigid “humic strands” that extended into the micropores of the black carbon blocked pore spaces, as was shown by N₂ adsorption at 77 K. At higher temperatures, these strands became more flexible and allowed nitrogen to penetrate the micropores. The implication is that traditional surface area measurement techniques may not offer an accurate picture of adsorption surface in cases where humic substances are adsorbed onto surfaces. It was also found that organic compound adsorption, where humic substances were present,
was suppressed in proportion to molecular size (e.g. benzene < naphthalene < phenanthrene and 1,2,4-trichlorobenzene << phenanthrene). In the cases where organic compounds are only able to adsorb on external sites, the authors cite molecular sieving in pores as an adsorption disrupter.

There is very limited information regarding sorption of vapor-phase PAHs to natural particles. Goss et al. (2004) measured adsorption of organic vapors to air-dry soils using inverse gas chromatography. The results showed that organic vapors adsorbed to both air-dry mineral surfaces and to soil organic matter. Both sorption sites must be considered in order to properly model the behavior.

In summary, soil organic matter plays a well-established key role in sorption of organic compounds. Carbons can play an important role, though their full porosity may or may not be usable depending upon the size of the sorbing species. Inorganic phases such as clays can also contribute to sorption of organics. Minerals can play some role, through it is generally less important than that of organic matter or carbon.

6.2 Experimental

Materials

PAHs used in the solubility experiments of this chapter are analogous to those described in Section 3.2.
Two types of adsorption experiments were conducted. The first made use of Ottowa Sand (SiO₂), supplied by Fisher Scientific (CAS Reg. No. 14808-60-7). The surface area of the sand was estimated by assuming that particles were spherical and by measuring and averaging particle diameters (± 0.001 inch) and density (mass/particle). The surface area of the sand is roughly 32 cm²/g or 0.0032 m²/g. Particle diameters and masses were measured using a micrometer and microbalance (section 3.2), respectively.

The second set of experiments used two types of soil samples that were obtained from a nearby, Providence, RI construction site. One sample was taken from a 19’ depth and identified as glacial till. The second was identified as backfill soil, and was sampled at a 4’ depth. Samples were homogenized by hand using a trowel, and then stored separately in sealed polyethylene buckets at room temperature. Before use or analysis, the soil was sifted to remove nonconforming materials (stones, roots, etc.), air-dried for 24 hours, and ground to a uniform consistency using a ceramic mortar and pestle.

Soil samples were analyzed for pH, cation exchange capacity, organic matter content, and USDA texture classification at the Soil and Plant Testing Laboratory at the University of Massachusetts Amherst. Surface area was determined by nitrogen sorption using a Quantachrome Automated Gas Sorption System. Results are summarized in Table 6.2.
Table 6.2 Physical and chemical properties of soil used in sorption studies

<table>
<thead>
<tr>
<th>Property</th>
<th>Backfill</th>
<th>Glacial Till</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>7.2</td>
<td>7.6</td>
</tr>
<tr>
<td>Cation Exchange Capacity [M\text{eq}/100g]</td>
<td>2.4</td>
<td>3.4</td>
</tr>
<tr>
<td>Organic Matter [%]</td>
<td>0.5</td>
<td>0.4</td>
</tr>
<tr>
<td>Surface Area [m\text{2}/g]</td>
<td>4.82</td>
<td>6.30</td>
</tr>
</tbody>
</table>

**USDA Texture Classification**

<table>
<thead>
<tr>
<th>USDA Texture Classification</th>
<th>Backfill</th>
<th>Glacial Till</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sand (0.05-2.0 mm)</td>
<td>69.6 %</td>
<td>56.9 %</td>
</tr>
<tr>
<td>Silt (0.002-0.05 mm)</td>
<td>25.3 %</td>
<td>33.1 %</td>
</tr>
<tr>
<td>Clay (&lt;0.002 mm)</td>
<td>5.1 %</td>
<td>10.0 %</td>
</tr>
<tr>
<td>Textural Class</td>
<td>Coarse Sandy Loam</td>
<td>Sandy Loam</td>
</tr>
</tbody>
</table>

**Sorption to Sand**

Batch PAH/sand experiments were conducted to determine the characteristics of PAH adsorption from the vapor phase onto a dry, nonporous material. Glass desiccators were used to hold the experimental containers, which are shown in Figure 6.10. The bottoms of the desiccators were filled with a thin layer of calcium sulfate desiccant in order to minimize humidity. Roughly 10 mg of PAH (either anthracene or pyrene) was added to open, ceramic crucibles. Ottawa sand was added to different crucibles. The filled crucibles were placed inside the desiccators, which were sealed and placed in a temperature controlled oven at 60 °C. It was hypothesized that PAHs would vaporize to maintain their equilibrium vapor pressure and that these vapors would adsorb to the surface of the sand particles, eventually reaching some equilibrium state. It should be noted that only
one PAH-containing crucible was used in each system. In other words, PAH mixtures were not examined. Samples of sand (10 g each) were periodically removed from desiccators over the course of 3 weeks, and analyzed for PAH content. This was accomplished using an accelerated solvent extractor and GC-MS system (described below).

Figure 6.10. Photo of a batch experiment used to characterize sorption of PAH to sand. This experiment was conducted in an oven at 60 °C (oven not shown).

A Dionex ASE 100 accelerated solvent extractor was used to quantify the adsorbed anthracene and pyrene. Samples of sand (10 g each) from the experiments above underwent extraction with approximately 50 ml of a 1:1 mixture of acetone and methylene chloride at 6000 psi and 100 °C for 15 minutes. The resulting
effluent was subsequently dried using a TurboVap evaporation system, dissolved and diluted in a known volume of methylene chloride (usually 5 ml), and analyzed by a calibrated PerkinElmer Clarus 680 combined gas chromatograph and mass spectrometer. The analytical procedure for EPA Method 8270C was followed. It was then possible to calculate the concentration of adsorbed PAH (mass PAH/mass sand) from the GC-MS data.

Sorption to Soil

In order to conduct vapor phase adsorption experiments with multiple soil types at varying temperatures, the method used for the PAH/sand systems (above) was slightly modified. In this new case, the desiccators were eliminated and 150 ml glass jars were used instead. The intent of this change was to reduce the size of each experimental system. Consequently though, much less sorbent could be used and there was initial, but unfounded concern that this would create an analysis challenge in which adsorbed PAH concentrations were below the lower detection limits of the analytical equipment.

In addition to the preparation steps described in the materials section above, soils were dried at 110 °C for 60 hours to remove residual moisture. As shown in Figure 6.2, the 150 ml glass jars were each filled with 25 g of dried soil. PAHs were then massed and placed within small glass vials. The glass vials were capped with stainless steel mesh to allow PAH vapors to escape the vials without restriction. The PAH-containing vials were then carefully placed in the jars with the soil. The jars were sealed with a glass stopper and placed within a temperature-controlled oven.
for 21 days before sampling. The revised experimental setup is shown in Figure 6.11.

Figure 6.11. Photos of a batch experiment used to characterize sorption of PAH to soil. This experiment was conducted in an oven at multiple temps (oven not shown).

The rate of adsorption was not tracked in this part of the study, and based on the result of the PAH/sand study, it was thought that the soil/PAH system might equilibrate within the 3-week time frame. Combinations of soil type (backfill or glacial till) and PAH (pyrene or anthracene) were varied in separate jars. Systems containing each possible combination of soil and PAH were prepared and each was equilibrated at six evenly spaced temperatures between 50 °C and 125 °C. Analyses
of the adsorbed PAHs were performed in an identical manner (ASE and GC-MS) to the previously discussed PAH/sand experiments.

6.3 Results and Discussion

The goal of this study was to examine the sorption of PAH vapors to real soil. Though other investigators have been interested in similar issues, no vapor to soil adsorption studies specifically addressed PAHs, and so, there is a significant absence of such information in the literature. This deficiency in data is accompanied by a lack of basic understanding with regards to sorption mechanism and experimental technique. Hence, the initial experiments of this study, which investigate the sorption of pure anthracene and pyrene vapors to sand, were meant to form a foundation from which more complex PAH-soil experiments could be based.

Consider the experimental design described in the previous section. It was initially hypothesized that each pure PAH would vaporize and that these PAH vapors would condense and adsorb as a monolayer onto the mineral surfaces of sand. Samples of sand were taken from the batch sorption systems at various time intervals and analyzed for PAH concentration. The results are given in Figure 6.12.
Figure 6.12. Adsorption of vapor phase PAHs onto sand at 60 °C.

An estimate was made of the concentration of adsorbed PAH that would represent monolayer coverage on the sand. This calculation depended on the geometry, e.g., surface area, of both the sorbent and sorbate. The surface area of the sand was roughly 32 cm²/g. The surface area of anthracene and pyrene was calculated using Spartan molecular-modeling software (roughly 1.0 x 10⁻¹⁸ m²/molecule). It was not obvious how much of each compound’s total surface would cover the mineral surface. In order to estimate the full range of surface areas available for adsorption, anthracene and pyrene molecules were assumed to be both
flat and spherical. The shaded area of Figure 6.12 thus represents the range of adsorbed PAH that might represent a monolayer. The lower end of this range represents the assumption that the molecules lay flat on the surface. Note that the sizes of anthracene and pyrene are quite similar, and hence, there is negligible difference between their estimated monolayer coverages.

The results given in Figure 6.12 suggest that both anthracene and pyrene adsorb to the surface of the sand as a monolayer and that this process may have reached equilibrium within 3 weeks. The concentration of pyrene stabilized at roughly 9.5 mg pyrene/kg sand. The adsorption behavior of anthracene cannot be as clearly interpreted. It is unclear if the variability in the last four data points represents experimental uncertainty in some mean concentration range or if there is some upward trend that would have continued had the experiments been conducted for a longer time. Based on the trend, it is suspected that the anthracene is nearing a saturation point of about 15 mg anthracene/kg sand.

Based on the results above, PAH adsorption onto soil was investigated using small scale, batch experiments. This part of the study did not consider adsorption rate, in that PAH-soil systems were held in an isothermal oven for 3 weeks and sampled only once. Since vapor phase concentration can be calculated using vapor pressure correlations and the ideal gas law, the bulk vapor phase concentration of PAHs in air was controlled by temperature. Temperature was carefully monitored and varied by no more than ±1°C.
Following equilibration for 3 weeks, soil was analyzed for PAHs and concentrations are plotted with respect to bulk air concentration in Figures 6.13 and 6.14. Subscripts “a” and “p” represent anthracene and pyrene, respectively.

Figure 6.13. Adsorption of anthracene vapor on two soils.
The data given in Figures 6.13 and 6.14 show that concentration of adsorbed anthracene and pyrene increase monotonically with the bulk concentration. This might support a saturation model in which sorption sites are limited in number. However, the magnitude of sorption is much lower in these soils than in sand and this is not what one would expect. This suggests that another mechanism is in play. This will be discussed below.
Figure 6.15. Anthracene adsorption data plotted as a Freundlich “isotherm.”

Figures 6.15 and 6.16 show the adsorption data of Figures 6.13 and 6.14 plotted as Freundlich “isotherms”. The best-fit Freundlich exponents ($n_i$) are about 0.70 and 0.75 for anthracene and pyrene, respectively. These values deviate from unity, indicating nonlinearity of the “isotherm” (see section 2.23).
Figure 6.16. Pyrene adsorption data plotted as a Freundlich “isotherm.”
Figures 6.17 and 6.18 show the adsorption data of Figures 6.13 and 6.14 plotted in the style given by the Langmuir isotherm. Fits are only crudely linear.

With regards to Figures 6.15 – 6.18, it is important to recognize that the data points represent adsorption experiments at different temperatures, which violates the concept of an isotherm. This brings into question the applicability of either the Langmuir or Freundlich “isotherm” to the results observed here. In other words, sorption behavior will vary with temperature and the Langmuir and Freundlich
Isotherms are meant to control this variable during analysis of adsorption. Hence, not much physical significance should be attached to the “isotherms” here.

Figure 6.18. Pyrene adsorption data plotted as a Langmuir “isotherm.”

The results shown in the previous six figures seem to suggest that adsorption of vapor phase anthracene and pyrene to dry soil increases monotonically with bulk air concentration and that there exists a sorption capacity in which sites become “filled” at high bulk air concentration. It needs to be recognized that the increase in concentration of PAH in the vapor phase with temperature competes with the
decreasing surface stability of adsorbed species with temperature. This behavior does not lend itself to prediction using a Freundlich or Langmuir model.

Based on the observed monolayer adsorption in the PAH-sand study (above) and on strong observations elsewhere that soil organic matter is responsible for sorption, the soil samples here should have adsorbed significantly more anthracene and pyrene than did the sand. This was not the case, as is shown in Figures 6.13 and 6.14. For example, after 3 weeks at 60 °C, the sand contained roughly 9.5 mg anthracene/kg sand and 15 mg pyrene/kg sand. Under similar conditions (65 °C for 3 weeks), the soil only contained about 2 mg PAH/kg soil. Since the soils used here consist of roughly 60% sand, the final values should have reflected at least two thirds of the value seen for sand, and likely much more. This suggests that the PAH-soil systems did not reach true equilibrium in the three-week time frame.

It is worth noting again that temperature variations were not of concern here and not responsible for the results. Furthermore, the accelerated solvent procedure is well documented and widely used by environmental laboratories. Based on the affinity of anthracene and pyrene to the organic solvents and on the high-temperature, high-pressure extraction conditions, inadequate extraction is not expected to be the source of the discrepancy. With these considerations acknowledged, it appears as though a mass transport limitation is causing the unexpectedly low sorption values observed in the PAH-soil systems. Though the soil is roughly 60% sand, the void fractions between these larger sand particles are filled with much smaller silt and clay particles. These fractions decrease the porosity
of the soil. Consequently, the effective diffusivity of a diffusing species is greatly reduced. Based on the estimation of Millington and Quirk (1961), effective diffusivity $D_{\text{eff}}$ can be calculated with respect to species-specific diffusivity in air $D_{\text{air}}$ and porosity $\varphi$.

$$D_{\text{eff}} = D_{\text{air}}^4 \varphi^{4/3}$$  \hspace{1cm} (6.3.1)

The characteristic length of diffusion is given by

$$L = \sqrt{D_{\text{eff}} t}$$  \hspace{1cm} (6.3.2)

The porosity of glacial till is between 10% and 20% (Bozkurt, 2009). The porosity of the sand used in this study was determined experimentally to be between 45% and 50%. If the characteristic diffusion lengths are equal for both cases, the time needed to reach a certain degree of saturation is between 3 and 10 times higher for actual soils than for sand. This means that hold times (3 weeks) were not nearly long enough and that only a small portion of the soil was exposed to the PAH vapors. This result is not much different from what others have seen and reported, in that there are often experimental problems associated with defining true equilibrium in these types of experiments.

Despite this lack of true equilibrium, the results obtained and reported in this study have value. The data may establish that vapor phase sorption to dry soil increases with temperature as would be expected, given the higher enthalpy of sublimation as compared with enthalpy of adsorption.
Future work and experimental design regarding this topic must carefully consider the mass transport limitations inherent in soil. These considerations will not be trivial. For example, a very thin layer of soil placed on tightly meshed stainless steel might eliminate mass transport limitations. However, the required minimum amount of soil is determined by the lower detection limits of the available analytical equipment and such an experiment might require that soil be thinly spread over a very large area. Furthermore, experiments need not be limited to batch studies. Rather, open-system column studies such as inverse gas-chromatographic methods can be considered.

6.4 Concluding Remarks

The sorption of vapor phase PAHs to natural particles is an important consideration in subsurface properties such as soil vapor extraction and vapor intrusion. The brief review of literature shows that PAH sorption is often studied in aqueous (and cosolvent) experiments. Though these issues are of great importance, there are very limited data on the adsorption of PAHs from the vapor phase.

The preliminary results obtained in this study suggest that vapor phase PAHs adsorb to mineral surfaces, i.e., sand, until a monolayer has formed. Results also suggest that adsorption of vapor phase PAHs to sand varies with bulk concentration in the vapor phase and that correlations might exist to describe such behavior. The experiments of this study on soils were, however, strongly influenced by mass transfer limitations that reduced the diffusion rate and availability of vapor phase
PAHs to the soil. This led to lower than expected sorption values because the systems were unable to reach true equilibrium in the experimental time frame.
Chapter 7. Conclusions and Recommendations for Future Work

The work presented in this study is meant to expand and enhance the current understanding of polycyclic aromatic hydrocarbon properties and behavior. Since PAHs are commonly encountered as mixtures of similarly structured compounds, this work has been largely focused on the thermodynamic, phase, and partitioning behavior of PAH mixtures. Though the environmental implications of PAH-containing contaminants have largely driven this work, the motivation for such characterization is grounded in both environmental and commercial interest.

Due to their abundance and ubiquity both as environmental contaminants and commercial chemicals, the “fate and transport” of PAH mixtures is quite important to a number of industries. A comprehensive understanding of the chemical properties and behavior of PAHs and their mixtures will improve fate and transport investigation, prediction, and control. The results given in this study are meant to do just that, in that they supplement and further develop the body of knowledge regarding PAH properties and their potential behavior in natural and commercial settings.

The value of this work is not limited to experimental results and discussion, but also extends to experimental design. Unique and inventive experimental procedures and subsequent data analysis were reported throughout this thesis, especially as regards vapor pressure measurement, mixture preparation, and sorption and aqueous solubility characterization. These procedures might serve as guides for others working in this or similar fields. As has been discussed, some of
these procedures and techniques are quite new and there is obvious room for modification and improvement.

The binary mixtures examined here, i.e., anthracene + pyrene and anthracene + benzo(a)pyrene, were highly non-ideal. Formation of eutectic phases, azeotropy, and accommodation of low-level impurities were observed in both cases. This behavior has been attributed to formation of cluster-like entities that define the thermodynamics and associated phase behavior of the mixtures.

The non-ideal behavior observed here for few-component mixtures is general. Even amongst the many similarities observed between the two binary mixtures, the systems are also very different in a number of ways. This means that specific, quantitative conclusions cannot be drawn with regards to other similar mixtures. Nevertheless, the important message is that PAH mixtures, and potentially other mixtures with a finite number of agents, may be surprisingly non-ideal. This is not what one would expect from “like dissolves like” theory and researchers in this field should take care not to assume ideality simply based on similarity of molecular structure and chemical properties.

PAH tars form as the number of mixture components increases. Tarlike behavior was observed and reported for 5- and 6- component PAH mixtures. In such cases, the complicated binary and ternary systems gave way to more ideal and simplified behavior as the mixtures approached true tar composition. The melting points and enthalpies of these tarlike mixtures approached a liquid limit. Results also suggested that the vapor pressure of these tarlike mixtures could be predicted
by ideal mixture theory, i.e., Raoult’s law. Despite this transition to a seemingly more environmentally relevant mixture, the phase behavior of such “tars” might become complicated as components are lost via evaporation (chapters 3 and 4), aqueous dissolution (chapter 5), and/or adsorption (chapters 6). In other words, as these mixtures weather in the environment, they may transition to few-component mixtures that could exhibit non-idealities similar to those reported above.

Since PAH mixtures often exist in subsurface environments, they will likely encounter natural particles (i.e., soil and sediment) and water, and these environmental media will affect their eventual fate and transport. With this in mind experiments were conducted to better characterize the aqueous solubility of PAH mixtures and absorption behavior of pure PAHs.

Results from this part of the study are somewhat consistent with those of the previous chapters, in that aqueous solubility of multicomponent, tarlike mixtures can be crudely predicted by ideal solid solution theory. Furthermore, dissolution behavior of binary anthracene + pyrene mixtures suggested that complicated mixture composition dependence might exist for few-component PAH mixtures. An important finding from this part of the study is that the commonly used dissolution theories reported by others for NAPLs may not be appropriate for mixtures that have weathered to a limited number of components. The reason for this discrepancy is that NAPL theory strictly applies to liquid mixtures and does not consider that multi-phase solids may exist in these systems.
The adsorption experiments conducted here were driven by a dearth of data surrounding the sorption of PAH vapor to environmental media. Other researchers have been largely focused on systems that contain water, and hence, have studied partitioning of PAHs from aqueous solution to natural particles. Though the results of this study were largely affected by mass transport limitations, they do suggest a PAH vapor/soil saturation model in which sorption sites are limited in number. This type of study is relevant to vapor intrusion and soil vapor extraction processes.

Though the experimental results presented here provide both qualitative and quantitative understanding of PAH mixture behavior under various conditions, further investigation should provide new and important insight regarding these topics. Characterization of aqueous solubility of PAH mixtures and adsorption of PAH vapor to natural particles are both complicated issues that will require further work. In the former case, solid PAH mixtures clearly exist in the environment and a more quantitative understanding of their dissolution behavior is necessary. A larger study with more mixtures and more samples might uncover and describe potentially complicated trends. Furthermore, future PAH vapor/soil sorption experiments must face the challenges associated with hindered mass transport and might also consider competitive adsorption (and subsequent desorption) associated with PAH mixtures.
Bibliography


Burgess, R. M.; Perron, M. M.; Friedman, C. L.; Suuberg, E. M.; Pennell, K. G.; Cantwell, M. G.; Pelletier, M. C.; Ho, K. T.; Serbst, J. R.; Ryba, S. A. Evaluation of the


EPA Priority Pollutants, Updated Friday, October 01, 2010.


Fu, J.; Suuberg, E. M., Brown University, Providence, RI, personal communication 2011.


Appendix 1. Pure PAH Vapor Pressure Data

Table A1.1. Anthracene vapor pressure data

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<td>3.1934</td>
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### Table A1.6. Fluorene vapor pressure data

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<th>1000K/$T$</th>
<th>lnP/Pa</th>
<th>P/Pa</th>
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