

Chapter 8

VAPOR PRESSURE (p_i^*)

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8.1 Introduction and Theoretical Background

The quantitative description of how much a compound likes or dislikes being in the gas phase as compared to other relevant condensed phases is an important aspect of our discussion about the partitioning of organic compounds in the environment. We have already addressed such favoring of phases very generally in Chapter 7. In this chapter, we focus on a special case, the equilibrium partitioning of an organic compound between the gas phase and the pure compound itself. In contrast to Chapter 7, we do not consider the compound in a dilute solution but at the maximum concentration possible in both the air (i.e., at saturation) and condensed phase. In this particular case, the gas–pure liquid or gas–pure solid partition constant of i is commonly expressed not in molar concentrations but as the ratio of the equilibrium partial pressure in the gas phase, p_i^* , to the mole fraction, x_i , in the pure condensed phase. By definition, the mole fraction of a pure substance in the condensed phase is equal to one ($x_i = 1$). Therefore, p_i^* is commonly referred to as the gas phase saturation (indicated by the superscript “*”) vapor pressure of a compound. It denotes the maximum possible partial pressure or concentration of a compound in the gas phase at a given temperature. Importantly, this vapor pressure provides direct quantitative information on the attractive forces among the compound’s molecules in its liquid or solid phase. Having such an insight into molecule–molecule interactions in the pure phase allows us to recognize how the chemical’s structure controls its fugacity and, therefore, to anticipate how placing the compound in different media affects such fugacity. This insight is main reason why the pure liquid phase is often used as reference state for the thermodynamic treatment of partitioning processes (see Section 4.1). Finally, we should note that the vapor pressure not only describes equilibrium partitioning between the gas phase and a condensed phase but also helps quantify the *rate of evaporation* of a compound from its pure phase or a mixture.

By simple observation, we know that at ambient temperatures (e.g., 25°C) and pressures (e.g., 1 bar), some organic chemicals in their *pure form* are present as gases, some as liquids, and others as solids. We should recall that when we talk about a pure chemical, we mean that only molecules of that particular compound are present in the phase considered. Hence, in a pure gas, the partial pressure of the compound is equal to the total pressure. As already addressed in Chapter 4, a pure compound will be a liquid or a solid at ambient conditions if the forces between the molecules in the condensed phase are strong enough to overcome the tendency of the molecules to “fly” apart. In other words, if the enthalpy terms (which reflect the “glue” among the molecules in the liquid) outweigh the entropy terms (which are measures of “freedom” gained when going from the liquid phase to the gas phase), then the free energy term is positive, and the material will exist as a liquid or solid. Conversely, if this free energy term is negative, then the compound is a gas at the given conditions. This variation in phase is illustrated by the series of n-alkanes, where the C₁– to C₄–compounds are gases ($p_i^* > 1$ bar), the C₅– to C₁₇–compounds are liquids, and the compounds with more than 18 carbon atoms are solids at 25°C and 1 bar total pressure (Fig. 8.1) This series of hydrocarbons exhibits a vapor pressure range of more than fifteen orders of magnitude ranging from 40.7 bar or 4.07×10^6 Pa (C₂H₆) down to about 10^{-14} bar or 10^{-9} Pa (n-C₃₀H₆₂). For methane, no vapor pressure is defined at 25°C because

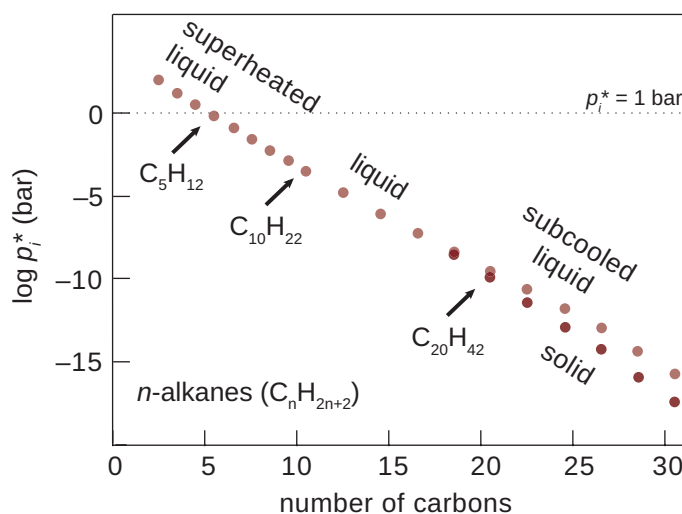


Figure 8.1 Vapor pressure at 25°C of *n*-alkanes as a function of chain length. The subcooled liquid vapor pressures have been calculated by extrapolation of p_{iL}^* values determined above the melting point (Eq. 8-7). Data from Daubert (1997) and Lide (1995).

methane cannot exist in a defined condensed form at this temperature, even at a very high pressure (see subsequent discussion).

Aggregate State and Phase Diagram: Normal Melting Point (T_m), Normal Boiling Point (T_b), and Critical Points (T_c, p_{ic}^*)

According to the Gibbs phase rule (number of degrees of freedom = number of chemical components – number of phases + 2; see Atkins, 2014), a system containing a single chemical distributed between two phases at equilibrium has only one degree of freedom. Therefore, by choosing a temperature of interest (i.e., defining the one degree of freedom), all other phase parameters are fixed, including the vapor pressure of the compound in the gas phase. This dependence of vapor pressure on temperature can be shown in a pressure–temperature plot (Fig. 8.2). Such a “phase diagram” allows us to assess the aggregate state (i.e., solid, liquid, gas, supercritical fluid) of the compound under various combinations of temperature and pressure. The diagram also depicts important single temperature/pressure points for the chemical of interest. Let us look at this phase diagram more closely by using four *n*-alkanes (Table 8.1) as illustrative examples. The points T_m , T_b , and T_c already have a subscript denoting that they are compound-specific parameters, so we omit the subscript *i*.

First, we inspect the *normal melting points* (T_m) of the compounds. T_m is the temperature at which the solid and the liquid phase are in equilibrium at 1.013 bar (= 1 atm) total external pressure. At 1 bar total pressure, we would refer to T_m as the *standard melting point*. As a simplification, we assume that small changes in pressure do not have a significant impact on the melting point. We also assume that T_m is equal to the *triple point temperature* (T_i). This triple point temperature occurs at only one set of pressure/temperature conditions under which the solid, liquid, and gas phase of a pure substance all simultaneously coexist in equilibrium.

Among our *n*-alkanes in Table 8.1, only *n*-eicosane has a T_m value that is above 25°C, so it is the only alkane in this group that is a solid at room temperature. The other

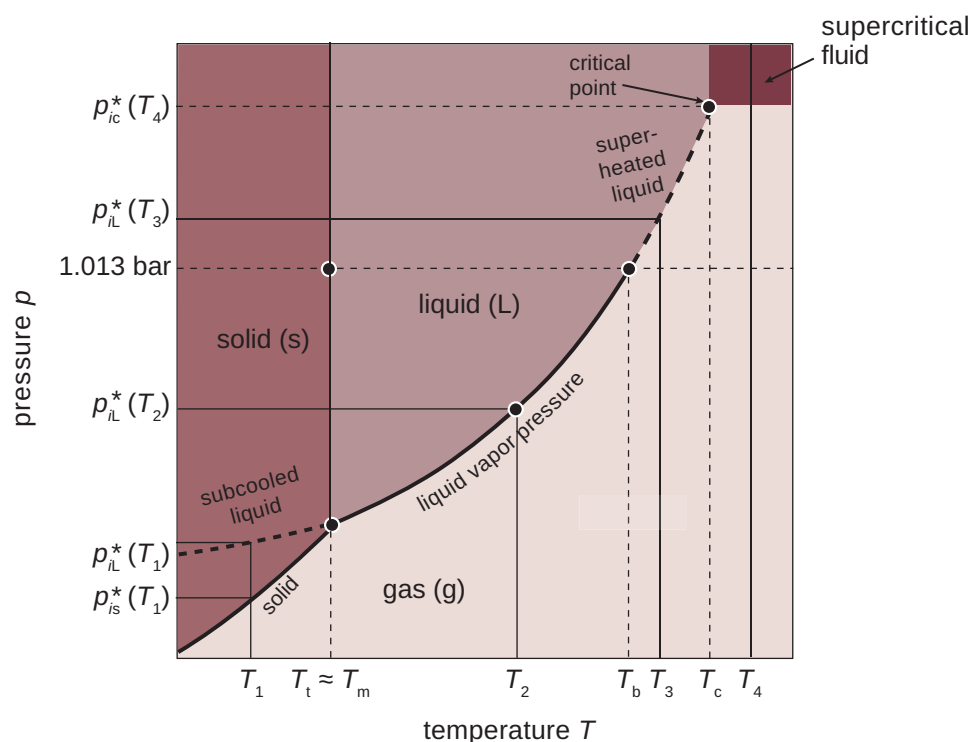


Figure 8.2 Simplified phase diagram of a pure organic chemical. The boundary between the solid and liquid phase has been drawn assuming the chemical's melting point (T_m) equals its triple point (T_t), the temperature–pressure condition where all three phases coexist. In reality, T_m is a little higher than T_t for some compounds and a little lower for others.

three compounds have much lower melting points, which means that, in these cases, we would have to lower the temperature at least to -29.7 , -138.4 , and -182.5°C in order to “freeze” *n*-decane, *n*-butane, and methane, respectively.

Let us now perform a little experiment with *n*-eicosane. We place pure (solid) *n*-eicosane in an open vessel (Fig. 8.3a) and in a closed vessel (Fig. 8.3b) at 25°C . In the open vessel, we have an ambient total pressure of 1 atm or 1.013 bar, exerted mostly by the nitrogen and oxygen molecules in the air. In contrast, in the closed vessel, we start out with a vacuum, that is, we allow no molecules other than eicosane in this

Table 8.1 Normal Melting Points (T_m), Normal Boiling Points (T_b), and Critical Points (T_c , p_{ic}^*) of some *n*-Alkanes^a

Compound	T_m ($^\circ\text{C}$)	T_b ($^\circ\text{C}$)	T_c ($^\circ\text{C}$)	p_{ic}^* (bar)	Location of Ambient Temperature (i.e., 25°C) in Fig. 8.2	Aggregate State at 25°C
Methane (CH_4)	-182.5	-164.0	-82.6	46.04	T_4	gas
<i>n</i> -Butane (C_4H_{10})	-138.4	-0.5	152.0	37.84	T_3	gas
<i>n</i> -Decane ($\text{C}_{10}\text{H}_{22}$)	-29.7	174.1	344.5	21.04	T_2	liquid
<i>n</i> -Eicosane ($\text{C}_{20}\text{H}_{42}$)	36.8	343.0	496.0	11.60	T_1	solid

^aData from Lide (1995).

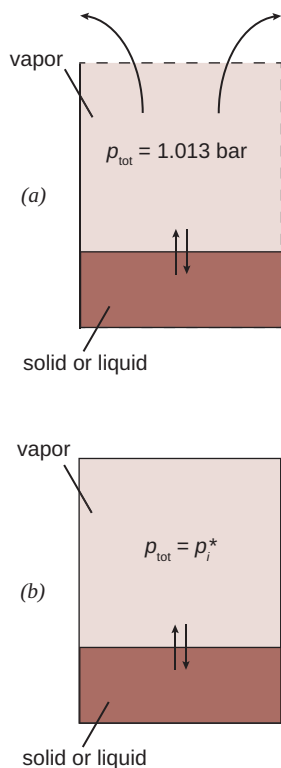


Figure 8.3 Open (a) and closed (b) vessel containing a pure condensed phase and a vapor phase. In case (a), the total pressure (1 bar) is exerted by the compound's molecules and by other gaseous species (e.g., O_2 , N_2), which do not significantly alter the composition of the condensed phase. In case (b), the total pressure is equal to the vapor pressure of the compound; that is, no other gaseous species are present.

vessel. Now we wait until equilibrium between the solid and vapor phase is reached, and then we measure the partial pressure of *n*-eicosane in the gas phase in each vessel. In the closed vessel, the total pressure will be equal to the vapor pressure, p_{is}^* , of solid eicosane, about 10^{-8} bar or 10^{-3} Pa. In our phase diagram in Fig. 8.2, the point on the bold line at T_1 represents this pressure/temperature point. Now the question is: what is the partial pressure of eicosane in the gas phase in equilibrium with the solid phase in the open vessel? Is it also equal to p_{is}^* ? The answer is yes because, particularly in the case of a solid compound, for pressures less than about 10 bar, the total system pressure has small influence on p_{is}^* . In general, at pressures near 1 bar we can assume that the difference in the partial pressures between the situations depicted in Figs. 8.3a and b would be less than 0.5% for most organic compounds (Atkins, 2014). However, in the open vessel, the compound would vanish because molecules could continuously leave the vessel and, thus, would have to be replenished from the condensed phase to keep a constant vapor pressure.

Returning to our experiment, if we now increase the temperature, we observe that p_{is}^* of *n*-eicosane increases. In our phase diagram, we move the solid line from T_1 towards T_m . At T_m , the compound melts and becomes a liquid. Above T_m , a further increase in temperature leads, of course, to an increasing vapor pressure, which we now denote as p_{iL}^* , as we are dealing with the vapor pressure of a *liquid* (L) compound (e.g., pressure/temperature point at T_2 in Fig. 8.2). We continue to raise the temperature until p_{iL}^* reaches 1 atm (1.013 bar), which equals the total external pressure in the open vessel. Now we have very different situations in the vessels: in the open vessel, the compound *boils*, whereas in vessel 2, boiling cannot occur, as there is no means of escape for the molecules. The temperature, T_b , at which p_{iL}^* is 1 atm is referred to as the *normal boiling point* temperature (or *standard boiling point* temperature, if p_{iL}^* is 1 bar). Historically, the standard pressure has been taken to be 1 atm (1.013 bar), which means that many T_b values are still reported as *normal* boiling points, which are somewhat higher than the *standard* boiling points. However, for practical purposes, we neglect these small differences and just refer to *the* boiling point, T_b . The boiling point of *n*-eicosane is 343°C (Table 8.1). We should recall that boiling means that in an open system, vaporization can occur throughout the bulk of the liquid, and the vapor can expand freely into the surroundings. Therefore, in contrast to the melting point, the boiling point of a compound depends strongly on the external pressure. A well-known example is the change in the boiling point of pure water at various pressures. At 1.013 bar, the T_b is 100°C , while at lower pressures, pure water boils at lower temperatures. At the summit of Mount Everest (0.357 bar external pressure), the T_b decreases to 73°C , making cooking pasta rather tedious.

At temperatures above the boiling point (e.g., T_3) and an external pressure of 1.013 bar, a compound exists only in the gas phase. A limited number of organic chemicals are gases at ambient temperatures. Examples are *n*-butane and methane, which have boiling points of -0.5 and -164°C respectively (Table 8.1). Other examples include some of the halogenated methanes, such as the companion compound methyl bromide (CH_3Br) and some freons (e.g., CCl_2F_2 and CClF_3).

In the closed vessel (Fig. 8.3b), increasing the temperature to above the boiling point creates a situation where we have a vapor pressure, p_{iL}^* , of greater than 1.013 bar,

which cannot occur in the open vessel. We take advantage of this situation in autoclaves and pressure cookers, which use elevated water temperatures to kill bacteria and cook food quickly. In such a case, we still have both a liquid and a gas phase (e.g., pressure/temperature point on bold broken line at T_3 in Fig. 8.2), and the liquid phase is referred to as a “*superheated*” liquid. Therefore, for compounds existing as gases at ambient temperature, we have to increase their partial pressure in the gas phase until we reach the vapor pressure of the superheated liquid to store them as liquids, for example, in a pressure bottle. For *n*-butane, often used as fuel for barbecues, this pressure is 2.5 bar, and for CCl_2F_2 , a freon used as a propellant and foaming agent, the corresponding p_{iL}^* value is 5.6 bar at 25°C.

Returning to our experiment with *n*-eicosane in the closed vessel, if we continue to raise the temperature, more and more molecules build up in the gas phase (increasing the gas density), while the density of the liquid continuously decreases. Finally, we reach a point where the density of the vapor is equal to that of the remaining liquid, meaning that we do not have two distinguishable phases anymore. This pressure/temperature point is called the critical point of the compound (T_c, p_{ic}^* , see Fig. 8.2). For *n*-eicosane, the T_c and p_{ic}^* values are 496°C and 11.6 bar. Above these values, the compound exists only as one phase, which is commonly referred to as a “*supercritical fluid*.” Methane has a critical temperature of –82.6°C (Table 8.1). Hence, liquid methane will exist only below this temperature, making condensing it to a liquid at ambient temperatures impossible. In our phase diagram, this means that methane belongs to those few chemicals for which the ambient temperature is above T_c (e.g., T_4 in Fig. 8.2). Other prominent examples of such chemicals are O_2 ($T_c = -118.6^\circ\text{C}$) and N_2 ($T_c = -147^\circ\text{C}$).

Before we turn to a quantitative description of the dependence of vapor pressure on temperature, we need to define one important additional vapor pressure value: the *subcooled liquid vapor pressure* of a compound. Imagine what occurs if we cool liquid eicosane from an elevated temperature (e.g., T_2 in Fig. 8.2) to a temperature below its melting (or freezing) point (e.g., T_1 in Fig. 8.2). Above the melting point ($T_m = 36.8^\circ\text{C}$), we observe a decrease in p_{iL}^* according to the solid line describing the liquid–gas boundary. Below the melting point, we follow a different solid line now describing the solid–gas boundary until we reach p_{is}^* (T_1). We note that, below the melting point, the decrease in vapor pressure with decreasing temperature is steeper than in the region above the melting point, where the compound is a liquid. This increase in slope is because the energy required to transfer molecules from the solid to the gas phase is higher than transferring them from the liquid to the gas phase. Hence, if we continued to move along the liquid–gas boundary below the melting point (dashed line in Fig. 8.2), at T_1 , we would reach another vapor pressure value, p_{iL}^* , which is larger than the corresponding p_{is}^* of the solid compound (examples in Fig. 8.1). This p_{iL}^* value, which is referred to as the vapor pressure of the *subcooled liquid*, is an important entity, because it tells us something about the molecular interactions of the compound in its pure liquid form at a temperature where the compound is actually a solid. Knowledge of the properties of the subcooled liquid compound helps us understand and quantify the molecular interactions in environments in which molecules exist in a liquid state (e.g., dissolved in water), although they would be solids if pure. Our interest in situations where organic compounds are dissolved in solvents like water is a major reason

why we have chosen the pure liquid compound as the reference state for describing partitioning processes.

Thermodynamic Description of the Vapor Pressure–Temperature Relationship

In Chapter 4, we have seen that the bulk phase equilibrium partition constant expressed on a mole fraction basis is related to the free energy of transfer by (Eqs. 4-23 to 4-25):

$$\ln K_{i12} = \ln(x_{i1}/x_{i2}) = -\Delta_{12}G_i/RT \quad (8-1)$$

By expressing x_{i1} by the equilibrium the partial pressure p_i^*/p_i^0 ($p_i^0 = 1$ bar, standard pressure) and by setting $x_{i2} = 1$ (pure organic phase), we then obtain:

$$\ln (p_i^*/1\text{bar}) = -\Delta_{12}G_i/RT \quad (8-2)$$

For liquid (subscript “L”)-vapor equilibrium, the free energy of transfer is commonly referred to as free energy of *vaporization* (subscript “vap”), while for solid (subscript “s”)-vapor equilibrium, it is called the free energy of *sublimation* (subscript “sub”). Hence, Eq. 8-2 is simplified for liquid vapor pressure to:

$$\ln p_{iL}^* = -\Delta_{\text{vap}}G_i/RT \quad (8-3)$$

and for solid vapor pressure:

$$\ln p_{is}^* = -\Delta_{\text{sub}}G_i/RT \quad (8-4)$$

Let us first consider the liquid vapor pressure both below and above the boiling point (Fig. 8.2). From Eq. 8-3, we can see that $\Delta_{\text{vap}}G_i$ will be positive at temperatures at which the vapor pressure is smaller than the standard pressure (i.e., 1 bar), which is, of course, the case at temperatures below the boiling point. At the boiling point, $p_{iL}^* = 1$ bar, and, therefore,

$$-RT \ln 1 = 0 = \Delta_{\text{vap}}G_i(T_b) = \Delta_{\text{vap}}H_i(T_b) - T_b\Delta_{\text{vap}}S_i(T_b) \quad (8-5a)$$

or

$$T_b\Delta_{\text{vap}}S_i(T_b) = \Delta_{\text{vap}}H_i(T_b) \quad (8-5b)$$

Hence, at the boiling point, the compound’s molecules in the liquid state can “fly apart” because their gain in entropy upon vaporizing now matches the enthalpic attractions that are trying to hold them together. Above the boiling point, $\Delta_{\text{vap}}G_i$ will be negative (because $T\Delta_{\text{vap}}S_i > \Delta_{\text{vap}}H_i$). That is, pressures greater than 1 bar must be applied to keep a liquid phase present.

As for any equilibrium partition constant, the temperature dependence of p_{iL}^* can be described by the *van’t Hoff* equation (Eq. 4-33):

$$\frac{d \ln p_{iL}^*}{dT} = \frac{\Delta_{\text{vap}}H_i(T)}{RT^2} \quad (8-6)$$

This equation is commonly referred to as the *Clausius-Clapeyron* equation. $\Delta_{\text{vap}}H_i$ is zero at the critical point, T_c . It rises rapidly at temperatures approaching the boiling point, then it rises more slowly at lower temperatures (Poling et al., 2001). Therefore, we can integrate Eq. 8.6 with the assumption that $\Delta_{\text{vap}}H_i$ is *constant* over the temperature range of interest (e.g., over the ambient temperature range from 0°C to 30°C). Over this narrow temperature range, we can then express the temperature dependence of p_{iL}^* by:

$$\ln p_{iL}^* = -\frac{A}{T} + B \quad (8-7)$$

where $A = \Delta_{\text{vap}}H_i/R$.

For liquids, plotting the observed $\log p_{iL}^*$ ($=\ln p_{iL}^*/2.303$) versus $1/T$ (K) over the ambient temperature range yields practically linear relations (Fig. 8.4), as expected from Eq. 8-7. Therefore, by calculating A and B over narrow temperature ranges with known vapor pressure data, Eq. 8-7 can be used to calculate vapor pressures at any other temperature *provided that the aggregate state of the compound does not change within the temperature range considered*. If the temperature range is extended, the fit of experimental data may be improved by introducing a third parameter, C , in Eq. 8-7 to reflect the temperature dependence of $\Delta_{\text{vap}}H_i$. The constant C captures the effect of changing enthalpy of vaporization over larger temperature ranges:

$$\ln p_{iL}^* = -\frac{A}{T+C} + B \quad (8-8)$$

Equation 8-8 is known as the Antoine equation and has been widely used to regress experimental data. Values for A , B , and C are available for many compounds (e.g., Haynes, 2014 and Daubert, 1997). When using Eqs. 8-7 and 8-8 to extrapolate vapor pressure data below the melting point, one gets an estimate of the vapor pressure of the subcooled liquid compound at that temperature (e.g., naphthalene in Fig. 8.4). For the solid vapor pressure, p_{is}^* , we can just substitute $\Delta_{\text{vap}}H_i$ by $\Delta_{\text{sub}}H_i$ in Eqs. 8-6 to 8-8 (i.e., $A = \Delta_{\text{sub}}H_i/R$).

The difference between the free energy of sublimation and the free energy of vaporization is referred to as the free energy of *fusion* (from the Latin, *fundere* meaning to melt). In other words, the energy required to convert molecules from their solid state directly to their vapor state is the same as the energy required to first melt the solid and then to vaporize them from their liquid state, even though sublimation does not involve ever having the liquid state exist. One can, therefore, obtain the free energy of fusion (melting) by rearranging then subtracting Eq. 8-3 from 8-4:

$$\Delta_{\text{fus}}G_i = \Delta_{\text{sub}}G_i - \Delta_{\text{vap}}G_i = RT \ln \frac{p_{iL}^*}{p_{is}^*} \quad (8-9)$$

In terms of enthalpy and entropy, this means:

$$\Delta_{\text{fus}}H_i = \Delta_{\text{sub}}H_i - \Delta_{\text{vap}}H_i \quad (8-10)$$

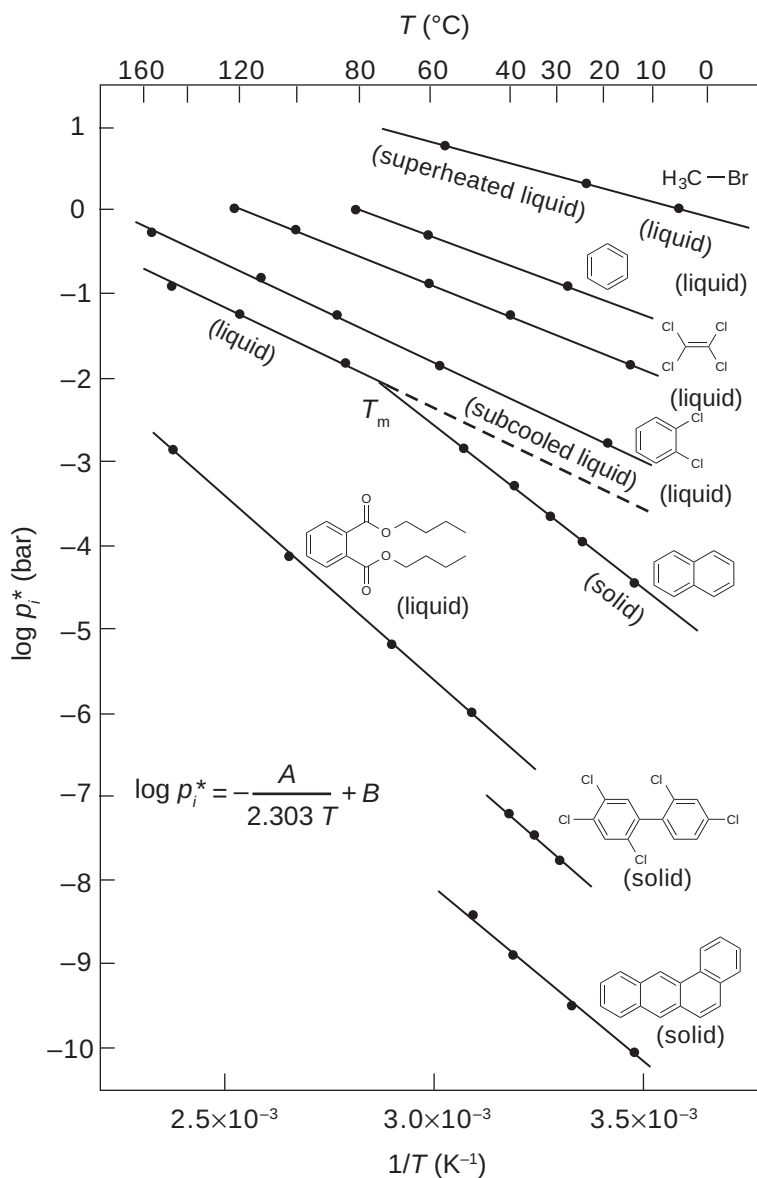


Figure 8.4 Effect of temperature on vapor pressure for some organic compounds. The decadic logarithm is used, thus the factor $1/2.303$ ($\ln p_i^* = 2.303 \log p_i^*$).

and:

$$\Delta_{\text{fus}} S_i = \Delta_{\text{sub}} S_i - \Delta_{\text{vap}} S_i \quad (8-11)$$

The thermodynamic expressions Eqs. 8-10 and 8-11 state that the intermolecular attraction forces that must be overcome to sublime the molecules of a substance are equal to the sum of the forces required to first melt and then vaporize them. Likewise, the increased randomness obtained as molecules sublime is the same as the sum of entropies associated with the sequence of melting and vaporizing. Consequently, if we can predict such thermodynamic terms for vaporization or melting, we already know the corresponding parameters for sublimation, and vice versa.

Knowledge of $\Delta_{\text{fus}}G_i$ at a given temperature is useful for estimating other properties of the subcooled liquid compound, in particular, its subcooled liquid aqueous solubility (Chapter 9). As can be qualitatively seen from Fig. 8.2, $\Delta_{\text{fus}}G_i$ decreases with increasing temperature (the solid and subcooled liquid vapor pressure lines approach each other when moving towards the melting point). At the melting point, T_m , $\Delta_{\text{fus}}G_i$ becomes zero, and, by analogy to the situation at the boiling point (Eq. 8-5), we can write:

$$T_m \Delta_{\text{fus}}S_i(T_m) = \Delta_{\text{fus}}H_i(T_m) \quad (8-12)$$

8.2 Molecular Interactions Governing Vapor Pressure and Vapor Pressure Estimation Methods

Enthalpy and Entropy Contributions to the Free Energy of Vaporization: Trouton's Rule of Constant Entropy at the Boiling Point

We now focus on the relation between chemical structure and vapor pressure. In Fig. 8.5, the enthalpy and entropy of vaporization at 25°C are plotted against the free energy of vaporization for a wide variety of apolar, monopolar, and bipolar compounds. In general, we see that the enthalpic contribution is larger than the entropic one, but also that these contributions are related. We can rationalize these findings by recalling that the entropy of vaporization reflects the difference of a molecule's freedom in the gas phase minus that in the liquid phase ($\Delta_{\text{vap}}S_i = S_{i\text{g}} - S_{i\text{L}}$). At ambient pressures, the freedom of the molecules in the gas phase is generally not that different between compounds. Therefore, we may assume that differences in $\Delta_{\text{vap}}S_i$ between different compounds are primarily due to differences in molecular freedom in the liquid phase. Hence, molecules that exhibit stronger intermolecular attractions (greater $\Delta_{\text{vap}}H_i$ values) have lower values of $S_{i\text{L}}$, causing higher values of $\Delta_{\text{vap}}S_i$.

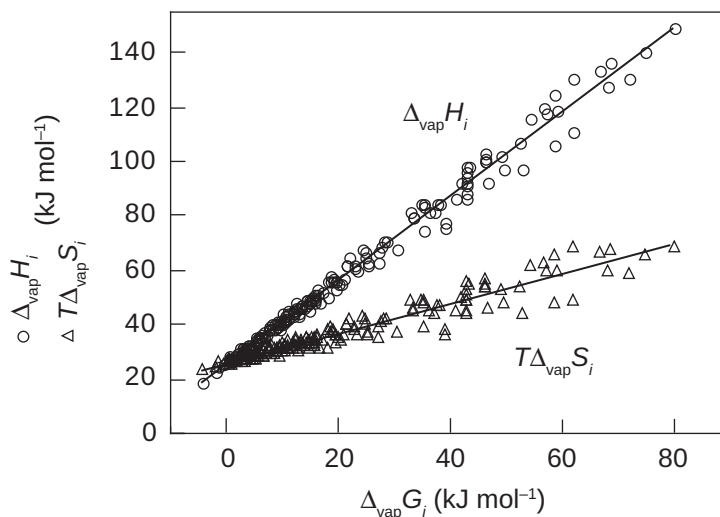


Figure 8.5 Plot of $\Delta_{\text{vap}}H_i$ and $T\Delta_{\text{vap}}S_i$ versus $\Delta_{\text{vap}}G_i$ for a wide variety of organic compounds at 25°C. At the intercept ($\Delta_{\text{vap}}G_i = 0$) the value for $\Delta_{\text{vap}}H_i$ ($= T\Delta_{\text{vap}}S_i$) obtained from a linear regression analysis is 25.8 kJ mol⁻¹.

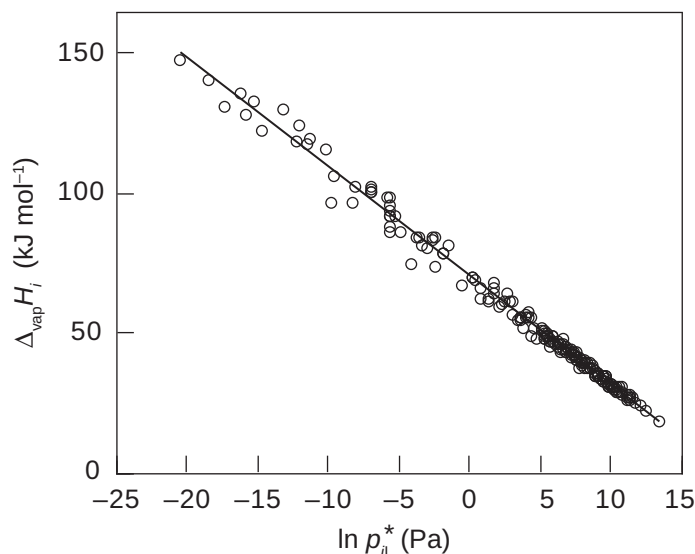


Figure 8.6 Plot of $\Delta_{\text{vap}}H_i$ versus $\ln p_{iL}^*$ for a large number of apolar, monopolar, and bipolar compounds (some bipolar outliers not included). Data from Goss and Schwarzenbach (1999).

The fact that the enthalpy and entropy terms correlate also means that $\Delta_{\text{vap}}G_i$ is proportional to $\Delta_{\text{vap}}H_i$.

We can, therefore, derive an extremely useful empirical relationship between $\Delta_{\text{vap}}H_i$ and $\log p_{iL}^*$ ($= -\Delta_{\text{vap}}G_i / 2.303RT$; Eq. 8-3) for a given temperature, T , which allows one to estimate $\Delta_{\text{vap}}H_i$:

$$\Delta_{\text{vap}}H_i(T) = -a \log p_{iL}^*(T) + b \quad (8-13)$$

At 25°C (298 K), the linear regression derived for the experimental data set of organic compounds shown in Fig. 8.6 is (Goss and Schwarzenbach, 1999):

$$\Delta_{\text{vap}}H_i (\text{kJ mol}^{-1}) = -8.79(\pm 0.07) \log p_{iL}^* (\text{Pa}) + 70.0(\pm 0.2) \quad (8-14)$$

As confirmed by MacLeod et al. (2007), Eq. 8-14 holds for a very large vapor pressure range (>15 orders of magnitude), particularly, for apolar and monopolar compounds. Importantly, Eq. 8-14 applies only to the vapor pressure of the *liquid* compound. For solids, the difference between p_{is}^* and p_{iL}^* can be estimated using the melting point temperature of the compound (see Eqs. 8-21 and 8-22).

Looking back at Fig. 8.5, the $\Delta_{\text{vap}}H_i$ intercept where $\Delta_{\text{vap}}G_i = 0$ is an interesting point; it represents a compound with a boiling point $T_b = 25^\circ\text{C}$. The corresponding $\Delta_{\text{vap}}H_i$ is 25.8 kJ mol⁻¹, from which the compound's entropy of vaporization at T_b can be calculated (Eq. 8-5):

$$\Delta_{\text{vap}}S_i(T_b) = \frac{\Delta_{\text{vap}}H_i(T_b)}{T_b} = \frac{25.8 \text{ kJ mol}^{-1}}{298 \text{ K}} = 86.6 \text{ J mol}^{-1} \text{ K}^{-1}$$

This $\Delta_{\text{vap}}S_i(T_b)$ value is typical for many organic compounds that boil at very different temperatures. A long time ago, Trouton (1884) recognized that the entropy of vaporization at the boiling point for many apolar and monopolar substances is between 85 and 90 J mol⁻¹ K⁻¹. This “constancy” of $\Delta_{\text{vap}}S_i(T_b)$ implies a close relationship exists between $\Delta_{\text{vap}}H_i(T_b)$ and T_b . Kistiakowsky (1923) utilized the Clapeyron equation and the ideal gas law to derive an expression to estimate individual $\Delta_{\text{vap}}S_i(T_b)$ in which the chemical’s boiling temperature is used:

$$\Delta_{\text{vap}}S_i(T_b) = (36.6 + 8.31 \ln T_b) \text{ J mol}^{-1} \text{ K}^{-1} \quad (8-15)$$

This expression reflects a weak relationship between the apolar or monopolar compound boiling temperature and entropy of vaporization, but substantially verifies Trouton’s empirical observation.

For bipolar organic liquids, especially for H-bonding liquids such as alcohols and amines, the tendency to orient in the liquid phase is greatly increased by these highly directional intermolecular attractions. The effect is reflected in the significantly larger entropies of vaporization (between 90 and 110 J mol⁻¹ K⁻¹) of bipolar chemicals like amines and alcohols. Fishtine (1963) provided a set of empirical factors, K_F , which correct the Kistiakowsky estimation for such polar interactions:

$$\Delta_{\text{vap}}S_i(T_b) = K_F(36.6 + 8.31 \ln T_b) \text{ J mol}^{-1} \text{ K}^{-1} \quad (8-16)$$

K_F values are equal to 1.0 for apolar and many monopolar compounds. For compounds exhibiting a weakly bipolar character (e.g., esters, ketones, nitriles), a modest correction with a K_F of about 1.04 can be made. Significant corrections are necessary for primary amines ($K_F = 1.1$), phenols ($K_F = 1.15$), and aliphatic alcohols ($K_F = 1.3$). For a more comprehensive compilation of K_F values, we refer to the literature (e.g., Sage and Sage, 2000). Using Eq. 8-16, and making some assumptions on the temperature dependence of $\Delta_{\text{vap}}H_i$, Mackay et al. (1982) employed an equation to estimate the liquid vapor pressure of a compound at the temperature T solely from its boiling point:

$$\log p_{iL}^*(T)(\text{bar}) \cong -(1/2.303) K_F (4.4 + \ln T_b) \left[1.8 \left(\frac{T_b}{T} - 1 \right) - 0.8 \ln \frac{T_b}{T} \right] \quad (8-17)$$

Equation 8-17 is particularly useful for prediction of vapor pressures of relatively low boiling compounds (i.e., $T_b < 300^\circ\text{C}$).

A pp-LFER Approach for Estimating the Liquid Vapor Pressure

Another strategy for estimating liquid vapor pressure utilizes a pp-LFER and the compound descriptors introduced in Eqs. 7-10 to 7-12. Since in the pure liquid only identical molecules are present, we can write an equation (Eq. 8-18) in which we express the size as well as the vdW London dispersive, and the Debye and Keesom contributions by L_i and S_i^2 respectively. We recall from Chapter 7, that L_i also

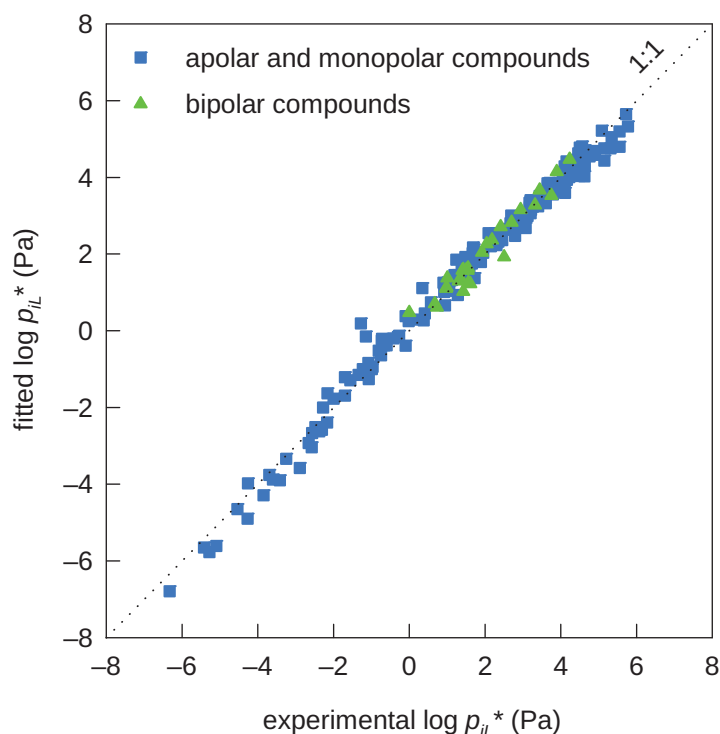


Figure 8.7 Fitted (Eq. 8-19) versus experimental p_{iL}^* values for 200 apolar, monopolar, and bipolar compounds taken from Appendix C.

takes into account entropy changes, which is particularly important when transferring a compound between the gas phase and a condensed phase, e.g., the pure liquid.

$$\log p_{iL}^*(T) = l_{\text{vap}}L_i + s_{\text{vap}}S_i^2 + h_{\text{vap}}A_iB_i + c \quad (8-18)$$

The system descriptor, h_{vap} , is a compounded H-bonding term. A multiple regression analysis using experimental data of a large number of apolar, monopolar, and bipolar compounds covering more than 12 orders of magnitude in $p_{iL}^*(25^\circ\text{C})$ yields the following equation:

$$\log p_{iL}^*(298\text{K}) (\text{Pa}) = -0.89L_i - 0.44S_i^2 - 5.43A_iB_i + 6.51 \quad (8-19)$$

(number of chemicals = 199; $r^2 = 0.99$; S.D. = 0.30)

In Eq. 8-19, all interaction terms exhibit a negative sign, as vapor pressure is an expression of an air–organic liquid partition constant. Figure 8.7 shows that Eq. 8-19 fits the experimental data quite well over a large vapor pressure range, and provides, therefore, an attractive alternative to Eq. 8-17 for estimating p_{iL}^* .

Entropy of Fusion and Vapor Pressure of Solids

As discussed in previous sections, one can obtain (subcooled) liquid vapor pressures via experimental measurements using gas chromatographic techniques (see Appendix C) or estimation methods (Eqs. 8-17 or 8-19). Now, turning to compounds that are solids at the temperature of interest, if no experimental p_{is}^* values are available, one has to first estimate the contribution of fusion; in other words, we have to predict the

solid vapor boundary below the melting point (solid line below T_m in Fig. 8.2). Since we are primarily interested in estimating the ratio p_{is}^*/p_{iL}^* , which is directly related to the free energy of fusion (Eq. 8-10), we can write the *van't Hoff* equation (Eq. 4-33) as:

$$\frac{d \ln p_{is}^*/p_{iL}^*}{dT} = \frac{\Delta_{fus}H_i(T)}{RT^2} \quad (8-20)$$

As a first approximation, if we assume that $\Delta_{fus}H_i$ is constant over the temperature range below the melting point and we substitute Eq. 8-12 into Eq. 8-20, we can integrate Eq. 8-20 from 1 ($p_{is}^* = p_{iL}^*$ at T_m) to p_{is}^*/p_{iL}^* and from T_m to T respectively. We then obtain for $T \leq T_m$:

$$\ln \frac{p_{is}^*}{p_{iL}^*} = -\frac{\Delta_{fus}S_i(T_m)}{R} \left[\frac{T_m}{T} - 1 \right] \quad (8-21)$$

Now, we are left with the problem of estimating the entropy of fusion at the melting point.

Unfortunately, $\Delta_{fus}S_i(T_m)$ is much more variable than $\Delta_{vap}S_i(T_b)$ since $\Delta_{fus}S_i(T_m)$ is equal to $S_{iL}(T_m) - S_{is}(T_m)$ and both of these entropies can vary differently with compound structure. They vary because molecular symmetry is an important determinant of the properties of a solid substance, whereas for a liquid, orientation of a molecule is not that important (Dannenfeler et al., 1993). Nevertheless, as demonstrated by Myrdal and Yalkowski (1997), a reasonable estimate of $\Delta_{fus}S_i(T_m)$ can be obtained by the empirical relationship:

$$\Delta_{fus}S_i(T_m) \cong 56.5 + 9.2 \tau - 19.2 \log \sigma \quad \text{J mol}^{-1} \text{K}^{-1} \quad (8-22)$$

where τ is the effective number of torsional bonds and σ is the rotational symmetry number that describes the indistinguishable orientations in which a compound may be positioned in space (see Box 8.1).

For compounds exhibiting no rotational symmetry axis, σ is equal to 1, which is the case for many of the more complex environmental chemicals. For benzene, on the other hand, $\sigma = 12$ as there are six indistinguishable forms looking from the top of the ring and there are six more when the ring is flipped over. For 1,4-dichlorobenzene, $\sigma = 4$ as only two two-fold rotational axes exist. Some examples of the application of Eq. 8-22 are given in Table 8.2. For a detailed discussion of the symmetry aspects (i.e., the derivation of σ), we refer to the articles by Dannenfeler et al. (1993) and Dannenfeler and Yalkowsky (1996). Finally, we should note that Eq. 8-22 does not work well for small spherical molecules and for polar compounds for which H-bonding has a significant impact on $\Delta_{fus}S_i(T_m)$. Hence, this empirical relationship could certainly be improved.

Box 8.1 Parameters Used to Estimate Entropies of Phase Change Processes

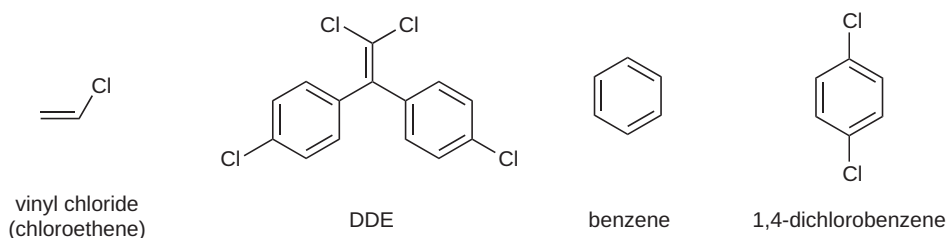
In phase change processes, the overall entropy change, $\Delta_{12}S_i$, can be understood by considering the degrees of freedom lost when molecules in one phase are introduced into a new phase. For example, when molecules in a solid state are converted into the same compound in a liquid state, one can envision the phase change process as involving three contributions to the change in molecular freedom: (1) translational, (2) conformational, and (3) rotational (Yalkowsky and Valvani, 1980; Dannenfelser and Yalkowsky, 1996):

$$\Delta_{12}S_i = \Delta_{12}S_{i\text{translational}} + \Delta_{12}S_{i\text{rotational}} + \Delta_{12}S_{i\text{conformational}}$$

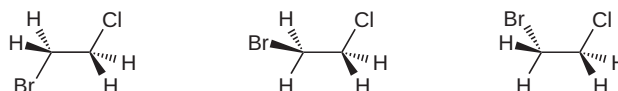
When molecules in a liquid state are transferred into a gaseous state, they gain additional translational and rotational freedom.

Translational freedom, reflected in $\Delta_{12}S_{i\text{translational}}$, is gained when ordered arrangements of molecules expand and become more randomized. For the process of fusion (i.e., opposite direction to freezing), the translational freedom gain involves 50 to 60 J mol⁻¹ K⁻¹. For vaporization (i.e., opposite direction to condensation), the translational freedom gain is about 86 J mol⁻¹ K⁻¹.

Molecules in a liquid state enjoy increased rotational freedom as compared to when they were held in a solid form. The magnitude of the accompanying entropy difference, $\Delta_{12}S_{i\text{rotational}}$, can be understood by considering the “symmetry” of a molecule, meaning the more symmetrical a molecule is, the less additional freedom it gains via rotation in space. This entropy contribution may be quantified by a parameter, σ , quantifying the number of indistinguishable ways a given molecule can exist in space. The more indistinguishable orientations, the easier it is to convert the molecules to a more packed phase, hence, making the absolute value of $\Delta_{12}S_{i\text{rotational}}$ smaller. One may begin by assessing whether a three dimensional view of a given molecule looks the same from above and below (i.e., is there a plane of symmetry in the plane of paper on which a molecule can be drawn?). A molecule like vinyl chloride does not look the same ($\sigma = 1$), while DDE does ($\sigma = 2$). Next, one may ask is there a way to rotate a molecule around an axis perpendicular to any plane of symmetry (e.g., perpendicular to the paper on which the molecule is drawn) and have orientations that look the same. In this sense, vinyl chloride and DDE have only one orientation that look the same, but 1,4-dichlorobenzene looks the same from above and below as well as if it is rotated 180° ($\sigma = 2 \times 2$). Benzene looks the same from above and below and every time it is rotated 60° ($\sigma = 2 \times 6$). The product of these numbers of indistinguishable orientations yields the symmetry number, σ . The higher a molecule’s symmetry number, the less change in rotational freedom associated with packing or unpacking of the molecules. In the case of fusion, $\Delta_{12}S_{i\text{rotational}} = R \ln \sigma = 19.2 \log \sigma$. When σ is 1, $\Delta_{12}S_{i\text{rotational}}$ is zero; when σ is 12, the absolute value is about 20 J mol⁻¹ K⁻¹. The sign depends on whether one considers unpacking (more freedom, so $\Delta_{12}S_{i\text{rotational}}$ has positive sign) or the packing (e.g., freezing or condensation) direction of phase change.

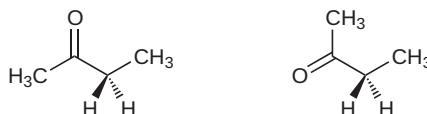


Finally, molecules in a liquid (or gas) state can assume different conformations due to their ability to rotate around single bonds. When a substance is packed into a liquid from a gas or into a solid from a liquid, the molecules have a reduced ability to assume various conformations. This loss of freedom is reflected in $\Delta_{12}S_{i \text{ conformational}}$. For example, consider 1-bromo-2-chloro-ethane. Viewing the two carbons and the chlorine substituent as co-existing in a plane, we recognize that the bromine atom can occur in the same plane opposite the chlorine atom, above the plane, or behind the plane:



This amounts to rotating around the single bond connecting the two carbons. Every bond capable of such rotation offers three distinguishable orientations. Therefore, if we increased the chain length by one $-\text{CH}_2-$ unit, $3 \times 3 = 9$ distinguishable conformations exist. Having only three atoms in such a chain does not enable conformation variation since three points always determine a single plane. Hence, $\Delta_{12}S_{i \text{ conformational}}$ increases by the number of bonds capable of rotation minus two (equivalent to number of non terminable sp^3 atoms in the chain; hydrogen is not a sp^3 atom).

Atoms in the chain that include double bonded moieties do not offer as much conformational variety. Consider methyl ethyl ketone; rotation around the bond between the carbonyl carbon and the C_3 allow two (not three) distinguishable conformers:



Therefore, the contribution of such atoms to $\Delta_{12}S_{i \text{ conformational}}$ needs to be discounted, which is done by applying a factor of 0.5 times the number of such sp^2 members of a chain. This discounting also applies to ring systems. Therefore, we can estimate a parameter, τ :

$$\tau = (\text{number of non terminable } \text{sp}^3 \text{ atoms}) + 0.5 * (\text{number of non terminable } \text{sp}^2 \text{ atoms}) + 0.5 * (\text{ring systems}) - 1$$

The number of distinguishable conformers is approximately 3^τ . Empirically, the observed data for the entropy of fusion at T_m are best fit using 2.85^τ . With this estimate, one finds $\Delta_{12}S_{i \text{ conformational}}$ is approximately $R \ln (\text{number of distinguishable conformers}) \approx R \ln(2.85^\tau) = 9.2 \tau$ (as in Eq. 8-22). For the case of 1-bromo-2-chloro-ethane with a τ of 1, $R \ln(2.85^\tau) = 9 \text{ J mol}^{-1} \text{ K}^{-1}$. As chains get longer, the magnitude of the contribution of $\Delta_{12}S_{i \text{ conformational}}$ to $\Delta_{12}S_i$ grows quickly (see Table 8.2).

Substitution of Eq. 8-22 into Eq. 8-21 then gives:

$$\ln \frac{p_{is}^*}{p_{iL}^*} = -(6.80 + 1.1\tau - 2.3 \log \sigma) \left[\frac{T_m}{T} - 1 \right] \quad (8-23)$$

Table 8.2 Comparison of Experimental and Predicted (Eq. 8-22) Entropies of Fusion at the Normal Melting Point^a

Compound	Experimental					Predicted (Eq. 8-22)
	T_m (°C)	$\Delta_{\text{fus}} H_i(T_m)$ (kJ mol ⁻¹)	$\Delta_{\text{fus}} S_i(T_m)$ (J mol ⁻¹ K ⁻¹)	τ	σ	$\Delta_{\text{fus}} S_i(T_m)$ (J mol ⁻¹ K ⁻¹)
Benzene	5.5	10.0	35.7	0	12	35.8
<i>n</i> -Butylbenzene	-88.0	11.2	60.5	2	2	69.1
1,4-Dichlorobenzene	52.7	17.2	52.8	0	4	45.0
Naphthalene	80.2	18.6	52.7	0	4	45.0
Phenanthrene	101.0	18.1	48.6	0	2	50.7
Fluoranthene	107.8	18.9	49.6	0	2	50.7
Pyrene	151.2	17.1	40.3	0	4	45.0
Decane	-29.7	28.8	118.3	7	2	115.1
Eicosane	36.8	69.9	225.6	17	2	207.1
Benzoic acid	122.4	18.1	45.8	0	2	50.7
2,2',4,5,5'-Pentachlorobiphenyl	77.0	18.8	53.6	0	1	56.5
p,p'-DDT	109.0	27.4	71.6	1	1	65.7

^aData from Hinckley et al. (1990) and Lide (1995).

which can be used to estimate p_{is}^* from the subcooled liquid vapor pressure p_{iL}^* , and *vice versa*. Finally, insertion of Eq. 8-23 into Eq. 8-9 yields an estimate of the free energy of fusion:

$$\Delta_{\text{fus}} G_i = +(56.5 + 9.2 \tau - 19.2 \log \sigma) [T_m - T] \quad \text{J mol}^{-1} \quad (8-24)$$

The entity, $\Delta_{\text{fus}} G_i$, will be important for estimating other properties of the subcooled liquid, such as water solubility (see Chapter 9).

8.3 Questions and Problems

Special note: Problem solutions are available on the book's website. Solutions to problems marked with an asterisk are available for everyone. Unmarked problems have solutions only available to teachers, practitioners, and others with special permission.

Questions

Q 8.1

Give at least five examples of environmentally relevant organic chemicals that are gases at 20°C (273K). Which of the companion compounds (Table 3.1) are liquids at both -20°C and +20°C (253K and 293K)?

Q 8.2

Why are certain chemicals gases at ambient conditions of temperature and pressure?

Q8.3

Propane ($T_b = -42.1^\circ\text{C}$, $T_c = 101.2^\circ\text{C}$) is a gas at 25°C . How can you “produce” liquid propane (give two options)?

Q8.4

What is the difference between the *normal* and the *standard* boiling point of a chemical?

Q8.5

Explain in words the terms *subcooled liquid*, *superheated liquid*, and *supercritical fluid*.

Q8.6

How are the (subcooled) liquid and solid vapor pressures of a given compound at a given temperature related to each other?

Q8.7

Which thermodynamic entities need to be known for assessing the temperature dependence of the vapor pressure of a given compound? How can this entity be derived from experimental data? How can it be estimated? What caution is advised when extrapolating vapor pressure data from one temperature to another temperature?

Q8.8

Explain the following observations:

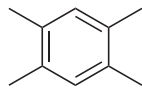
(a) The two isomeric polycyclic aromatic hydrocarbons, phenanthrene and anthracene, are solids at 25°C . Although these compounds have almost the same boiling point (339°C and 341°C respectively), their vapor pressures at 25°C differ by more than one order of magnitude.

(b) Although they have approximately the same size, *n*-hexane ($V_i = 95\text{ cm}^3\text{ mol}^{-1}$) exhibits a 20 times larger vapor pressure than styrene ($V_i = 96\text{ cm}^3\text{ mol}^{-1}$), and a 1000 times larger vapor pressure than 3-methylphenol ($V_i = 92\text{ cm}^3\text{ mol}^{-1}$).

(c) The liquid vapor pressure of 2,6-dimethylphenol is almost one order of magnitude larger than the one of its isomer, 3,4-dimethylphenol.

Problems**P8.1* Basic Vapor Pressure Calculations**

(a) Consider the chemical 1,2,4,5-tetramethylbenzene (abbreviated TeMB and also called durene, structure in margin). In an old *CRC Handbook of Chemistry and Physics*, you find vapor pressure data that are given in mm Hg (see margin).



1,2,4,5-tetramethylbenzene

$$M_i = 134.2 \text{ g mol}^{-1}$$

$$T_m = 79.5^\circ\text{C}$$

$$T_b = 195.9^\circ\text{C}$$

Experimental vapor pressure
data for TeMB

T (°C)	p_i^* (mm Hg)
45.0 ^s	1
74.6 ^s	10
104.2	40
128.1	100
172.1	400
195.9	760

^sTeMB is a solid at these temperatures.

Estimate the vapor pressure, p_i^* , of TeMB (in bar and Pa) at 20°C and 150°C using the experimental vapor pressure data given.

(b) Estimate the free energy ($\Delta_{\text{fus}} G_i$, in kJ mol⁻¹), the enthalpy ($\Delta_{\text{fus}} H_i$, in kJ mol⁻¹), and the entropy ($\Delta_{\text{fus}} S_i$, in kJ mol⁻¹ K⁻¹) of fusion of TeMB at 20°C using the vapor pressure data previously given.

P8.2 A Solvent Spill in Your Class Room

You teach Environmental Organic Chemistry, and for a demonstration of partitioning processes of organic compounds, you bring a glass bottle containing 10 L of the common solvent, tetrachloroethene (PCE), into your classroom. After closing the door, you stumble, and you drop the bottle. The bottle breaks, and the solvent spills onto the floor. Soon, you can smell the solvent vapor in the air. (The odor threshold of PCE is between 8 and 30 mg m⁻³). Answer the following questions:

(a) What is the maximum PCE concentration that you can expect in the air in the room ($T = 20^\circ\text{C}$)? How much of the solvent has evaporated if you assume that the air volume is 50 m³? (Neglect any adsorption of PCE on the walls and furniture.)

(b) If the same accident happened in your sauna (volume 15 m³, $T = 80^\circ\text{C}$), what maximum PCE concentration would you and your friends be exposed to there?

In an old *CRC Handbook of Chemistry and Physics* (Lide, 1995), you find the following vapor pressure data for PCE:

T (°C)	25	50	75	100
p_i^* (kPa)	2.42	8.27	22.9	54.2

Use both the experimental data as well as Eqs. 8-19 and 8-14 to solve this problem. Compare the predicted with the experimental data. Any comments?

P8.3 How Much Freon is Left in the Old Pressure Bottle Left at a Dump Site?

In a dump site, you find an old 3-liter pressure bottle with a pressure gauge that indicates a pressure of 2.7 bar. The temperature is 10°C. From the label, you can see that the bottle contains Freon 12 (dichlorodifluoromethane, CCl₂F₂). You wonder how much Freon 12 is still left in bottle. Try to answer this question.

In an old *CRC Handbook of Chemistry and Physics* (Lide, 1995), you find the following data on CCl₂F₂:

T (°C)	-25	0	25	50	75
p_i^* (kPa)	123	308	651	1216	2076

Using these data, estimate the free energy ($\Delta_{\text{cond}} G_i$), the enthalpy ($\Delta_{\text{cond}} H_i$), and the entropy ($\Delta_{\text{cond}} S_i$) of condensation of Freon 12 at 25°C. Note that condensation is the opposite of vaporization (watch out for the signs of the three quantities).

P8.4 What Are the Differences Between Freon 12 and its Replacement HFC-134a?
(From Roberts, 1995)

Hydrofluorocarbon 134a (1,1,1,2-tetrafluoroethane, F_3C-CH_2F) is used as a replacement for Freon 12 (see Problem 8.3) for refrigeration applications. Why is such a replacement necessary and what is the advantage of HFC-134a from an environmental protection point of view?

Some vapor pressure data for Freon 12 is given in Problem 8.3. The vapor pressure data of HFC-134a has been determined very carefully and is as follows:

T (°C)	−40.0	−30.0	−20.0	−10.0	0	+10.0
p_i^* (kPa)	51.6	84.7	132.9	200.7	292.9	414.8

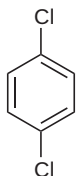
- Determine the normal boiling points (in °C) of these compounds from the data provided.
- At what temperature (in °C) will they have an equal vapor pressure?
- Compare the enthalpies ($\Delta_{\text{vap}}H_i$) and entropies ($\Delta_{\text{vap}}S_i$) of vaporization of the two compounds at ambient temperatures. Can you rationalize any differences you observe between the two compounds?
- Automobile air conditioners commonly operate at temperatures between 30 and 50°C. Are the vapor pressures of the two compounds significantly (i.e., greater than 10%) different in this temperature region?

P8.5 A Public Toilet Problem

Pure 1,4-dichlorobenzene (1,4-DCB) is still used as a disinfectant and air freshener in some public toilets. As an employee of the health department of a large city you are asked to evaluate whether the 1,4-DCB present in the air in such bathrooms may pose a health problem to the cleaning personnel who are exposed to this compound for several hours every day. In this context, you are interested in the maximum possible 1,4-DCB concentration in the bathroom air at 20°C. Calculate this concentration in g m^{-3} air, assuming that:

- you go online and get the vapor pressure data given below from *CRC Handbook of Chemistry and Physics* (Haynes, 2014: <http://www.hbcpnetbase.com>),
- you have no time to look for vapor pressure data, but you know the boiling point ($T_b = 174.0^\circ\text{C}$) and the melting point ($T_m = 53.1^\circ\text{C}$) of 1,4-DCB, or
- you are a pp-LFER freck.

Compare the three results.

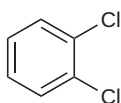


1,4-dichlorobenzene

What would be the maximum 1,4-DCB concentration in the air of a public toilet located in Death Valley (Temperature 60°C)? Any comments?

T (°C)	-45.5 ^s	-21.8 ^s	8 ^s	46.7 ^s	99	173.6
p_i^* (kPa)	0.001	0.01	0.1	1	10	100

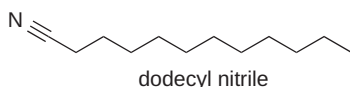
^sIndicates the compound is a solid at this temperature.



1,2-dichlorobenzene

P 8.6 True or False?

Somebody bets you that at 60°C, the vapor pressure of 1,2-dichlorobenzene (1,2-DCB) is smaller than that of 1,4-dichlorobenzene (1,4-DCB), but that at 20°C, the opposite is true. Is this person right? If yes, at what temperature do both compounds exhibit the same vapor pressure? (Try to answer these questions by using only the T_m and T_b values given in Appendix C.)



dodecyl nitrile

$M = 181.3 \text{ g mol}^{-1}$
 $T_m = 4^\circ\text{C}$
 $T_b = 277^\circ\text{C}$
 density = 0.82 g mL^{-1}
 index of refraction = 1.4361

P 8.7 Vapor pressure of Alkyl Nitriles from Biomass Burning

Simoneit et al. (2003) discovered that biomass burning results in the introduction of alkyl nitriles into the atmosphere. One such alkyl nitrile is dodecyl nitrile. In order to prepare to estimate the fate of dodecyl nitrile, you are asked to find its physical chemical properties. Now, estimate the vapor pressure (Pa) of dodecyl nitrile at 25°C.

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