Lecture Notes 1: Physical Equilibria – Vapor Pressure

Our first exploration of equilibria will examine physical equilibria (no chemical changes) in which the only changes occurring are matter changes phases.

As is the case with all equilibria we will see that the stable state depends on the free energy of the system and that at equilibria all species that are present have the same free energy

Free energy is the balance between energy (on our case we will specifically look at the enthalpy) and entropy. The balance between these two varies with the temperature.

Areas of physical equilibria we will examine are

• Phase transitions. Changes between the solid, liquid, and gaseous forms of a substance. For example: why does diethyl ether boil at a lower temperature than ethanol?

• Mixtures. How do energy and entropy govern the mixing of two substances? For example: why do oil and water not mix.

• Colligative properties. How does making a mixture affect the phase transitions of the system? For example: why does salt water freeze at a lower temperature than pure water?

To understand this, we will draw on two large areas from CH301

Thermodynamics and Intermolecular Forces

REVIEW these two areas.

The first topic we will examine is vapor pressure. You should have covered this topic briefly during your discussion of intermolecular forces.

Definition of vapor pressure: the partial pressure of a substance in equilibrium with its condensed phase (liquid or solid). The pressure of the vapor over a liquid (solid) at equilibrium.

The stability of any given state is given by its free energy. At constant temperature and pressure we utilize the Gibb's Free Energy

$$G = H - TS$$

G is the free energy. H is the enthalpy. T is the temperature. S is the entropy. The lower the free energy, the more stable the state. Thus lower enthalpy is more stable and higher entropy is more stable at a given T.

For phases we have a competition. Intermolecular forces lead to attractions between the molecules. These means the molecules have a lower enthalpy (energy) when they are close together. This favors the solid state. In contrast, from an entropy standpoint, the higher the entropy the lower the free energy. This favors the gas phase as it has the highest entropy. The favored state then depends on the temperature. When the temperature is low, the energy dominates and substances are solid. When the temperature is high, the entropy dominates and substances are gaseous. The exact temperature of a phase change depends on the substance (intermolecular forces).

Entropy

The highest entropy state for any substance at a given temperature would be if the atoms/molecules were scattered out as far as possible. Thus from an entropy standpoint everything should be a gas exploring the far reaches of the universe. However, all substances have intermolecular forces (interatomic forces) (IMF) that lead to attractions between the molecules. (it might be good to rattle off a few of the IMFs here, just in case IMF term doesn't ring a bell w/ students—they're likely to remember ion-ion, dipole, London, etc..) This means that they have a lower energy when they are close together as compared to far apart. Thus the IMF are "holding" the molecules close together. The stronger these forces are, the more difficult it is for the molecules to wander away from each other. Conversely, the lower the IMF the easier 'the wandering' is. However, no matter the magnitude of the IMF there can always be a few molecules that escape. The number of these molecules and thus the partial pressure of the substance varies with the IMF. Thus at a given temperature, if the IMF are strong, the vapor pressure is low as only a few molecules can overcome the attractions of the molecules for each other. In contrast, a liquid with weak IMF will have many molecules in the gas phase and thus a higher vapor pressure.

In CH301 you likely ranked the boiling point of molecules based on their IMF. Boiling point and vapor pressure are the same concept. The boiling point is the temperature at which the vapor pressure equals the total pressure. When comparing vapor pressures we need to be discussing the same temperature. Thus at room temperature, the substance with the lowest boiling point will have the highest vapor pressure (easiest to get into the gas phase). The highest boiling point will have the lowest vapor pressure.

In general the trend is to rank things according to the accepted magnitude (or strength) of IMF.

Generally dispersion (instantaneous dipoles) forces are the weakest, dipole-dipole interactions stronger, H-bonding next, followed by ionic forces (which are more bonding than IMF).

However, as you may or may not have discovered, these trends are not set in stone. Everything has dispersion forces and they can be very large. In addition, some molecular dipoles can be weak. Thus it is very possible for completely non-polar molecules to have stronger IMF than similar polar molecules. For example, the boiling point of CCl_4 (no dipole) is higher than that of $CHCl_3$ (polar).
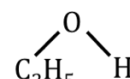
What will always correlate is the vapor pressure and the IMF. Larger IMF = lower vapor pressure.
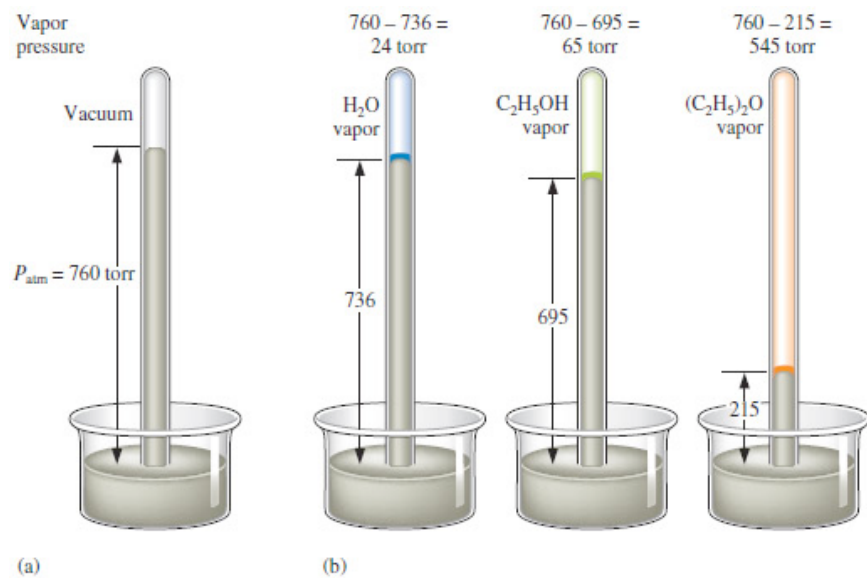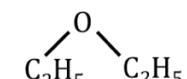
For example. This figure from the text shows the vapor pressure of three liquids.
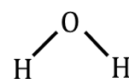
Water
24 Torr

Ethanol
65 Torr

Diethyl Ether
545 Torr

They are measured by comparing the pressure they exert versus the atmospheric pressure. On the far left is the apparatus with no liquid. It consists of an evacuated tube placed into a pool of mercury. The pressure from the atmosphere pushes the mercury up into the tube. The height it rises is a measure of the pressure and depends on the density of the fluid (mercury) and gravity. In the next example, a small amount of water is placed in the tube. Some of the water vapor evaporates. The pressure of this gas is the vapor pressure. Now the liquid in the tube is forced back down the tube slightly such that the height of the liquid represents the difference of the pressure inside the tube (the vapor pressure of water) and outside the tube (the atmosphere). The two other pictures illustrate ethanol and diethyl ether.

Note at this temperature, water has the lowest vapor pressure (24 Torr) , ethanol is next (65 Torr) and diethyl ether is the highest (545 Torr). This is the trend we expect from the IMF. Water is polar and has strong H-bonds, ethanol is also polar but it has weaker H-bonds (only one H that can H-bond vs. the two that water has), and finally diethyl ether is the weakest as it has no H-bonds (no hydrogens bonded to the oxygen)

How does the vapor pressure change with temperature? We would expect it to get larger as the temperature is raised. Why? As T increases we start to favor the higher entropy state. That is the gas phase. Let's look at some data to see what happens to the vapor pressure of water as the temperature changes.

E 16.7 The Vapor Pressure of Water as a Function of Temperature	
T (°C)	P (torr)
0.0	4.579
10.0	9.209
20.0	17.535
25.0	23.756
30.0	31.824
40.0	55.324
60.0	149.4
70.0	233.7
90.0	525.8
100.0	760.0

As we expected, as the temperature increases the vapor pressure rises. We also see that the rise is not linear. It is in fact exponential.

We can derive an expression for this dependence based on what we know from thermodynamics.
What are we looking at? A liquid in equilibrium with its vapor at a pressure P at a temperature T. When the system is at equilibrium the two phases have the same free energy thus

$$\Delta G_{vaporization} = G_{gas} - G_{liq} = 0$$

The free energy of the liquid is approximately independent of the pressure, thus the free energy at pressure P is about the same as that at the standard pressure (the one with the zero superscript)

Thus $\quad G_{liq} = G_{liq}^0$

However, the free energy of the gas is a strong function of the pressure. Approximating the gas as idea, it is given by

$$G_{gas}(P) = G_{gas}^0 + RT\ln(P/P^0) = G_{gas}^0 + RT\ln(P) \quad \text{if we take the standard pressure P° as 1.}$$

Putting this all together we see

$$\Delta G_{vaporization} = G_{liq}^0 - [G_{gas}^0 + RT\ln(P)] = \Delta G_{vap}^0 - RT\ln(P) = 0$$
$$\Delta G_{vap}^0 = RT\ln(P)$$

Thus the pressure depends on the standard free energy for vaporization.

$$\Delta G_{vap}^0 = \Delta H_{vap}^0 - T\Delta S_{vap}^0 \qquad \text{thus} \qquad \ln(P) = \frac{-\Delta G_{vap}^0}{RT} = \frac{-\Delta H_{vap}^0}{RT} + \frac{\Delta S_{vap}^0}{R}$$

If we assumed that ΔH_{vap}^0 and ΔS_{vap}^0 are independent of temperature, then the entropy term is a constant. The temperature dependence is only from ΔH_{vap}^0. This was the part that depended on the IMF.
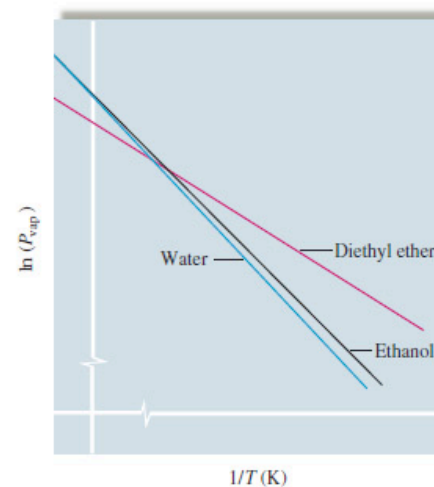Taking the exponential of both sides we get

$$P = Ke^{-\Delta H_{vap}^0/RT} \quad \text{where K is a constant . This is an important relationship that we will see crop up many times in dealing with equilibria.}$$

The final conclusion! The vapor pressure increases exponentially with temperature.
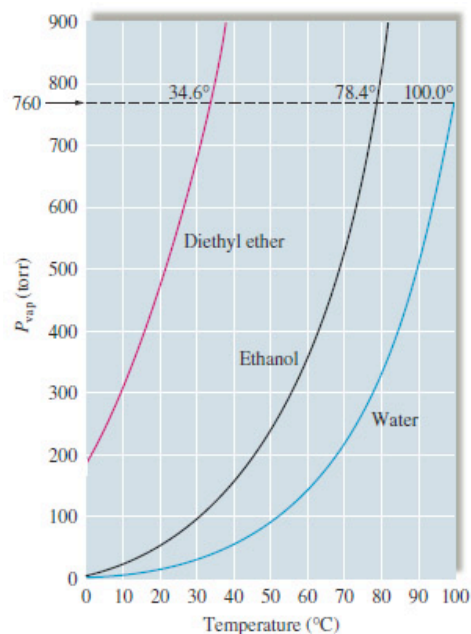
(a)

(b)

This figure shows the vapor pressure of water, ethanol, and diethyl ether as a function of temperature. Note the exponential function of temperature. The strongest IMF in water leads to the larges ΔH^0_{vap}. Thus the lowest vapor pressure at each temperature.

If we take our expression for the vapor pressure as a function temperature and look at two data points P_1 at T_1 and P_2 at T_2 we find the following (after some algebra).

$$\ln\left(\frac{P_2}{P_1}\right) = \frac{-\Delta H^0_{vap}}{R}\left[\frac{1}{T_2} - \frac{1}{T_1}\right]$$

This is the Claussius-Clapyeron Equation. There are many forms in which you might find this equation, however they are all equivalent.

Note: this also means that if you plot ln(P) vs 1/T the graph will be a straight line. The slope will be given by $-\Delta H^0_{vap}/R$.

Looking at the second part of the figure you can see that ΔH^0_{vap} must be largest for H_2O (as it has the most negative slope).

Let's use this new equation to find the vapor pressure at one temperature given data at a different temperature.

One question we might ask, is at what temperature will ethanol boil? The boiling point of a liquid is the point at which its vapor pressure is equal to the total pressure. Since the pressure is general one atmosphere, the normal boiling point of ethanol will be the temperature at which its vapor pressure is one atmosphere (760 Torr). To find this point, we need two things. The standard enthalpy of vaporization for ethanol and the vapor pressure at some other temperature.

We have the vapor pressure at 25°C as it was our example from earlier. This is 65 Torr. Then we need the ΔH^0_{vap} . For this we'll need a table of data (or will have to find it from two data points using the equation). I looked this up and found it to be 38.6 kJ mol^{-1}.

Note: for the Clausius-Clapyeron equation we have several key ideas regarding units. First, for pressure we can use any units we like as long as they are the same for P$_1$ and P$_2$. For temperature, everything must be in Kelvin. For R we need to have units of J. For ΔH^0_{vap} the units are usually kJ, so we need to convert to Joules.

What do we have?
ΔH^0_{vap} =38.6 kJ mol^{-1} = 38,600 J mol^{-1}
R = 8.314 J K^{-1}mol^{-1}
P$_1$= 65 Torr
T$_1$ = 298.15 K
P$_2$ = 760 Torr
T$_2$ = ????

$$\ln\left(\frac{P_2}{P_1}\right) = \frac{-\Delta H^0_{vap}}{R}\left[\frac{1}{T_2}-\frac{1}{T_1}\right]$$ this can be re-arranged (being careful with the algebra) such that $$\frac{1}{T_2}=\frac{1}{T_1}-\frac{R}{\Delta H^0_{vap}}\ln\left(\frac{P_2}{P_1}\right)$$

$$\frac{1}{T_2}=\frac{1}{298.15K}-\frac{8.314\ \text{J K mol}^{-1}}{38600\ \text{J mol}^{-1}}\ln\left(\frac{760\ \text{Torr}}{65\ \text{Torr}}\right)$$

T$_2$ = 354 K

The actual answer is 351 K. Not bad considering all our approximations!
The difficult part of this problem (actually the only part) is the algebra and the units. Otherwise it is simply plugging numbers into an equation.

Final note.

We now have a quantitative way to calculate the vapor pressure for a substance as a function of temperature.

What is in this equations? ΔH^0_{vap} which depends on the IMF. The temperature. That is all. Those are the two things that affect the vapor pressure of a pure substance.

What about the volume of the liquid? Doesn't matter. As long as there is liquid, at a given temperature it will have a given vapor pressure. What if the container is large? What if it is small? None of this matters. At a given temperature, a pure liquid (or solid) has a given vapor pressure. End of story (unless you make a mixture. But that is lecture 4)