Chapter 8: Physical Equilibria

Our first foray into equilibria is to examine phenomena associated with two phases of matter achieving equilibrium in which the free energy in each phase is the same and there is no change in the overall values of system state functions.

The areas of physical equilibria we will investigate are:

- The interface between phases: gas ← → liquids ← → solid. Solution properties like freezing and boiling will be given a thorough thermodynamic treatment.
- Mixtures formed when phases are soluble or miscible in one another. Dissolving solids or gases in liquids or mixing two liquids.
- Colligative properties that derive from mixing of two phases. These are essential properties of biological and chemical systems.

We will draw on the following theoretical treatments from CH 301:

intermolecular force theory (chapter 5) **thermodynamics (chapters 6 and 7)**

So review them!!

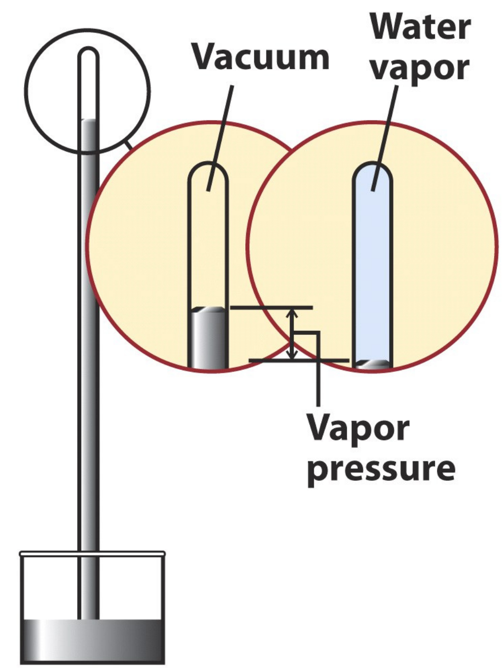
Specifically, review the intermolecular force and thermodynamic lecture notes on the CH301 web site. Pay special attention to the introductory treatment of phases and phase transitions that are presented at various times during these lectures.

Section 8.1-8.3: Vapor Pressure

Vapor Pressure. Vapor pressure was introduced in Chapter 5 as a solution property. We learned that vapor pressure rankings could be qualitatively determined from a ranking of intermolecular forces.

Definition of vapor pressure: the pressure exerted by the vapor of a substance that exists in a condensed (liquid or solid) phase.

Just looking at this picture suggests vapor pressure is a surface phenomenon. The more surface the more vapor. The depth of the condensed phase doesn't matter. The reason is that the particles in the condensed phase with the greatest ability to enter the vapor phase are on the surface.



IMF Theory and vapor phase ranking: It is intuitive that the stronger the intermolecular force holding a substance together, the less likely it is to enter the vapor phase. Similarly, the smaller the IMF force, the greater the vapor pressure.

Here is the ranking and trend, contrasting IMF and assorted compounds:

As the intermolecular forces increase , the vapor pressure decreases

Instantaneous dipoles < dipole-dipole < hydrogen bonding < ionic

He > CH_4 > C_3H_8 > CCl_4 > $CHCl_3$ > CH_3OH > H_2O > NaCl

It is pretty easy to generate these qualitative rankings of vapor pressure by first ranking IMF. Look at the table of values for different compounds at 25°C to see the correlation:

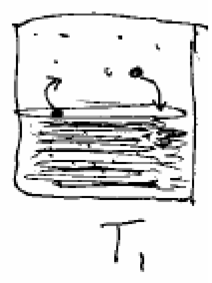
TABLE 8.2 Vapor Pressures at 25°C

Substance	Vapor pressure (Torr)
benzene	94.6
ethanol	58.9
mercury	0.0017
methanol	122.7
water*	23.8

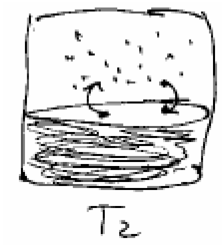
*For values at other temperatures, see Table 8.3.

Now can we create a **quantitative** measure of vapor pressure?

First recognize that vapor pressure is an equilibrium phenomenon that is temperature dependent.



← note that at equilibrium, as vapor encounters the surface it condenses and the energy released promotes a different particle into the vapor.



← also note that at the higher T more particles achieve separation energy to enter vapor.

In the table of water vapor pressures, note that as the temperature increases, the vapor pressure increases until the boiling point is reached—100 degrees at 1 atmosphere. Also note what appears to be an exponential-like increase in P as T increases.

TABLE 8.3 Vapor Pressure of Water

Temperature (°C)	Vapor pressure (Torr)
0	4.58
10	9.21
20	17.54
21	18.65
22	19.83
23	21.07
24	22.38
25	23.76
30	31.83
37*	47.08
40	55.34
60	149.44
80	355.26
100	760.00

*Body temperature.

Can we derive an expression that predicts this relationship? First note that at equilibrium,

$$\Delta G_{vap} = G_{gas} - G_{liquid} = \emptyset$$

$$G_{liquid} = G^\circ_{liquid}$$ because it is pressure independent

$$G_{gas} = G^\circ_{gas} + RT\ln P$$ where RTlnP = correction for change in pressure, so:

$$\Delta G_{vap} = G^\circ_{gas} + RT\ln P - G^\circ_{liquid} = G^\circ_{gas} - G^\circ_{liquid} + RT\ln P$$

$$\therefore \Delta G^\circ_{vap} = -RT\ln P$$

(the standard free energy of vaporization)

But

$$\Delta G^\circ_{vap} = \Delta H^\circ_{vap} - T\Delta S^\circ_{vap}$$

So: $$\ln P = -\frac{\Delta G^\circ_{vap}}{RT} = -\frac{\Delta H^\circ_{vap}}{RT} + \frac{\Delta S^\circ_{vap}}{R}$$

A constant, assuming ideal gas behavior because a mole of any kind of gas has about the same entropy.

Or multiplying through by e^x

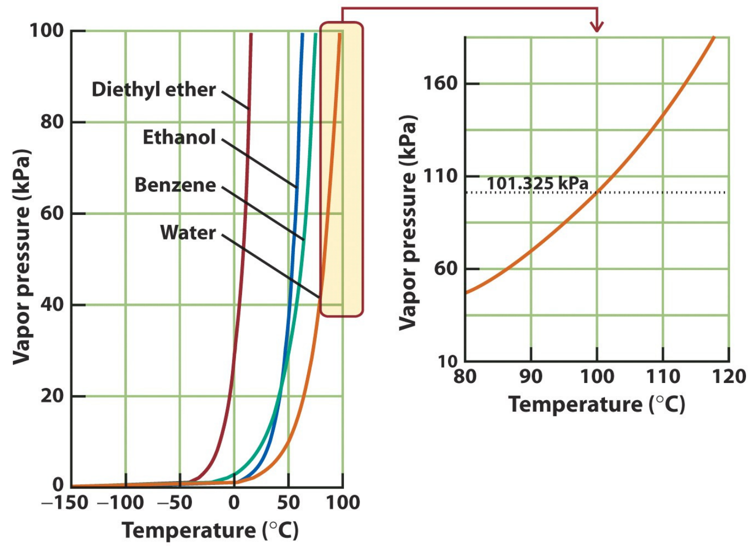
$$P = K e^{-\Delta H_{vap}/RT}$$

This is a very famous mathematical relationship that shows up all the time in nature.

What does the above equation suggest for a function? An exponential increase in P with T.

Note this functional relationship not just for water but for other compounds. And note that

Note that as delta H^{o}_{vap} decreases with increasing IMF, the boiling point increases and that this correlates with IMF.



And now for something really useful that scientists do: Combining equations to eliminate a variable—or how to create the famous Clausius Clapeyron equation.

Given that ΔS°_{vap} is assumed to be constant in the expression:

$$\ln P = \frac{-\Delta H^{\circ}_{vap}}{RT} + \frac{\Delta S^{\circ}_{vap}}{R}$$

We can rearrange the equation to put everything in terms of $\frac{\Delta S^{\circ}_{vap}}{R}$, identify two states of the system P_1, T_1 and P_2, V_2, set them equal and do mad algebra. When it is all over,

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

This is the famous **Clausius-Clapeyron equation** that allows us to use one value of P_1 and T_1 to predict the vapor pressure anywhere else on the graph.

So let's test this by using the equation to find the boiling point of water (hey, at least we'll know if our answer is right since at 100 degrees the vapor pressure should be 760 torr). Selecting a P and T, from our table of H_2O vapor pressures, Like 20C and 17.54 torr, and given $\Delta H^\circ_{vap}\ H_2O = 40.7\ kJ/mole$. We need to work in the correct units so convert 17.54 torr into Pa.

1 torr = 133.3 Pa, so 17.54 torr (133.3Pa/1torr) = 2338.1 Pa

$$\ln\frac{P_2}{P_1} = \frac{\Delta H_{vap}^\circ}{R}\left(\frac{1}{T_1}-\frac{1}{T_2}\right) \xRightarrow{\text{rearranging}} \frac{1}{T_1} = \frac{1}{T_2} + \frac{R}{\Delta H_{vap}^\circ}\ln\frac{P_2}{P_1}$$

$$\frac{1}{T_1} = \frac{1}{(20+273)} + \left(\frac{8.3145\ J/Kmol}{40{,}700\ J/mole}\right)\ln\left(\frac{2338.1\,Pa}{101{,}325\,Pa}\right) \Leftarrow \text{1atm in Pa}$$

Solving: T1 = 378 K or 105 degrees C which is pretty good considering all the approximations. So there we have it, an equation that models the vapor pressure curve for any compound as a function of temperature!!!