Lecture 26: First Order Phase Transitions

A first order phase transition (in a single component system) is characterized by a discontinuity in one or more state variables.

Example of water at 373.15 K and 1 atm:

Property	Liquid	Gas
Molar volume, V_m	0.018 L	30.62 L
Molar enthalpy of formation, $\Delta H_{f,m}$	−283.44 kJ/mol	−242.56 kJ/mol
Molar entropy of formation, $\Delta S_{f,m}$	79.83 J/mol/K	186.60 J/mol/K
Molar heat capacity, $C_{P,m}$	77.06 J/mol/K	33.58 J/mol/K
$\Delta U_{f,m}$, $\Delta A_{f,m}$		

Verify these numbers.

Enthalpy of vaporization = −242.56+283.44 = 40.88

Table 4.2: 40.7 kJ/mol

Entropy of vaporization = 186.60 – 79.83 = 106.77

Table 4.2: 109.1 kJ/mol/K

$$\Delta G_{vap} = \Delta H_{vap} - T_{bp}\Delta S_{vap} = 0 \quad \text{(why?)}$$

$$\Rightarrow \Delta S_{vap} = \Delta H_{vap}/T_{bp}$$
$$= 40{,}700/373.15 = 109.1$$

Q. What is the cause of a phase transition?

A. Multiple minima in μ

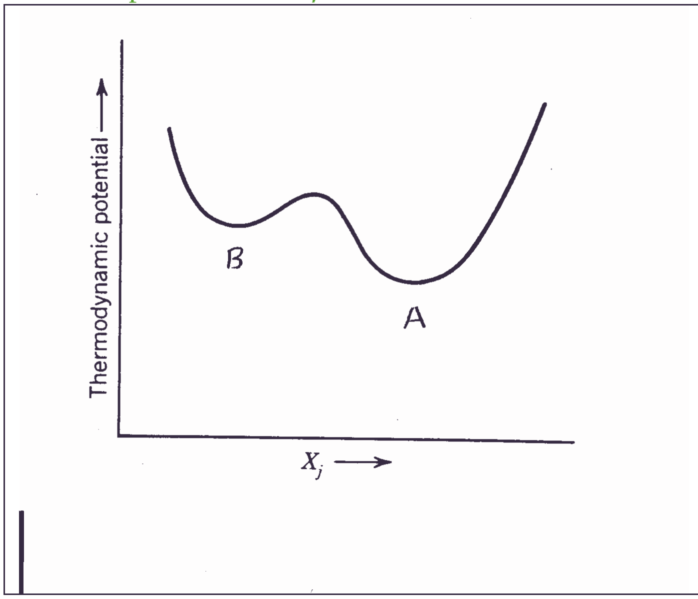


Figure 26.1 Dependence of G_m on an extensive variable, such as V_m. The slope is an intensive variable, such as the pressure, which provides a restoring force that drives the system towards a homogeneous equilibrium state.

Explanation: This might be, for example, a plot of G_m vs V_m for water at constant T. The minimum point at B represents the molar volume of liquid water, and that at A is V_m of water vapor (which lower density). The only point on the graph that actually exists in nature at this temperature is the minimum at A. The difference between the two minima is $\Delta G_{m,melting.}$ If some dropplets happen to form at B, they vaporize spontaneously because $\Delta G_{m,vaporization}$ is negative.

Minimum A is stable, minimum B is metastable.
A random fluctuation might temporarily reach B.

Q. How can the phase transition A → B occur spontaneously?
A. One way is to reduce the temperature until minimum B is lower than A.

Note: If we cool slowly enough, the system might remain trapped in A for a while.

Example: crystallization out of a super-cooled liquid.
See Figure 2, where X = V_m.

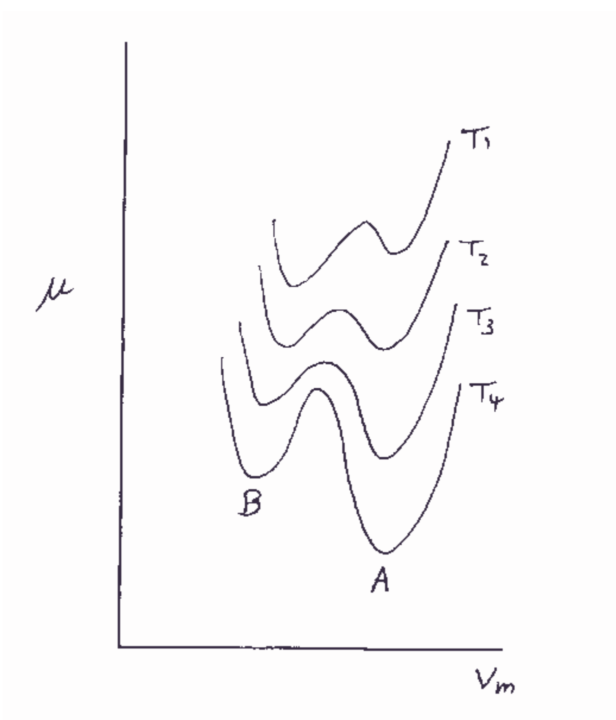


Figure 26.2 Plot of chemical potential vs. molar volume, illustrating a phase transition, as the temperature is reduced from T_4 to T_1. At T_4, the vapor phase , A, is more stable than the liquid, B. At T_3, A and B are in equilibrium, and at B is more stable.

Q. What happens if the barrier between the two minima is very large?

A. Phase A becomes metastable.
Example: diamond → graphite.

. How does μ vary with T?

$$dG = -SdT + VdP$$

A: For a single component system,

$$d\mu = -S_m dT + V_m dP$$

$$\left(\frac{\partial \mu}{\partial T}\right)_P = -S_m$$

This slope is necessarily negative.

It follows that μ always decreases with temperature.

$S_{solid} < S_{liquid} < S_{gas} \Rightarrow$ as the temperature increases a material first melts and then boils. (Depending on where the curves in Figure 3 cross, it possible for the solid to go directly to the vapor phase.)
Figure 3 shows the value of the minimum of μ vs T.
(At each T, the three plotted points correspond to a different isotherm in Figure 2.)

A phase transition occurs when $\Delta\mu \leq 0$.

The equals sign denotes equilibrium.

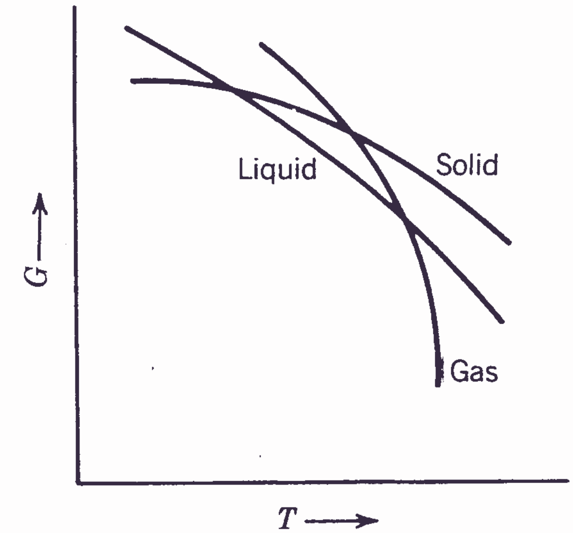


Figure 26.3 Phase transition from solid to liquid to gas.

Q. How does μ vary with P?

$$\left(\frac{\partial \mu}{\partial P}\right)_T = V_m$$

A. It follows that μ always increases with pressure.

Usually, $V_{m,solid} < V_{m,liquid}$
Always, $V_{m,liquid} < V_{m,gas}$

It follows that compressing a gas liquefies it.

Explanation: Because $V_{m,gas}$ is greater than $V_{m,liquid}$, μ_{gas} increases with pressure more than does μ_{liquid}. If P is large enough, μ_{gas} will exceed μ_{liquid}. When this happens, ΔG_m for condensation becomes negative, and the process becomes spontaneous.
Compressing a liquid usually freezes it. (Exception is ice.)

Lecture 27. "Topography" of a phase transition: the phase diagram.

The phase diagram is a map showing the regions of T and P (or any other suitable pair of intensive variables) where different phases are the most stable. The boundaries between "countries" denote equilibrium between phases.

We will prove later that for a single component system, no more than three phases can be in equilibrium.

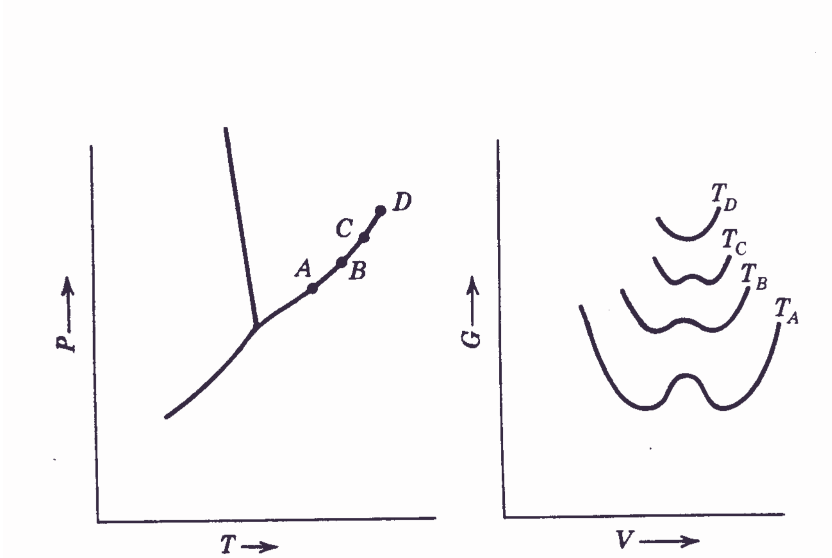


Figure 27.1 A "typical" phase diagram.

Note the boundaries of co-existence of two phases,
The triple point of co-existence of three phases, and the critical point where two phases merge into one.

Along curve ABCD, the liquid and vapor are in equilibrium, but the barrier falls until the two phases merge at the critical point, D.

We can think of this map in two different, but equivalent ways.

1. Graph of vapor pressure vs. temperature.

2. Graph of boiling temperature vs pressure.

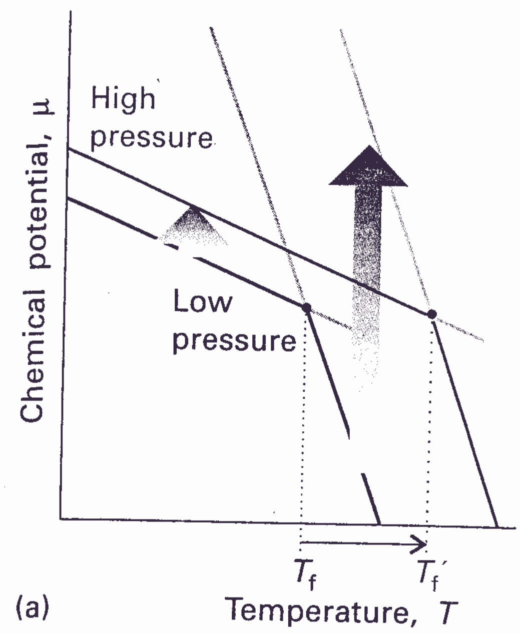
Slopes of the boundaries on a phase diagram

The boundary between a gas and a condensed phase:

1. S is always positive $\Rightarrow \mu$ vs T always has a negative slope.

2. $S_{m,gas} > S_{m,condensed} \Rightarrow$ the slope of μ vs T is always steeper for the gas.

3. $V_{m,gas} > V_{m,condensed} \Rightarrow$ the temperature of vaporization always increases with pressure, giving a positive slope of P vs T.



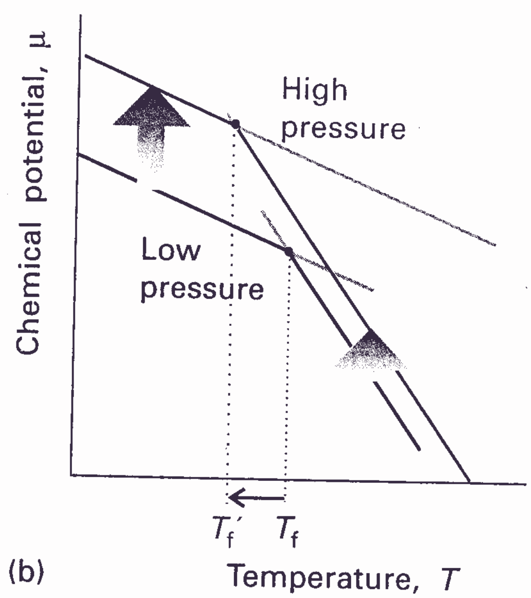


Figure 27.2

(a) $V_{m,condensed} < V_{m,gas}$

The figure also applies for $V_{m,solid} < V_{m,liquid}$

The result is that the transition temperature increases with P, making the phase boundary slope to the right.

(b) $V_{m,solid} < V_{m,liquid}$

The result is that the transition temperature decreases with P, making the phase boundary slope to the left.

The boundary between a gas and a condensed phase:

Points 1 and 2 still hold.

3'. $V_{m,liquid}$ is usually greater $V_{m,solid}$ ⇒ the temperature of melting usually increases with pressure, giving a positive slope of P vs T. But is
But, if $V_{m,liquid}$ is less than $V_{m,solid}$ (as for water), the P-T slope will be negative.

Lecture 28. Quantitative properties of a phase diagram

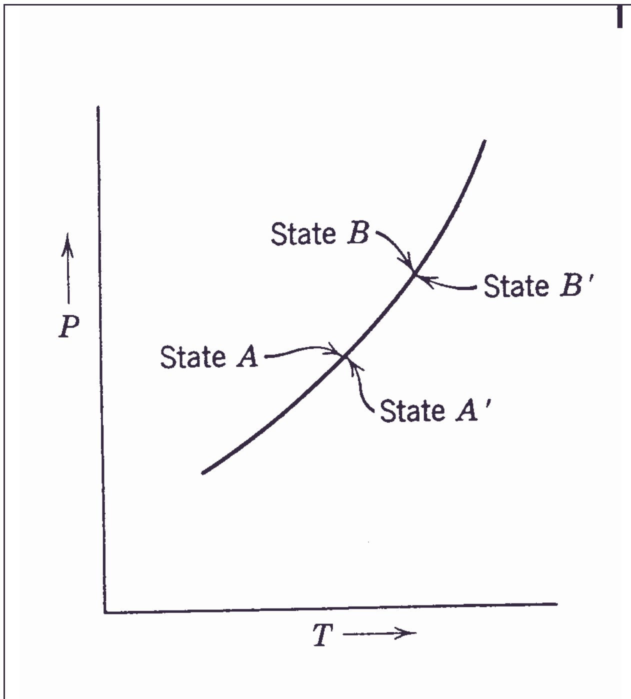


Figure 28.1
At any two points of equilibrium, A and B, on the boundary curve,

$$\mu_A = \mu'_A$$

$$\mu_B = \mu'_B$$

$$\therefore \mu'_B - \mu'_A = \mu_B - \mu_A$$

But

$$\mu_B - \mu_A = -S_m dT + V_m dP$$

$$\mu'_B - \mu'_A = -S'_m dT + V'_m dP$$

$$\therefore -S_m dT + V_m dP = -S'_m dT + V'_m dP$$

The Clapeyron Equation:

$$\frac{dP}{dT} = \frac{S'_m - S_m}{V'_m - V_m} = \frac{\Delta S_{m,vap}}{\Delta V_{m,vap}} = \frac{\Delta H_{m,vap}}{T\Delta V_{m,vap}}$$

Boundary between a gas and a condensed phase:

$$\Delta S_m > 0, \ \Delta V_m > 0$$

P-T slope is therefore positive.

$$\Delta V_m \cong V_{m,gas} = ZRT/P$$

$$\frac{dP}{dT} = \frac{\Delta H_m}{T(ZRT/P)}$$

$$\frac{dP}{P} = \frac{\Delta H_m}{ZR}\frac{dT}{T^2}$$

$$\frac{d\ln P}{d(1/T)} = -\frac{\Delta H_m}{ZR}$$

Slope of ln P vs 1/T gives $-\Delta H_m/Z$.

For constant ΔH_m and Z=1, we get the Clapeyron-Clasusius equation:

$$\ln\left(\frac{P_2}{P_1}\right) = -\frac{\Delta H_m}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

$$P \propto \exp\left(-\frac{\Delta H_m}{RT}\right)$$

If we choose T_1 to be the boiling point at P_1 = 1 atm, then

$$P = e^{\frac{\Delta H_m}{RT_{bp}}} e^{\frac{-\Delta H_m}{RT}}$$

Note: $\Delta H_{sub} = \Delta H_{fus} + \Delta H_{vap}$

The solid-liquid boundary:

$$S_{m,liquid} > S_{m,solid}$$

If $V_{m,liquid} > V_{m,solid}$, the P-T slope is positive.

If $V_{m,liquid} < V_{m,solid}$, the P-T slope is negative.

Treating both ΔH_m and ΔV_m as constant,

$$\int_{P_1}^{P_2} dP = \frac{\Delta H_m}{\Delta V_m} \int_{T_1}^{T_2} \frac{dT}{T}$$

$$P_2 - P_1 = \frac{\Delta H_m}{\Delta V_m} \ln \frac{T_2}{T_1}$$

Problem: A sled is equipped with two runners 1.5 m long and 4 mm wide. What is the minimum weight of the sled (plus cargo) if it is to run on a liquid layer above the ice at -4^0?

Answer:

$$\frac{dP}{dT} = \frac{\Delta S_m}{\Delta V_m}$$

$$\Delta P = \frac{\Delta S_m}{\Delta V_m} \Delta T$$

But we also know that $\Delta P = mg/A$, where A is the contact area of the runners.

Problem: The boiling point of water on the top of a certain mountain is 90^0 C. How tall is the mountain?
(Assume T=280 K at the mountain top and a molar mass of 28 for air.)

Answer: First calculate the vapor pressure of water at the mountain top.

$$P = \exp\left(-\frac{40,700}{8.31452}\left(\frac{1}{363.15}-\frac{1}{373.15}\right)\right) = 0.697\,atm$$

Next, use the barometric formula,

$$P = e^{-Mgh/RT}$$

$$h = \frac{\Delta H_{vap}}{Mg}\left(\frac{T}{T_{bp}}-\frac{T}{T_{bp}^{0}}\right) = 3.06\,km$$

How can we calculate the temperature and pressure of a phase transition, given only the equation of state?

We have a stability criterion that tells us that certain conditions are unstable:

$$\kappa_T = -\left(\frac{\partial P}{\partial V_m}\right)_T > 0$$

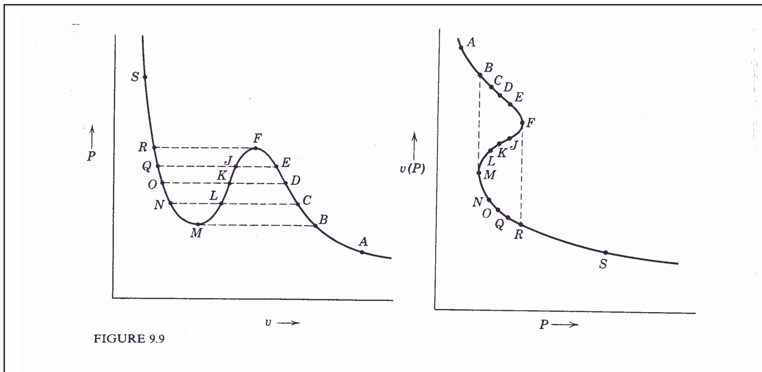


Figure 28.2 Van der Waals Eq. of state and its inverse. Note that the inverse is multi-valued.

The unstable region is between F and M. Where exactly does the phase transition occur? What is the value of V_m?

We calculate μ(V_m) for a fixed T, using point A as a reference:

$$\mu_B = \mu_A + \int_{P_A}^{P_B} V_m(P)dP$$

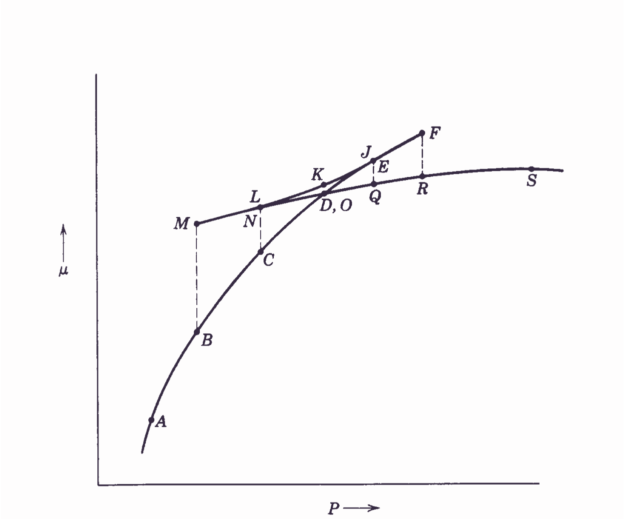


Figure 28.3 Calculation of the chemical potential for a van der Waals gas.

We find that μ(p) increases between P_A and P_F, decreases from P_F to P_M, and then increases again. The equilibrium state is always on the lowermost branch of μ(P). The phase transition occurs at points D → O, where $P_D = P_O$ and Vm has a discontinuity.

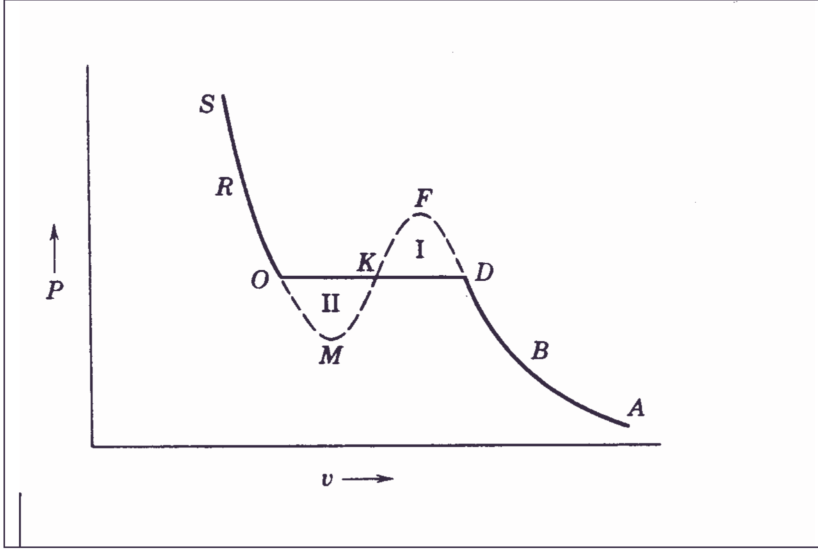


Figure 28.4 The phase transition occurs along line DKO, with areas I and II equal. Point D is a vapor, and point O is a liquid. Point K doesn't actually exist.

What is the value of the transition pressure?

$$\mu(P_O) = \mu(P_D)$$

$$\oint_{D\to O} V_m(p)dP = 0$$

$$\int_{P_D}^{P_F} V_m(P)dP + \int_{P_F}^{P_K} V_m(P)dP + \int_{P_K}^{P_M} V_m(P)dP + \int_{P_M}^{P_O} V_m(P)dP = 0$$

$$\int_{P_D}^{P_F} V_m(P)dP - \int_{P_K}^{P_F} V_m(P)dP = \int_{P_M}^{P_K} V_m(P)dP - \int_{P_M}^{P_O} V_m(P)dP = 0$$

This equation shows that the two areas are equal.

The Lever Rule

The points along the “tie line” OKD exist only in an average sense.

$$\langle V_m \rangle = x_D V_{m,D} + x_O V_{m,O}$$

x_D = mole fraction of the vapor = x_{liq}
x_O = mole fraction of the liquid = x_{vap}

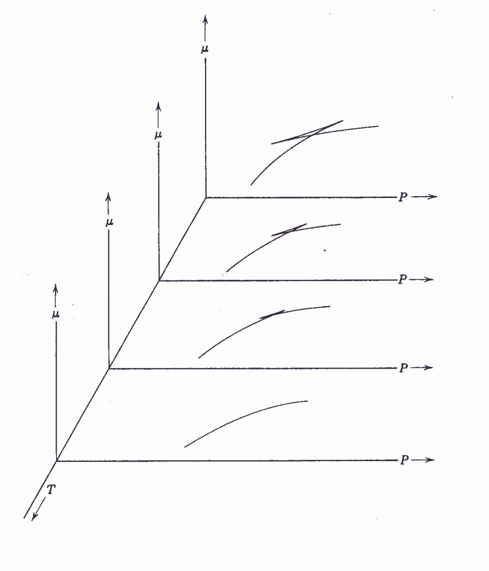
$$(x_{liq} + x_{vap}) \langle V_m \rangle = x_{liq} V_{m,liq} + x_{vap} V_{m,vap}$$

$$x_{liq}\left[\langle V_m \rangle - V_{m,liq}\right] = x_{vap}\left[V_{m,vap} - \langle V_m \rangle\right]$$

$$\frac{x_{liq}}{x_{vap}} = \frac{V_{m,vap} - \langle V_m \rangle}{\langle V_m \rangle - V_{m,liq}}$$

$$x_{liq} + x_{vap} = 1$$

V_m is discontinuous; $\langle V_m \rangle$ is continuous.

	*Figure 28.5* Temperature dependence of the phase transition. The lowermost curve corresponds to the triple point.

Lecture 29. Phase diagrams: A quantitative example; external pressure and surface tension

The following are the physical properties of benzene, collected from various tables.

Boiling point = T_{bp} = 80.1 C = 353.25 K

Melting point = T_{mp} = 5.5 C = 278.65 K

Density of liquid = ρ_{liq} = 0.879 g/cm^3
Density of solid = ρ_{sol} = 0.891 g/cm^3

Triple point: T_t = 5.50 C = 278.65 K
P_t = 36 Torr = 4800 Pa

Critical Point: T_c = 562.7 K
P_c = 48.6 atm
$V_{m,c}$ = 260 cm^3/mol
$Z_c = P_cV_{m,c}/RT_c$ = 0.274

$\Delta H_{m,fus}$ = 10,600 J
$\Delta H_{m,vap}$ = 30,800 J

Surface tension = γ = 28.88 mN/m

Let's sketch out the phase diagram.

$V_{m,liq}$ = 78/0.879 cm^3/mol = 8.874 x 10^{-5} m^3/mol

$V_{m,sol}$ = 78/0.891 cm^3/mol = 8.754 x 10^{-5} m^3/mol

ΔV_m = 1.195 x 10^{-6} m^3/mol

Equation of solid-liquid boundary:

$$\frac{dP}{dT} = \frac{\Delta S_{m,fus}}{\Delta V_m} = \frac{\Delta H_{m,fus}}{T\Delta V_m} = \frac{8.91x10^9}{T} \text{ pa K}^{-1}$$

$$P - P_t = 8.91x10^9 \ln\frac{T}{T_t}$$

e.g., T=6.0 C = 279.15 K ⇒ P = 1.6 x 10^7 Pa = 157 atm

Solid-vapor boundary:

$$\ln\frac{P}{P_t} = \frac{\Delta H_{m,sub}}{R}\left(\frac{1}{T_t} - \frac{1}{T}\right)$$

$\Delta H_{m,sub} = \Delta H_{m,fus} + \Delta H_{m,vap}$ = 41,400 J

$$\ln\frac{P}{P_t} = 17.8692 - 4{,}979/T$$

e.g., T = 5.0 C = 278.15 K ⇒ P = 0.9684 P_t = 34.86 Torr

Liquid-vapor boundary:

$$\ln\frac{P}{P_t} = \frac{\Delta H_{m,vap}}{R}\left(\frac{1}{T_t} - \frac{1}{T}\right) = 13.31656 - 3704/T$$

e.g., T = 6.0 C = 279.15 K ⇒ P = 1.0241 P_t = 36.87 Torr

Estimate of the normal boiling point:

Set P = 760 Torr and solve for T: Find $T_{bp} \cong 361.6$ K

Question: What is the effect of external pressure on the vapor pressure?

Answer: At equilibrium, $\mu_{liq} = \mu_{vap}$. At constant T,

$$d\mu_{vap} = V_{m,vap}dP_{vap} = \frac{RTdP_{vap}}{P_{vap}}$$

$$d\mu_{liq} = V_{m,liq}dP_{liq} = V_{m,liq}dP_{ext}$$

$$RT\ln\frac{P_{vap}}{P_{vap}^*} = V_{m,liq}\Delta P_{ext}$$

$$P = P^* e^{\frac{V_{m,liq}\Delta P_{ext}}{RT}}$$

P^* is the vapor pressure of the liquid without any external pressure.

Example: What is the vapor pressure of benzene in an atmosphere of 100 atm of helium at its normal melting point?

$$\ln\frac{P_{vap}}{P_{vap}^*} = \frac{V_{m,liq}P_{ext}}{RT} = \frac{8.874x10^{-5}x1.01375x10^7}{8.31451x278.65} = 0.4227$$

$P_{vap} = 54.94$ Torr

Surface Tension

In order to lower its energy, a liquid spontaneously alters its shape so as to maximize the number of molecules in the condensed phase.

The work done do distort the surface area, σ, at constant volume and temperature, is given by

$$dw = \gamma d\sigma$$

γ is the surface tension, having units of $J/m^2 = N/m$

dW is the change in Helmholtz free energy, dA.

The pressure inside a droplet increases as a result of the surface distortion from planarity.

Force inside = Force outside + Force from surface tension

$$F_{in} = F_{out} + F_{surface}$$

$$F_{in} = 4\pi r^2 P_{in}$$

$$F_{out} = 4\pi r^2 P_{out}$$

$$F_{surface} dr = w = \gamma d\sigma = \gamma d(4\pi r^2) = 8\pi\gamma r dr$$

$$F_{surface} = 8\pi\gamma r$$

$$\Delta P = P_{in} - P_{out} = 2\gamma/r$$

What is the pressure differential for a droplet of benzene with r = 0.01 mm?

$$\Delta P = 2 \text{ x } 0.02888/10^{-5} \text{ Pa} = 5776 \text{ Pa} = 43.3 \text{ Torr}$$

This pressure differential leads to an enhanced vapor pressure above a meniscus (in a capillary, for example).

$$P = P^* e^{\frac{V_{m,liq}\Delta P_{ext}}{RT}} = P^* e^{\frac{2\gamma V_{m,liq}}{rRT}}$$

In the present case, this effect is very small: P/P* = 1.0002

Lecture 31. Capillary Rise

The pressure below a meniscus is lowered by $2\gamma/r$ as compared to the external pressure.

This allows the liquid to rise in a capillary until the surface force is balanced by the hydrostatic force.

$$\rho g h = 2\gamma/r$$

$$h = 2\gamma/\rho g r$$

For a 0.5 mm radius capillary,

h = 115.5/(879 x 9.81) = 0.0134 m = 1.34 cm

Lecture 31. Partial Molar Quantities

We know from previous lectures that by definition,

$$dU = TdS - pdV + \mu dn$$

We will now derive a very remarkable result, known as the Euler relation,

$$U = TS - PV + \mu n$$

This expression stems from the fact that S, V, and n are extensive variables, and that T, P, and μ are intensive. The technical terminology is that U is a *homogeneous first order function* of S, V, and n: For any constant λ,

$$U(\lambda S, \lambda V, \lambda n) = \lambda U(S, V, n)$$

For example, doubling S, V, and n is equivalent to doubling U.

Next, differentiate both sides with respect to λ, using the chain rule,

$$\frac{\partial U(\lambda S, \lambda V, \lambda n)}{\partial(\lambda S)}\frac{\partial(\lambda S)}{\partial\lambda} + \frac{\partial U(\lambda S, \lambda V, \lambda n)}{\partial(\lambda V)}\frac{\partial(\lambda V)}{\partial\lambda} + \frac{\partial U(\lambda S, \lambda V, \lambda n)}{\partial(\lambda n)}\frac{\partial(\lambda n)}{\partial\lambda}$$

$$= \frac{\partial U(\lambda S, \lambda V, \lambda n)}{\partial(\lambda S)}S + \frac{\partial U(\lambda S, \lambda V, \lambda n)}{\partial(\lambda V)}V + \frac{\partial U(\lambda S, \lambda V, \lambda n)}{\partial(\lambda n)}n$$

$$= U(S, V, n)$$

Next, set $\lambda=1$,

$$\frac{\partial U}{\partial S}S + \frac{\partial U}{\partial V}V + \frac{\partial U}{\partial n}n = U$$

But we recognize that the derivatives are the intensive variables.

$$T = \left(\frac{\partial U}{\partial S}\right)_{V,n}, -P = \left(\frac{\partial U}{\partial V}\right)_{S,n}, \mu = \left(\frac{\partial U}{\partial n}\right)_{V,P}$$

Therefore, $U = TS - PV + \mu n$

Next, calculate the perfect differential of U,

$$dU = TdS + SdT - PdV - VdP + \mu dn + nd\mu$$

But we also know from the First Law that

$$dU = TdS - PdV + \mu dn.$$

Subtracting, we obtain the Gibbs-Duhem relation,

$$SdT - VdP + nd\mu = 0.$$

We can easily generalize to a mixture of two (or more) substances:

$$U = TS - PV + \mu_A n_A + \mu_B n_B$$

$$dU = TdS - PdV + \mu_A dn_A + \mu_B dn_B$$

$$SdT - VdP + n_A d\mu_A + n_B d\mu_B = 0$$

At constant temperature and pressure,

$$n_A d\mu_A + n_B d\mu_B = 0$$

We can apply this method to any extensive, homogeneous first order variable. Consider the volume of a mixture of liquids,

$$V = V_A n_A + V_B n_B + \ldots$$

Where

$$V_A = \left(\frac{\partial V}{\partial n_A}\right)_{p,T,nB,n_C,\ldots}$$

$$V_B = \left(\frac{\partial V}{\partial n_B}\right)_{p,T,n_A,n_C,\ldots}$$

V_A is the increase in the total volume when a small amount dn_A of substance A is added to the solution.

The Gibbs-Duhem relation for a binary mixture is

$$n_A dV_A + n_B dV_B = 0$$

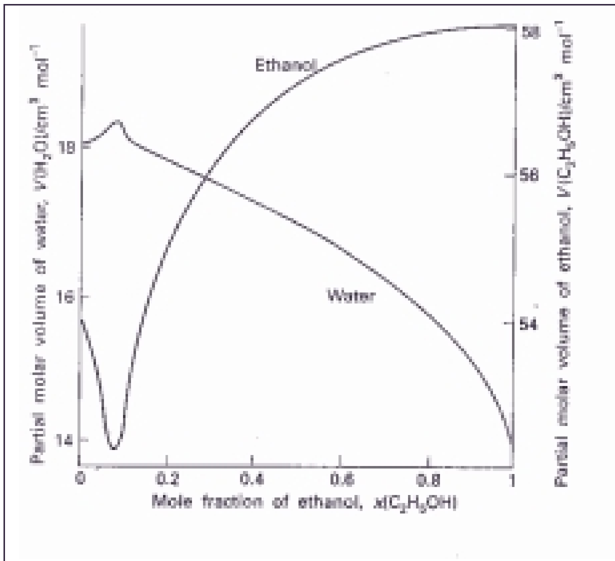
or

$$dV_B = -\frac{n_A}{n_B} dV_A$$

When one goes up the other goes down.

Lecture 32. Liquid mixtures

Example from text: ethanol, water mixture



Partial molar volumes of an ethanol, water mixture.
(Fig. 7.1 from Atkins.)

We will use the notation of M_A to designate the molecular weight of A, n_A for the number of moles of A, and m_A for the mass of A, so that

$$m_A = n_A M_A,$$

and

$$R = m_A/m_B$$

Molar volumes for pure liquids: $V_{m,A} = M_A/\rho_A$

$$V_{m,W} = V_W(x_E = 0) = 18 \text{ cm}^3\text{/mol}$$

$$V_{m,E} = V_E(x_E = 1) = 58 \text{ cm}^3\text{/mol}$$

(Note: Fig. 7.1 is inconsistent with the tabulated value of ρ_E, which gives a value of 58.4.)

Partial molar volumes for a solute added to a pure solvent:

$$V_W(x_E = 1) = 14\ cm^3/mol$$

$$V_E(x_E = 0) = 54\ cm^3/mol$$

Partial molar volumes for a 50% mixture:

$$V_W(x_E = 0.5) = 17\ cm^3\ /mol$$

$$V_E(x_E = 0.5) = 57\ cm^3/mol$$

Example: What is the volume of a mixture of one liter of ethanol and one liter of water?

1 L water = 1000 gm = 55.51 moles
1 L ethanol = 1000x0.789 gm = 17.13 moles
mole fraction of ethanol = x_E = 17.13/72.64 = 0.236

From the figure, V_W = 0.0175 L, V_E = 0.0560 L ⇒

V = 0.0175(55.51) + 0.0560(17.31) = 1.94 L

Self –test problem, 7.1: Given that a 1:1 mixture (by mass) of ethanol to water has a density of 0.914 g/cm^3, if the partial molar volume of water is 17.4 cm^3/mol, find the partial molar volume of ethanol.

From the Euler relation we know that

$$V_E = (V - n_W V_W)/n_E$$

where

$$V = (m_E + m_W)/\rho$$

$$n_W = m_W/M_W,\ \ n_E = m_E/M_E$$

It follows that

$$V_E = \frac{(m_W + m_E)/\rho - m_W V_W / M_W}{m_E / M_E}$$

$$= \frac{\frac{1+m_E/m_W}{\rho} - \frac{V_W}{M_W}}{\frac{m_E}{m_W}\frac{1}{M_E}}$$

$$= \frac{(1+R)/\rho - V_W/M_W}{R/M_E}$$

Here, R = 1, ρ = 0.914, V_W = 17.4, M_W = 18.015, and M_E = 46.07 ⇒ V_E = 56.3 cm^3

Application of the Gibbs – Duhem relation

Expressing the partial molar volumes as functions of n_A and n_B, we integrate over n_1:

$$V_B(n_A,n_B) - V_{B,m} = -\int_{V_A(n_A=0)}^{V_A(n_A)} \left(\frac{n_A}{n_B}\right) dV'_A = -\int_0^{n_A} \left(\frac{n'_A}{n_B}\right)\left(\frac{\partial V_A}{\partial n'_A}\right)_{n_B} dn'_A$$

where $V_{B,m}=V_B^*$ is the volume of the pure liquid B.

Example:

$$\mathrm{V} = \mathrm{n_A V_A^*} + \mathrm{n_B V_B^*} + \tfrac{1}{2} C\sqrt{n_A n_B}$$

Doubling n_A and n_B causes V to double.

In terms of mole fractions, divide by $n_A + n_B$,

$$V_m = x_A V_{m,A} + x_B V_{B,m} + C\sqrt{x_A x_B}$$

Suppose you are given that

$$V_A = V_{A,m} + cb$$

where b is the molality of A,

$$b = \frac{n_A}{m_B} = \frac{n_A}{n_B M_B}$$

and c is a constant. Calculate V_B and V.

$$V_A = V_{A,m} + \frac{c}{M_B}\frac{n_A}{n_B}$$

$$dV_A = \frac{c}{M_B n_B} dn_A$$

$$dV_B = -\frac{cn_A}{M_B n_B^2} dn_A$$

Above is the Gibbs-Duhem eq. Integatting it gives the following:

$$V_B = V_{B,m} - \frac{cn_A^2}{2M_B n_B^2}$$

$$V = n_A V_A + n_B V_B = n_A V_{A,m} + n_B V_{B,m} + \frac{c}{2M_B}\frac{n_A^2}{n_B}$$

Vapor pressure of a liquid mixture

Suppose you have a liquid mixture of A and B, with mole fractions x_A and x_B. What is the composition of the vapor phase?

For an ideal liquid mixture,

$$P_A = x_A P_A^*$$

$$P_B = x_B P_B^*$$

This is Raoult's Law for an ideal solution.

What is the composition of the vapor?

$$y_A = \frac{P_A}{P_A + P_B} = \frac{x_A P_A^*}{x_A P_A^* + x_B P_B^*}$$

$$y_B = \frac{P_B}{P_A + P_B} = \frac{x_B P_B^*}{x_A P_A^* + x_B P_B^*}$$

Suppose that A is more volatile than B. Which phase is richer in A?

Our assumption is that $P_A^* > P_B^*$.

$$y_A = \frac{x_A}{x_A + x_B P_B^* / P_A^*} > x_A$$

(Explanation: $x_A + x_B = 1$. Here the denominator is smaller than 1.)

Conclusion: The gas phase is richer in A.

Even if a solution is non-ideal, it may still have a linear vapor pressure if it is dilute. This is called an "ideal dilute solution," which satisfies Henry's Law.
If A is the solvent and B the solute

$$P_B = x_B K_B.$$

An ideal liquid solution is not one in which the molecules do not interact. Rather, it is a mixture in which the interactions of all species are the same (both like and unlike).

Lecture 33. The Chemical Potential of Liquids

The shower problem: What happens when you step out of the shower (aside from the fact that the phone rings)?

Evaporating water removes heat and makes you feel cold. Let's calculate how much heat is removed, and determine whether the process occurs spontaneously.

Suppose that room temperature is 298 K, and that one mole of water evaporates. (Probably 0.1 mole is more realistic.) Because the process is irreversible, we need to find some other path to calculate changes. (It would have better to assume that all the temperatures are the same a your body temperature, but we will ignore this detail.)

What is $\Delta H_{vap}(H_2O, 298\ K)$? Construct a cycle:

$$\begin{array}{ccc} H_2O(liq, 298\ K) & \xrightarrow{1} & H_2O(gas, 298\ K) \\ \downarrow 2 & & \uparrow 4 \\ H_2O(liq, 373\ K) & \xrightarrow[3]{} & H_2O(gas, 373\ K) \end{array}$$

$\Delta H_1 = \Delta H_2 + \Delta H_3 + \Delta H_4$

$\Delta H_{2,m} = C_{P,m}(H_2O, liq) \times (373\text{-}298) = 5.647$ kJ/mol

$\Delta H_{3,m} = \Delta H_{vap,m}(H_2O, 373\ K) = 40.656$ kJ/mol

$\Delta H_{4,m} = -C_{P,m}(H_2O, gas) \times (373\text{-}298) = -2.519$ kJ/mol

$\therefore \Delta H_{vap,m}(H_2O, 298\ K) = 40.656 + 3.126 = 43.784$ kJ/mol

(Table 2.3 lists 44.016 kJ/mol. Why?)

This heat of vaporization that is absorbed by the water accounts for your feeling cold.

Now let's calculate the entropy changes.

$\Delta S_{298,m} = \Delta S_2 + \Delta S_3 + \Delta S_4$

$\Delta S_{2,m} = C_{P,m}(H_2O, liq)\ \mathit{ln}\ (373/298) = 16.90\ J\ mol^{-1}K^{-1}$

$\Delta S_{3,m} = \Delta H_{vap,m}(H_2O, 373\ K)/373 = 109.0\ J\ mol^{-1}K^{-1}$

$\Delta S_{4,m} = C_{P,m}(H_2O, gas)\ \mathit{ln}\ (298/373) = -7.54\ J\ mol^{-1}K^{-1}$

$\therefore \Delta S_{298,m} = 118.36\ J\ mol^{-1}K^{-1}$

Question: Is this process spontaneous?

Answer: Calculate $\Delta G_m = \mu = \Delta H_m - T\Delta S_m$ to find out.

At 373K, ΔG_m is clearly zero. Is it positive or negative at 298 K?

$\Delta G_{298,m} = \Delta H_{298,m} - 298\Delta S_{298,m}$
$= 43{,}784 - 298(118.36) = 8{,}513$ J/mol

Incidentally, you could have obtained nearly this result using the Gibbs-Helmholtz equation. Try it!

It is positive! What is going on?

Resolution: The above result is for P^o = 1 bar, whereas the water vapor pressure is lower. In general,

$$\Delta G_m(T,P) = \Delta G_m^o + RT \ln \frac{P}{P^o}$$

At equilibrium at 298 K,

$$\Delta G_m(298,P) = 8{,}513 + RT \ln\left(\frac{P}{P^o}\right) = 0 \Rightarrow P = 25 Torr$$

Chemical potentials of two phases

Equilibrium occurs when $\mu_{liq} = \mu_{vap}$

Strictly speaking, we should use the fugacities rather than partial pressures. We will use phase A for illustration:

$$\mu_{A,liq} = \mu_{A,gas} = \mu_{A,gas}^o + RT \ln\left(\frac{f_{A,gas}}{f_{A,gas}^o}\right)$$

where "o" refers to a fugacity of 1bar.

For Henry's Law, $f_{A,gas} = K_A x_A$.

For Raoult's Law, $f_{A,gas} = P_A^* x_A$, where the * refers to the vapor pressure of the pure liquid.

Theorem: If the solute obeys Henry's law, the solvent obey's Raoult's Law.

We will prove it using the Gibbs-Duhem relation for μ:

$$n_A d\mu_A + n_B d\mu_B = 0$$

Divide through by $n = n_A + n_B$,

$$x_A d\mu_A + x_B d\mu_B = 0$$

$$x_A\left(\frac{\partial \mu_A}{\partial x_A}\right)_{P,T} + x_B\left(\frac{\partial \mu_B}{\partial x_A}\right)_{P,T} = 0$$

But $dx_A = -dx_B$ for a binary mixture. Therefore,

$$x_A\left(\frac{\partial \mu_A}{\partial x_A}\right)_{P,T} - x_B\left(\frac{\partial \mu_B}{\partial x_B}\right)_{P,T} = 0$$

$$\left(\frac{\partial \mu_A}{\partial \ln X_A}\right)_{P,T} = \left(\frac{\partial \mu_B}{\partial \ln X_B}\right)_{P,T}$$

Let A be the solvent and B the solute.

From Henry's Law, $\left(\frac{\partial \mu_B}{\partial \ln x_B}\right)_{P,T} = RT$

Therefore, for the solvent $\left(\frac{\partial \mu_A}{\partial \ln x_A}\right)_{P,T} = RT$

Integrating, $\mu_A = RT \ln x_A + C$

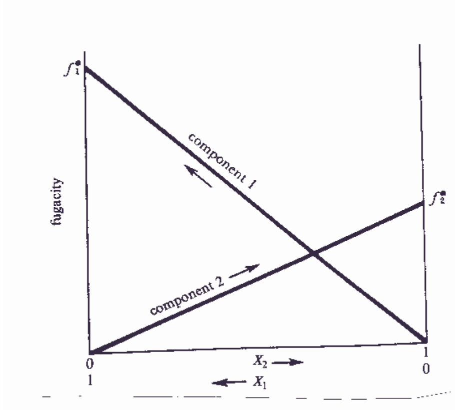
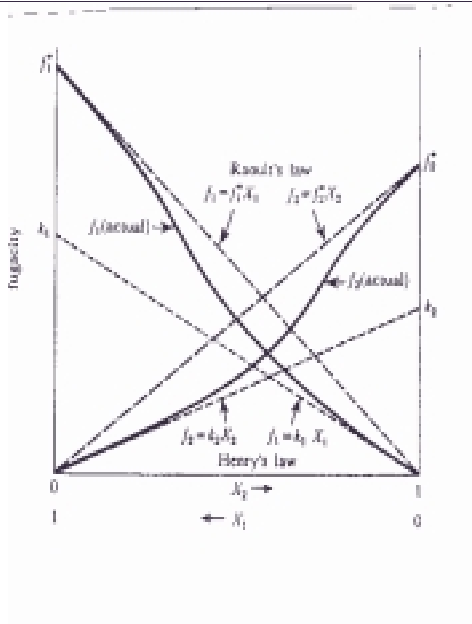
This result is valid in the limits of $x_B \rightarrow 0$, $x_A \rightarrow 1$.

Therefore, $C = \mu_A^*$, giving Raoult's Law.

The gas phase composition is therefore

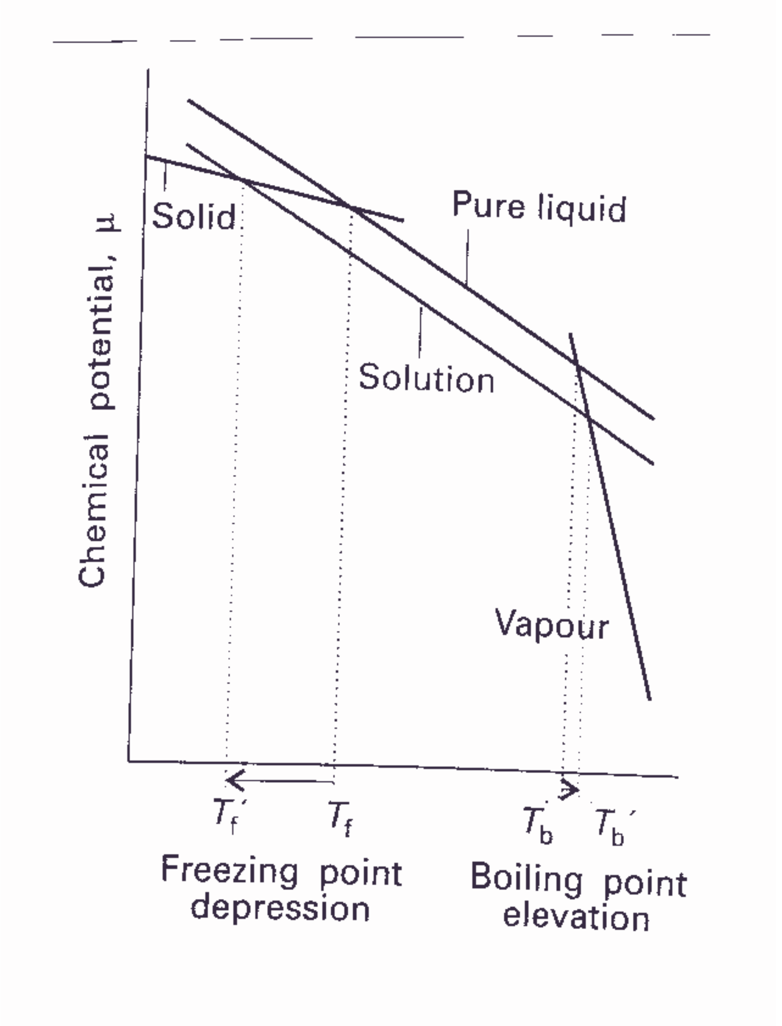
$$y_A = \frac{x_A P_A^*}{x_A P_A^* + K_B P_B^*}$$

$$y_B = \frac{K_B P_B^*}{x_A P_A^* + K_B P_B^*}$$

		Liquid Solutions. Left: Ideal mixture illustrating Raoult's Law. Right: Non ideal mixture, showing ideal dilute behavior.

Lecture 34. Colligative Effects

Suppose component B is totally non-volatile. Also, suppose that it remains behind in the liquid phase when the solvent freezes. Then its only effect is to lower μ_A(liq). The net result is to lower the freezing point and raise the boiling point of A. The phenomenon is conceptually related to vapor pressure elevation by an external pressure.



Colligative effects:
Boiling point elevation and freezing point depression.

The key concept is that the chemical potential of the solvent, A, equals that of the vapor, which is pure A.

$$\mu_A(liq) = \mu_A^*(liq) + RT\ln x_A = \mu_A(vap)$$

The text shows directly that the boiling point is elevated by an amount

$$\Delta T_b = \frac{RT_b^2}{\Delta H_{vap,A,m}}$$

The same reasoning holds for freezing. The chemical potential of the solid, which is assumed to be pure A, equals that of the solvent:

$$\mu_A(liq) = \mu_A^*(liq) + RT \ln x_A = \mu_A(solid)$$

The freezing point is depressed by an amount

$$\Delta T_f = \frac{RT_f^2}{\Delta H_{A,\,fus,m}}$$

In both cases, ΔT is independent of the properties of the solute.

Suppose the solvent does not freeze, but instead the solute, B, precipitates. Then the same reasoning gives

$$\mu_B(solution) = \mu_B^*(liq) + RT \ln x_B = \mu_B(solid)$$

We can use this relation to calculate the solubility of B:

$$\ln x_B = -\frac{\Delta H_{B,\,fus,m}}{R}\left(\frac{1}{T} - \frac{1}{T_f}\right)$$

This is analogous to saying that a liquid-vapor phase diagram may be viewed as either a boiling point curve or a vapor pressure curve.

Lecture 35. Entropy and Energy of Mixing

Microscopic approach: S = k lnW, where W is the number of equivalent configurations.

Suppose you have a crystal with N sites, and you wish to fill it with N_A atoms of type A and N_B atoms of type B, with $N = N_A + N_B$. Assume that the interaction energies AA, BB, and AB are equivalent. What is the entropy of the crystal?

Assume that the A atoms are indistinguishable, as are the B atoms. The atoms can be permuted among the N sites N! different ways, but of these $N_A!$ permutations of A and $N_B!$ permutations of B are indistinguishable. Therefore

$$W = \frac{N!}{N_A!\,N_B!}$$

Assume that $N_A, N_B >> 1$

Sterling approximation: $\ln N! \approx N\ln - N$

$$S/k \approx N\ln N - N - N_A \ln N_A + N_A - N_B \ln N_B + N_B$$
$$= (N_A + N_B)\ln N - N_A \ln N_A - N_B \ln N_B$$
$$= N_A(\ln N - \ln N_A) + N_B(\ln N - \ln N_B)$$

$$\Delta S_{mixing} = -kN_A \ln \frac{N_A}{N_A + N_B} - kN_B \ln \frac{N_B}{N_A + N_B}$$

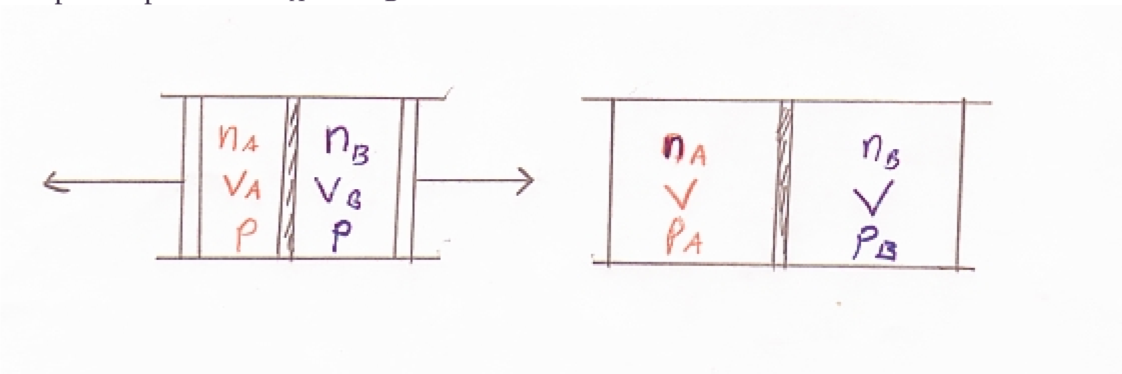
$$= -kN_A \ln x_A - kN_B \ln x_B > 0$$

Number of moles = $(N_A + N_B)/N_{avog} = n_A + n_B = n$

$$\Delta S_{mixing,m} = -Rx_A \ln x_A - Rx_B \ln x_B$$

Macroscopic approach: Suppose you have two ideal gases, $\{n_A, V_A\ P, T\}$ and $\{n_B, V_B\ P, T\}$. Mix them irreversibly to the final equilibrium condition, $\{n_A, n_B, V, P, T\}$. Calculate the entropy change using a reversible path.

Step 1. Expand each gas separately, reversibly, and isothermally to a final volume, V, and partial pressures P_A and P_B:



$P_A = n_ART/V$

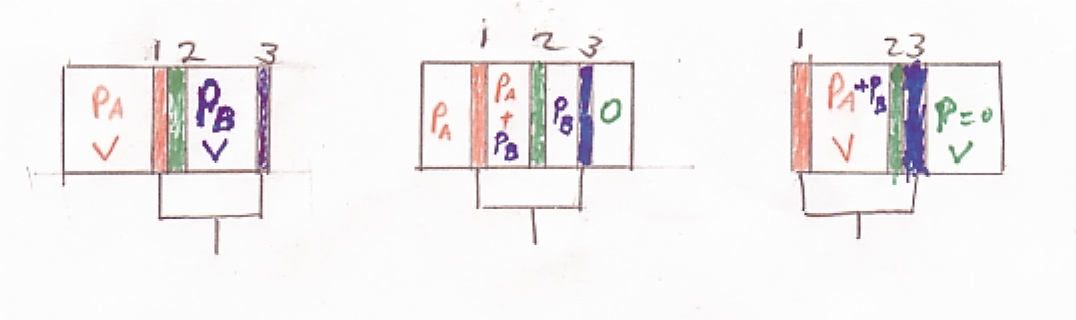
$P_B = n_BRT/V$

$P = P_A + P_B$

$V = V_A + V_B$

$$\Delta S_1 = n_A R \ln \frac{V}{V_A} + n_B R \ln \frac{V}{V_B}$$

Step 2. Mix the gases reversibly, while maintaining a total volume V.



Membrane 1 is permeable only to A. The partial pressure P_A is the same on both sides of the membrane.

Membrane 2 is permeable only to B. The partial pressure P_B is the same on both sides of the membrane.

Membrane 3 is impermeable to both A and B.

Membranes 1 and 3 are connected by a movable piston having area $\mathcal{A}$. Membrane 2 is stationary.

The force pushing the piston to the right equals
$P_A \cdot \mathcal{A} + P_B \cdot \mathcal{A}$.

The force pushing the piston to the left equals
$(P_A + P_B) \cdot \mathcal{A}$.

Net force on the piston is zero ⇒ w = 0.

$\Delta U = 0$ because T is constant.

The process is reversible. $\therefore q_{rev} = 0 \Rightarrow \Delta S_2 = 0$

$$\therefore \Delta S_{mixing} = \Delta S_1 = n_A R \ln \frac{V}{V_A} + n_B R \ln \frac{V}{V_B}$$

$$\therefore \Delta S_{mixing} = -n_A R \ln x_A - n_B R \ln x_B$$

$$\therefore \Delta S_{mixing,m} = -x_A R \ln x_A - x_B R \ln x_B$$

General result:

$$\Delta S_{mixing,m} = -R\sum_i x_i \ln x_i$$

The entropy of a mixture of perfect gases is the sum of the entropies that each pure gas would have if it occupied the same volume as the mixture at the same temperature.

What is the energy of mixing?

Consider the case of an ideal gas.

$$\left(\frac{\partial \Delta G_{mixing}}{\partial T}\right)_{P,n_A,n_B} = -\Delta S_{mixing}$$

$$\Delta G_{mixing}(T) = \Delta G_{mixing}(T=0) - \int_0^T \Delta S_{mixing}(T')dT'$$

But we proved that for an ideal gas, ΔS_{mixing} is independent of temperature.

$$\therefore \ \Delta G_{mixing} = -T\Delta S_{mixing}$$

Your textbook attacks the problem in the opposite direction. First it solves for ΔG_{mixing} and then determines ΔS_{mixing}.

Before mixing, the chemical potential is just the sum for the pure materials:

$$G_{unmixed} = n_A\mu_A + n_B\mu_B$$

$$= n_A\left\{\mu_A^o + RT\ln\left(\frac{P}{P^o}\right)\right\} + n_B\left\{\mu_B^o + RT\ln\left(\frac{P}{P^o}\right)\right\}$$

After mixing, the partial pressures have dropped to P_A and P_B:

$$G_{mixed} = n_A\left\{\mu_A^o + RT\ln\left(\frac{P_A}{P^o}\right)\right\} + n_B\left\{\mu_B^o + RT\ln\left(\frac{P_B}{P^o}\right)\right\}$$

(Note the typo in the book.)

The free energy of mixing is the difference between these two quantities:

$$\Delta G_{mixing} = n_A RT \ln\left(\frac{P_A}{P}\right) + n_B RT \ln\left(\frac{P_B}{P}\right)$$

Assuming Dalton's Law,

$$\Delta G_{mixing} = n_A RT \ln x_A + n_B RT \ln x_B$$

$$\Delta G_{mixing,m} = x_A RT \ln x_A + x_B RT \ln x_B$$

What is the entropy of mixing?

$$\Delta S_{mixing,m} = -\left(\frac{\partial \Delta G_{mixing,m}}{\partial T}\right)_{P,n_A,n_B} = -R(x_A \ln x_A + x_B \ln x_B)$$

What is the enthalpy of mixing?

$$\Delta H = \Delta G + T\Delta S = 0$$

This result is not surprising because we assumed that the gas is ideal. What are the results for real gases?

$$G_{unmixed} = n_A \mu_A + n_B \mu_B$$
$$= n_A \left\{ \mu_A^o + RT \ln\left(\frac{f_A^*}{f^o}\right) \right\} + n_B \left\{ \mu_B^o + RT \ln\left(\frac{f_B^*}{f^o}\right) \right\}$$

$$G_{mixed} = n_A \left\{ \mu_A^o + RT \ln\left(\frac{f_A}{f^o}\right) \right\} + n_B \left\{ \mu_B^o + RT \ln\left(\frac{f_B}{f^o}\right) \right\}$$

$$\Delta G_{mixing} = n_A RT \ln\left(\frac{f_A}{f_A^*}\right) + n_B RT \ln\left(\frac{f_B}{f_B^*}\right)$$

$$\Delta G_{mixing,m} = x_A RT \ln\left(\frac{f_A}{f_A^*}\right) + x_B RT \ln\left(\frac{f_B}{f_B^*}\right)$$

Because ϕ=f/P depends on temperature, it no longer follows that $\Delta S_{mixing} = -\Delta G_{mixing}/T$ and that $\Delta H_{mixing}=0$. However, for gases it is a good approximation (the rule of Randall and Lewis) that

$$\frac{f_A}{f_A^*} \approx x_A$$

so that for gases it is still true that $\Delta H_{mixing} \approx 0.$

What is the story for solutions?

For solvent A, having vapor pressure P_A,

$$\mu_A(liq) = \mu_A^* + RT \ln\left(\frac{P_A}{P_A^*}\right) = \mu_A^* + RT \ln a_A$$

where we have defined the activity, a_A. For an ideal (Raoult) solvent, $a_A = x_A$.

For an ideal-dilute solute,

$$\mu_B(liq) = \mu_B^* + RT \ln\left(\frac{P_B}{P_B^*}\right) = \mu_B^* + RT \ln\left(\frac{K_B x_B}{P_B^*}\right)$$

$$\mu_B(liq) = \mu_B^\# + RT \ln x_B$$

where $$x_B = \frac{P_B}{K_B}$$

Finally, for a real solute,

$$\mu_B(liq) = \mu_B^{\#} + RT \ln a_B$$

where $$a_B = \frac{P_B}{K_B}$$