

## CHAPTER 14: EQUILIBRIA BETWEEN DIFFERENT PHASES

Liquid/vapor equilibrium

$$\Delta F = \Delta U - T\Delta S$$

Energy tends to hold molecules together  
Entropy favors evaporation into vapor

$N_c$  = # in condensed phase

$N_v$  = # in vapor phase

$N = N_c + N_v = \text{const}$

$$dG = (\mu_v - \mu_c) dN_v = 0$$

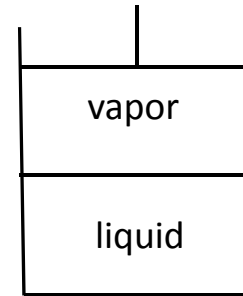
$\Rightarrow \mu_v = \mu_c$  at equilibrium

$$\mu_v = kT \ln \left( \frac{p}{p_{\text{int}}^o} \right)$$

$p_{\text{int}}^o = q_0^o kT$  -Depends on internal degrees of freedom,  
- is a constant (i.e., independent of p)

Need equation for  $\mu_c$  : adopt a lattice model

We will use such models for both liquids and solids



hold  $T, p$  constant

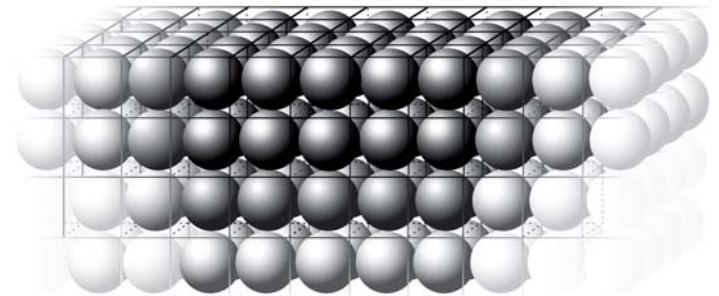


Figure 14.1 Molecular Driving Forces 2/e (© Garland Science 2011)

Lattice: one arrangement  $\Rightarrow S = 0$

$$U = \frac{Nz w_{AA}}{2}$$

$$F = U - TS = U = Nz \frac{w_{AA}}{2}$$

$$\mu_c = \left(\frac{\partial F}{\partial N}\right)_{T,V} = \frac{z w_{AA}}{2}$$

$$\mu_v = \mu_c \Rightarrow kT \ln\left(\frac{p}{p_{int}^o}\right) = \frac{z w_{AA}}{2}$$

$$p = p_{int}^o e^{z w_{AA} / 2kT}$$

$$\ln\left(\frac{p_2}{p_1}\right) = \frac{z w_{AA}}{2R} \left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

**Note:**  $p$  = applied pressure, in general  $\neq$  vapor pressure

ideal gas

$$p = \left(\frac{N}{V}\right) kT$$

$\rho$  = density

From two equations up

using results from Figure 14.4  $w_{AA} = 20.3kT / mol$  for liq. water

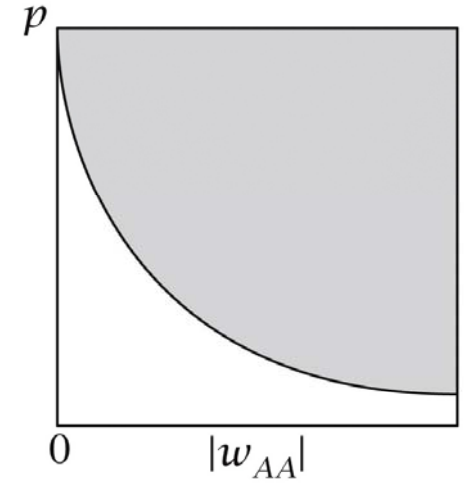


Figure 14.3 Molecular Driving Forces 2/e (© Garland Science 2011)

Remember  $w_{AA}$  is negative

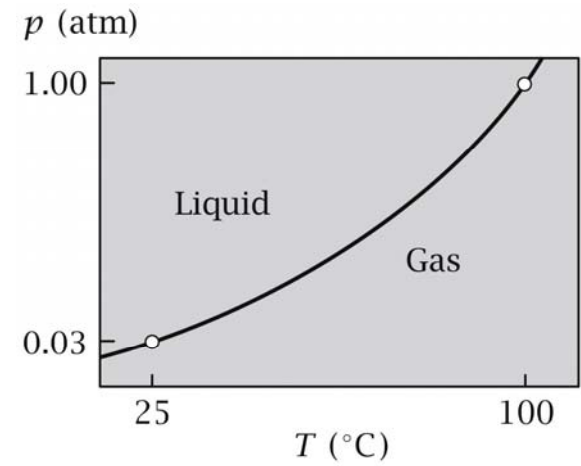


Figure 14.4 Molecular Driving Forces 2/e (© Garland Science 2011)

## Phase equilibrium

Suppose you have  $(p_1, T_1)$  and  $(p_2, T_2)$  on the equilibrium curve

$$\mu_L(T_1, p_1) = \mu_G(T_1, p_1); \quad \mu_L(T_2, p_2) = \mu_G(T_2, p_2)$$

assume chemical potential at point 2 is close to that at point 1

$$\mu_L(T_2, p_2) = \mu_L(T_1, p_1) + d\mu_L(T, p)$$

$$\mu_G(T_2, p_2) = \mu_G(T_1, p_1) + d\mu_G(T, p)$$

$$d\mu_G(T, p) = d\mu_L(T, p)$$

$$d\mu(T, p) = \left( \frac{\partial \mu}{\partial T} \right)_{p,N} dT + \left( \frac{\partial \mu}{\partial p} \right)_{T,N} dp$$

$\uparrow$   
 $-s$

$\uparrow$   
 $v$

using molar quantities

We also know that we can write  $d\mu$  in terms of the partial derivatives

$$d\mu_G = -s_G dT + v_G dp = d\mu_L = -s_L dT + v_L dp$$

$$\frac{dp}{dT} = \frac{s_G - s_L}{v_G - v_L} = \frac{\Delta s}{\Delta v}$$

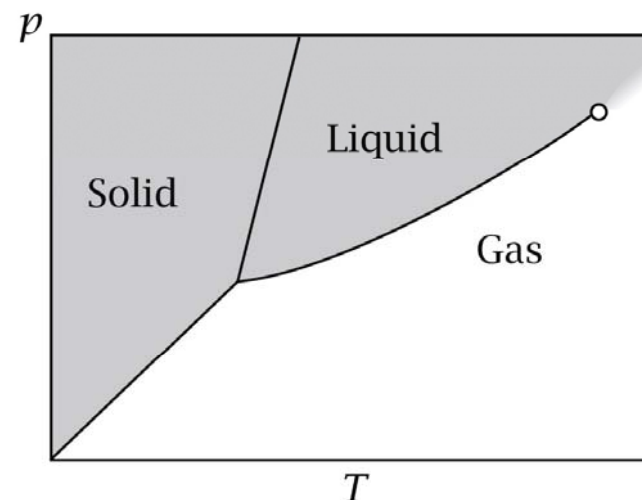


Figure 14.5 Molecular Driving Forces 2/e (© Garland Science 2011)

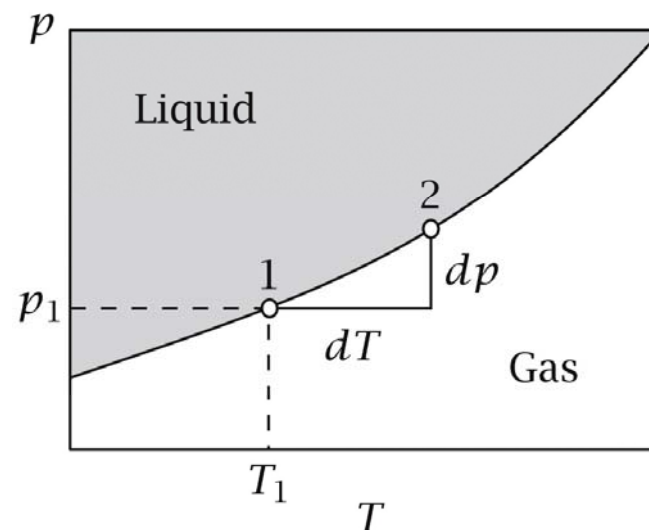


Figure 14.6 Molecular Driving Forces 2/e (© Garland Science 2011)

at the phase transition:  $\Delta\mu = \Delta h - T\Delta s = 0$

$$\frac{dp}{dT} = \frac{\Delta h}{T\Delta v} \quad \left| \quad \text{Clapeyron Equation} \right.$$

$\Delta v = v_G - v_C \approx v_G = RT / p$  for ideal gas

$$\frac{d \ln(p)}{dT} = \frac{\Delta h}{RT^2} \quad \left| \quad d \ln(p) = \frac{dp}{p} \right.$$

Clausius-Clapeyron  
Equation

$$\int_{p_1}^{p_2} d \ln(p) = \frac{\Delta h}{R} \int_{T_1}^{T_2} \frac{dT}{T^2} \quad \left| \quad \text{assumes } \Delta h \text{ is independent of } T, p \right.$$
$$\ln(p_2 / p_1) = -\frac{\Delta h}{R} \left( \frac{1}{T_2} - \frac{1}{T_1} \right)$$

Boiling point of water at high altitudes (Ex. 14.2)

$$\frac{1}{T_2} = \frac{1}{T_1} - \frac{R}{\Delta h_{\text{vap}}} \ln\left(\frac{p_2}{p_1}\right)$$

boils at  $T_1 = 373\text{K}$ ,  $p_1 = 1\text{atm}$

$$p_2 = 0.5\text{atm} \rightarrow T_2 = 354\text{K} (81^\circ\text{C})$$

$$\frac{dp}{dT} = \frac{\Delta s}{\Delta v}$$

If  $dp/dT$  is +,

the phase with the greater entropy has the greater volume

$\Rightarrow$  vapor has greater  $S$  than liquids

Also, in general, liquid has  $>$  volume than solid

For  $H_2O$  solid-liquid phase boundary  $dp/dT$  is negative

$\Rightarrow$  liquid water has smaller volume per molecule than ice

$\Rightarrow$  ice floats on liquid  $H_2O$

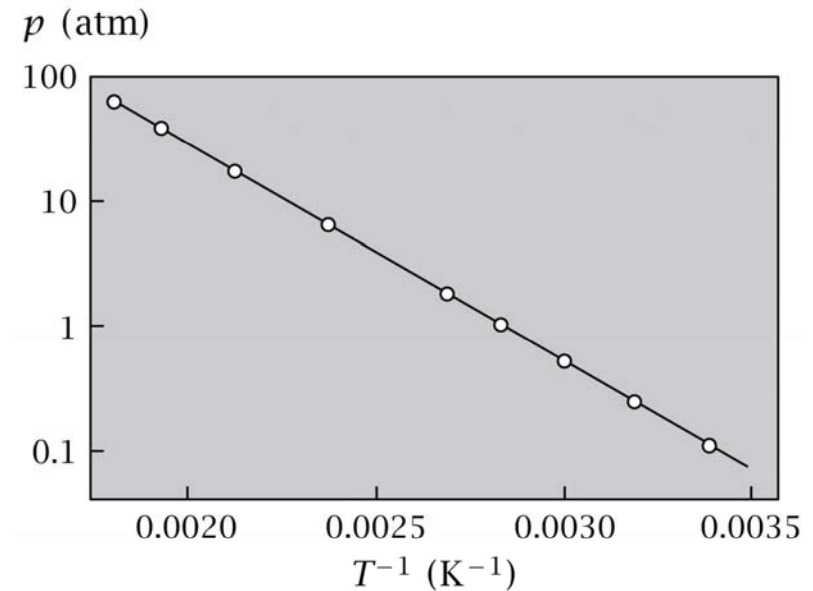


Figure 14.7 Molecular Driving Forces 2/e (© Garland Science 2011)

$$\left[ \begin{array}{l} kT \left( \frac{p}{p_{\text{int}}^0} \right) = \frac{zW_{AA}}{2} \\ \ell n \left( \frac{p_2}{p_1} \right) = -\frac{\Delta h}{R} \left( \frac{1}{T_2} - \frac{1}{T_1} \right) \end{array} \right. \quad \left. \begin{array}{l} \ell n \left( \frac{p_1}{p_{\text{int}}^0} \right) = \frac{zW_{AA}}{2kT_1} \\ \ell n \left( \frac{p_2}{p_{\text{int}}^0} \right) = \frac{zW_{AA}}{2kT_2} \\ \Rightarrow \ell n \left( \frac{p_2}{p_1} \right) = \frac{zW_{AA}}{2k} \left( \frac{1}{T_2} - \frac{1}{T_1} \right) \end{array} \right.$$

$$\Rightarrow \Delta h_{\text{vap}} = \frac{-zW_{AA}}{2}$$

To vaporize a liquid one has to break bonds

Cavities

to remove one particle:

$$\Delta U_{\text{remove}} = -zW_{AA}$$

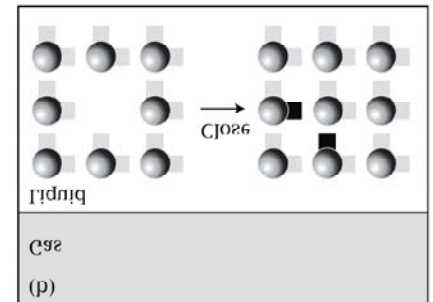
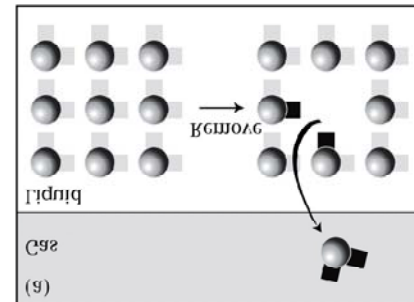
$$\Delta U_{\text{close}} = zW_{AA} / 2$$

$$\Delta U_{\text{remove} + \text{close}} = -zW_{AA} / 2$$

when a molecule evaporates from the liquid,  
does it leave from the surface or the interior?

Does not matter as  $\mu$  is the same in both cases.

Figure 14.8 Molecular models of evaporation from the surface and from the interior of a liquid.



## Surface tension



sphere – smallest ratio of surface to volume



increase surface relative to volume

sphere

take  $r = 1$ ,

$$vol = \frac{4}{3}\pi \sim 4$$

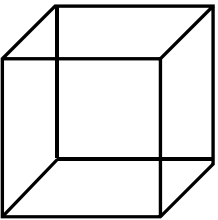
$$area/vol \sim 3$$

$$area = 4\pi \sim 12$$

cube: side = 1  $\Rightarrow$  volume = 1

$$area = 6 \times 1$$

$$area/vol = 6$$



Another look at refrigerators and heat pumps.

- (1) boiling breaks bonds  $\rightarrow$  energy becomes  $KE$
- (2) condense – get that energy back

liquid, low  $p$

absorbs heat from inside fridge (cools)

boils,  $>H$

condenses to liquid  $\rightarrow$  releases heat to surroundings ( $<H$ )

reduce  $p$  of liquid (*via* expansion)

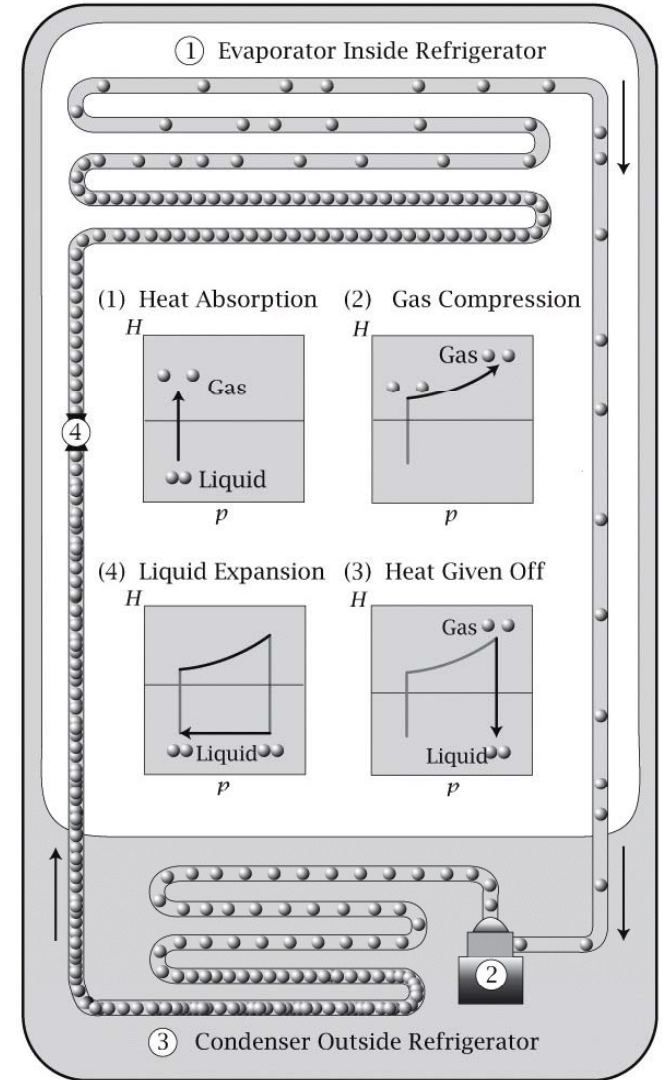
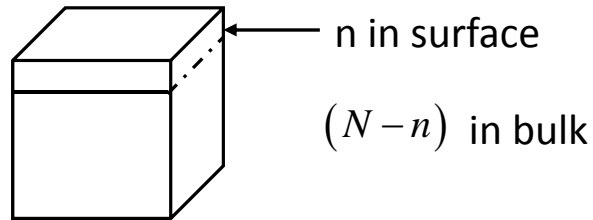


Figure 14.9 Molecular Driving Forces 2/e (© Garland Science 2011)



deviation from spherical drop opposed by surface tension



bulk:  $z$  nearest neighbor  
 surface:  $(z-1)$  nearest neighbors

$$U = \frac{zw_{AA}}{2}(N-n) + \frac{(z-1)w_{AA}}{2}n = \frac{w_{AA}}{2}(Nz-n)$$

$$\gamma = \left( \frac{\partial F}{\partial A} \right)_{T,V,N}$$

For lattice model of liquid

$$S = 0 \Rightarrow F = U$$

$$\gamma = \left( \frac{\partial U}{\partial n} \right)_{T,V,N} \left( \frac{\partial n}{\partial A} \right)$$

$$\gamma = -\frac{w_{AA}}{2a}$$

$$A = na, \quad a = \text{area per particle}$$

free energy for transferring particles from bulk to the surface