

CHAPTER 9

Need to generalize beyond $p \cdot V$ work

E.g., droplets and lipid bilayers can vary surface area

$$G(T, p, N, A), \quad A = \text{area}$$

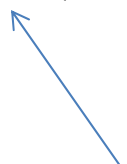
extensive degree of freedom \leftrightarrow conjugate force

	$p \rightarrow V$	
	$T \rightarrow S$	
surface tension	$\gamma \rightarrow A$	area
force	$f \rightarrow L$	length
potential	$\psi \rightarrow Q$	charge
mag. field	$B \rightarrow I$	mag. moment

In general $[f, X]$

$$U = U(S, V, N, X)$$

$$dU = TdS - pdV + \sum \mu_k dN_k + fdL + \gamma dA + \psi dQ + BdI + \sum f_j dX_j$$

$$f_j = \left(\frac{\partial U}{\partial X_j} \right)_{S, V, N, X_{i \neq j}}$$


Consider surface tension

Assume composition does not change

$$dU = TdS - pdV + \gamma dA$$

$$dG = dU + pdV + Vdp - TdS - SdT$$

$$dG = Vdp - SdT + \gamma dA, \quad \gamma = \left(\frac{\partial G}{\partial A} \right)_{p,T}$$

Maxwell relations

example $\left(\frac{\partial S}{\partial V} \right)_T = \left(\frac{\partial p}{\partial T} \right)_V$ ← easy to measure

To see where these come from

$F = F(T, V)$ is a state function

$$dF = \left(\frac{\partial F}{\partial V} \right)_T dV + \left(\frac{\partial F}{\partial T} \right)_V dT$$

\uparrow \uparrow
 $-p$ $-S$

$$\left(\frac{\partial S}{\partial V} \right)_T = \left(\frac{\partial p}{\partial T} \right)_V$$

$$\frac{\partial^2 F}{\partial T \partial V} = \frac{\partial^2 F}{\partial V \partial T}$$

$$\left(\frac{\partial}{\partial T} \left(\frac{\partial F}{\partial V} \right)_T \right)_V = \left(\frac{\partial}{\partial V} \left(\frac{\partial F}{\partial T} \right)_V \right)_T$$

$$\left(\frac{\partial p}{\partial T} \right)_V = \left(\frac{\partial S}{\partial V} \right)_T$$

Suppose you want $\left(\frac{\partial S}{\partial p}\right)_{T,N}$

variables T, p, N

The natural function is $G(T, p, N)$

$$dG = -SdT + Vdp + \sum \mu_j dN_j \quad \left| \quad -\frac{\partial S}{\partial p} = \frac{\partial^2 G}{\partial p \partial T} \quad \frac{\partial V}{\partial T} = \frac{\partial^2 G}{\partial T \partial p} \right.$$
$$-\left(\frac{\partial S}{\partial p}\right)_{T,N} = \left(\frac{\partial V}{\partial T}\right)_{p,N}$$

Susceptibilities

coefficient of thermal expansion

$$\alpha = \frac{1}{V} \left(\frac{\partial V}{\partial T}\right)_p = -\frac{1}{V} \left(\frac{\partial S}{\partial p}\right)_T \quad \left| \quad \text{using the relation} \right.$$

we found above

so measuring α gives info on $\left(\frac{\partial S}{\partial p}\right)_T$

usually $\alpha > 0 \Rightarrow > p$ leads to $< S$

Ideal gas

$$\alpha = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_p = \frac{1}{T}$$

$$pV = nkT$$

$$V = \frac{nkT}{p}$$

$$\left(\frac{\partial V}{\partial T} \right)_p = nk / p$$

$$\frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_p = \frac{nk / p}{nkT / p} = \frac{1}{T}$$

increase T generally loosens bonds $\rightarrow \alpha > 0$

Note the change in sign of α of water just above 0 °C.

So water has maximum density near 4 °C

Liquid water is more dense than ice.
Again, rather unusual behavior.

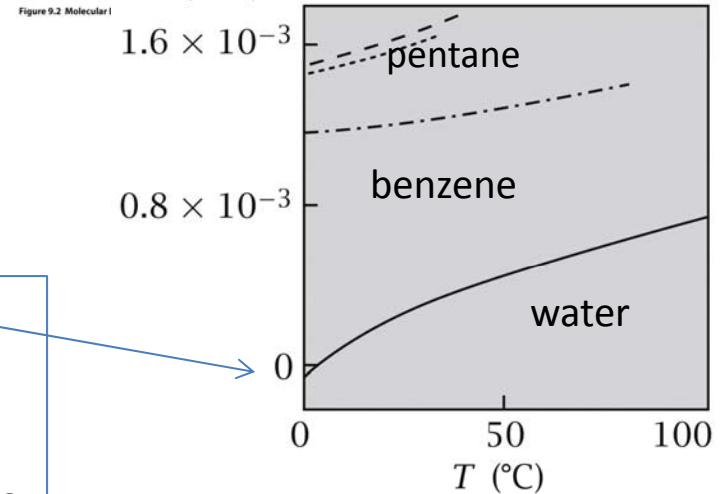
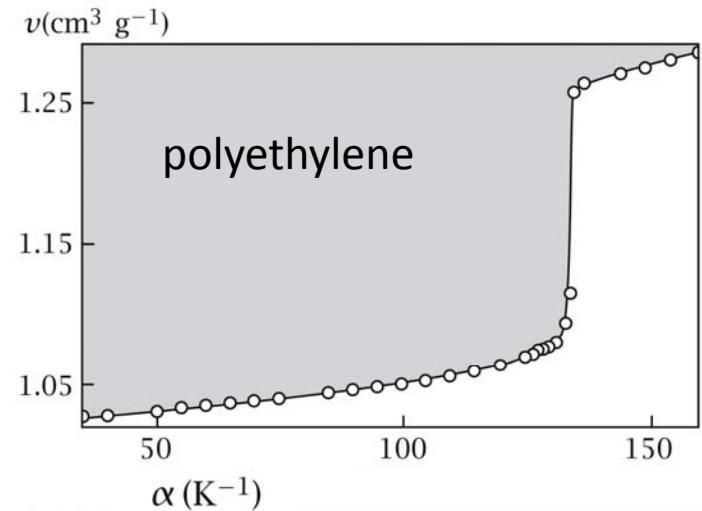


Figure 9.3 Molecular Driving Forces 2/e (© Garland Science 2011)

Ex. 9.3 Can show $\Delta S = -\int_{p_1}^{p_2} \alpha(p) V(p) dp$

isothermal compressibility

$$\kappa = -\frac{1}{V} \left(\frac{\partial V}{\partial p} \right)_T$$

$$\text{ideal gas } \kappa = \frac{1}{p}$$

$$pV = NkT$$

$$V = \frac{NkT}{p}$$

$$\left(\frac{\partial V}{\partial p} \right)_T = -\frac{NkT}{p^2}$$

$$-\frac{1}{V} \left(\frac{\partial V}{\partial p} \right)_T = \frac{+NkT / p^2}{NkT / p} = \frac{1}{p}$$

organic liquids undergo larger volume changes upon heating than does liquid water.

Also, water is less compressible than organic liquids

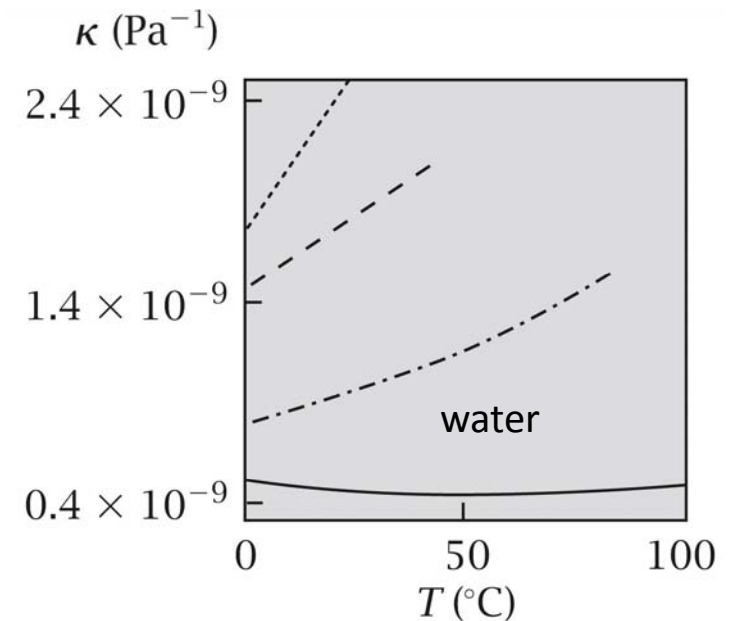


Figure 9.5 Molecular Driving Forces 2/e (© Garland Science 2011)

Suppose you wanted $\left(\frac{\partial U}{\partial V}\right)_T$?

$$U = U(T, V), \quad S = S(T, V)$$

$$dU = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV$$

$$dS = \left(\frac{\partial S}{\partial T}\right)_V dT + \left(\frac{\partial S}{\partial V}\right)_T dV$$

$$dU = TdS - pdV$$

$$\left(\frac{\partial U}{\partial V}\right)_T dV + \left(\frac{\partial U}{\partial T}\right)_V dT = T \left[\left(\frac{\partial S}{\partial V}\right)_T dV + \left(\frac{\partial S}{\partial T}\right)_V dT \right] - pdV$$

$$\text{If } T \text{ is constant } \left(\frac{\partial U}{\partial V}\right)_T dV = T \left(\frac{\partial S}{\partial V}\right)_T dV - pdV$$

$$\uparrow \\ \left(\frac{\partial p}{\partial T}\right)_V \text{ from Table 9.1}$$

$$\left(\frac{\partial U}{\partial V}\right)_T dV = T \left(\frac{\partial p}{\partial T}\right)_V dV - pdV = 0 \text{ for ideal gas}$$

Thermodynamics of a rubber band

$$U = U(S, V, L), \quad L = \text{length}$$

$$dU = TdS - pdV + fdL, \quad f = \text{force of retraction}$$

expt. at constant T, p

$$dG = -SdT + Vdp + fdL$$

$$f = \left(\frac{\partial G}{\partial L} \right)_{T,p} = \left(\frac{\partial H}{\partial L} \right)_{T,p} - T \left(\frac{\partial S}{\partial L} \right)_{T,p}$$

$$\left(\frac{\partial S}{\partial L} \right)_{T,p} = - \left(\frac{\partial f}{\partial T} \right)_{p,L}$$

$$G = H - TS$$

$$dG = dH - TdS - SdT$$

slope \Rightarrow stretching involves ordering

$$\left(\frac{\partial H}{\partial L} \right)_{T,p} = f - T \left(\frac{\partial f}{\partial T} \right)_{p,L}$$

Entropy of rubber band decreases with increasing T

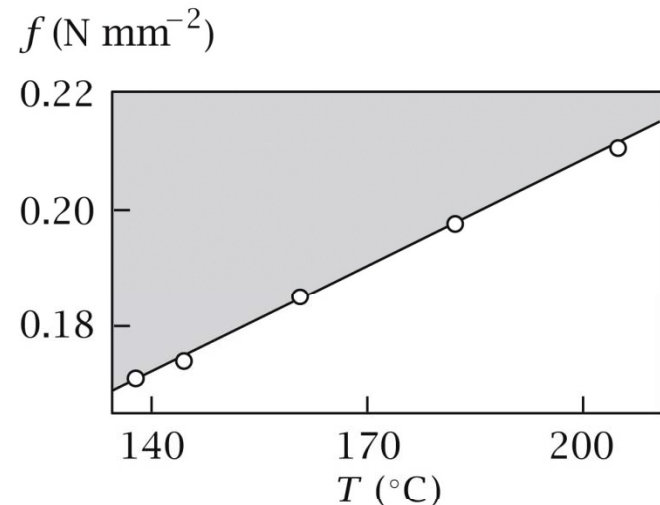


Figure 9.6 Molecular Driving Forces 2/e (© Garland Science 2011)

Surfactant molecules on a liquid surface

$$\pi = (T, A, N) = \text{lateral pressure}$$

N surfactant molecules in A lattice sites: $N \ll A$

$$W = A^N \ll \text{assumes you can tell which molecule is which} \gg$$

$$S = Nk \ln A$$

suppose T, p constant

$$dG = -SdT + Vdp - \pi dA$$

$$\pi = - \left(\frac{\partial G}{\partial A} \right)_{T,p} = - \left(\frac{\partial H}{\partial A} \right)_{T,p} + T \left(\frac{\partial S}{\partial A} \right)_{T,p} \quad \left| \quad \begin{array}{l} \text{sign} \Rightarrow \text{free energy} \\ > \text{ as you compress} \\ \text{the molecules} \end{array} \right.$$

$$\left(\frac{\partial S}{\partial A} \right)_{T,p} = \left(\frac{\partial \pi}{\partial T} \right)_{p,A}$$

$$\left(\frac{\partial \pi}{\partial T} \right)_{p,A} = \frac{Nk}{A}$$

$$\pi = \frac{NkT}{A} :$$

Analogous to the ideal gas law

The pressure is purely entropic.

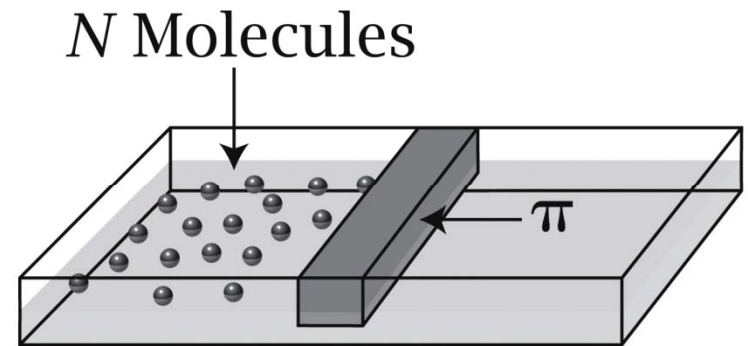


Figure 9.7 Molecular Driving Forces 2/e (© Garland Science 2011)

Langmuir trough

Multicomponent systems

$v = V / n =$ molar volume, $n = \#$ moles assuming
single component system

Multicomponent system: n_1, n_2, \dots, n_m

$$v_j = \left(\frac{\partial V}{\partial n_j} \right)_{T, p, n_{i \neq j}}$$

$$dV = \sum_j v_j dn_j, \quad dn_j \text{ is change in \# moles of species } j$$

can also define partial specific volumes $\left(\frac{\partial V}{\partial w_j} \right)$, where w_j is the weight of j .

Ideal solutions: v_j would be independent of the composition

In fact, mixing water and alcohol V_{tot} not necessarily $= V_a + V_w$

if you assume v_w is fixed at the pure water value

$$\text{can define } v_{app}(alc) = \frac{V - n_w v_w}{n_a}$$

↑
apparent

shrinkage when the liquids are mixed
salts (e.g., MgSO_4) have – partial molar
volumes in water

Chemical potentials

$$dG = -SdT + Vdp + \sum \mu_j dN_j, \text{ etc.}$$

$$\mu_j = \left(\frac{\partial G}{\partial N_j} \right)_{T,p,N_{i \neq j}} = \left(\frac{\partial U}{\partial N_j} \right)_{V,S,N_{i \neq j}} = \left(\frac{\partial F}{\partial N_j} \right)_{T,V,N_{i \neq j}} = \left(\frac{\partial H}{\partial N_j} \right)_{S,p,N_{i \neq j}}$$

but partial molar volumes are measured at fixed T, p

So need $\partial G / \partial n_j$

$$\mu_j = \frac{\partial G}{\partial n_j} = \frac{\partial H}{\partial n_j} - T \frac{\partial S}{\partial n_j} = h_j - Ts_j$$

$$dG = -SdT + Vdp + \sum (h_j - Ts_j) dn_j \quad \text{partial molar}$$

Notice the two types of entropy terms

for condensed phases $G \approx F$

consider inserting 1 water molecule into liquid water

$$\mu = \left(\frac{\partial G}{\partial N} \right)_{T,p} = \left(\frac{\partial F}{\partial N} \right)_{T,V}$$

$$F = G - pV \quad \left| \quad \text{consider fixed } T, p \right.$$

$$\left(\frac{\partial F}{\partial N} \right)_{T,p} = \left(\frac{\partial G}{\partial N} \right)_{T,p} - p \left(\frac{\partial V}{\partial N} \right)_{T,p}$$

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

$$\left(\frac{\partial F}{\partial N} \right)_{T,p} - \left(\frac{\partial F}{\partial N} \right)_{T,V} = -0.44 \text{ cal / mol}$$

Here we made use of

$$\mu = \left(\frac{\partial G}{\partial N} \right)_{T,p} = \left(\frac{\partial F}{\partial N} \right)_{T,V}$$

which is very small

$$\Delta G - \Delta F \approx 0$$

in gas phase $\Delta G - \Delta F = RT$