

CHAPTER 8

So far, we considered systems where we control q and or w

Actually, in many cases, it is the intensive variables p and/or T that are controlled.

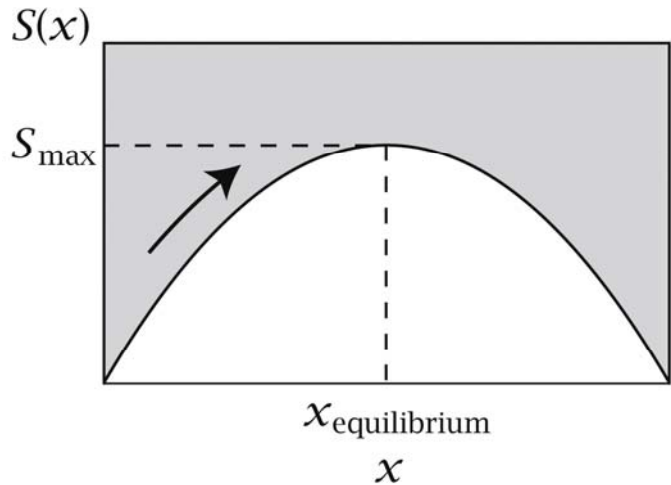
To deal with these cases, we need to introduce new thermodynamic variables.

When T is constant: energy exchanges between system and surroundings (heat bath)

$$(U_{sys} + U_{surr} = const)$$

When p is constant, system and surroundings exchange volume

Const. μ , particles exchange between system and surroundings



if system + local surroundings
are isolated from the rest of
the universe, then their combined
 $S \rightarrow$ maximum

Figure 8.2. Molecular Driving Forces 2/e (© Garland Science 2011)

If extremum of a function, e.g. $S(U)$, predicts equilibrium
 U is a natural variable of S
 T is not a natural variable of S

Define $F = F(T, V, N)$, where T, V, N are natural variables of F
extremum of $F \rightarrow$ equilibrium, where T is constrained

Helmholtz
free energy

$$dS_{comb} = dS_{sys} + dS_{bath} \quad dS_{comb} \geq 0$$

$$dU_{sys} + dU_{bath} = 0$$

For combined system (subsystem + heat bath) if isolated \rightarrow
equilibrium is state of maximum $S(U, V, N)$

$$dS_{bath} = \frac{1}{T} dU_{bath}, \quad \text{if } V, N \text{ fixed}$$

$$dS_{bath} = -\frac{dU_{sys}}{T}$$

$$dS_{sys} - \frac{dU_{sys}}{T} \geq 0 \quad \Rightarrow \quad dU_{sys} - TdS_{sys} \leq 0$$

$$\text{Let } F = U - TS \rightarrow dF = dU - TdS - SdT$$

$$= dU - TdS, \quad \leftarrow \text{at const } T \quad \left| \begin{array}{l} \text{definition of Helmholtz} \\ \text{free energy} \end{array} \right.$$

In a system with T, V, N const., equilibrium $\Leftrightarrow F$ is a minimum

equilibrium: a balance between U and S , with T determining the balance

lattice model of dimer formation: consider the case of two atoms and V sites

dimer and dissociated states

V sites, $W = V - 1$ dimer possibilities
for large $V - 1 \approx V$

$$F_{\text{dimer}} = U_{\text{dimer}} - TS_{\text{dimer}} = -\varepsilon - kT \ln V$$

$$W_{\text{monomers}} = W_{\text{total}} - W_{\text{dimer}}$$

$$= \frac{V!}{2!(V-2)!} - (V-1) = \frac{V(V-1)}{2} - V - 1$$

$$= \left(\frac{V}{2} - 1\right)(V-1) \approx \frac{V^2}{2}$$

$$F_{\text{monomer}} = U_{\text{monomer}} - TS_{\text{monomer}} = -TS_{\text{monomer}}$$

$$= -Tk \ln \left(\frac{V^2}{2}\right)$$

dimer $U = -\varepsilon (\varepsilon > 0)$

otherwise $U = 0$

$$S = k \ln W$$

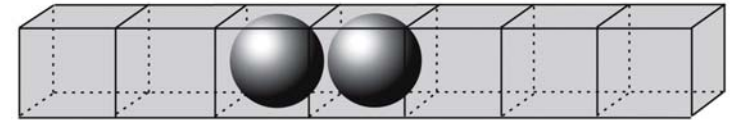


Figure 8.3 Molecular Driving Forces 2/e (© Garland Science 2011)

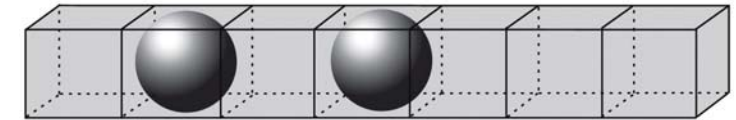


Figure 8.4 Molecular Driving Forces 2/e (© Garland Science 2011)

dimer is more stable at low T
monomers more stable at high T

When are they equally stable?

$$\begin{array}{l}
 -\varepsilon - kT_0 \ln V = -kT_0 \ln \left(\frac{V^2}{2} \right) \\
 \varepsilon = kT_0 \ln \frac{V}{2}
 \end{array}
 \left| \begin{array}{l}
 -\varepsilon - kT_0 \ln V = -2kT_0 \ln V + kT_0 \ln 2 \\
 -\varepsilon = -kT_0 \ln V + kT_0 \ln 2 \\
 \varepsilon = kT_0 \ln V - kT_0 \ln 2 \\
 \varepsilon = kT_0 \ln \left(\frac{V}{2} \right)
 \end{array} \right.$$

stronger bonds \Rightarrow greater ε values \Rightarrow
 higher T needed to break the bond

energy dominates at low T
 entropy dominates at high T

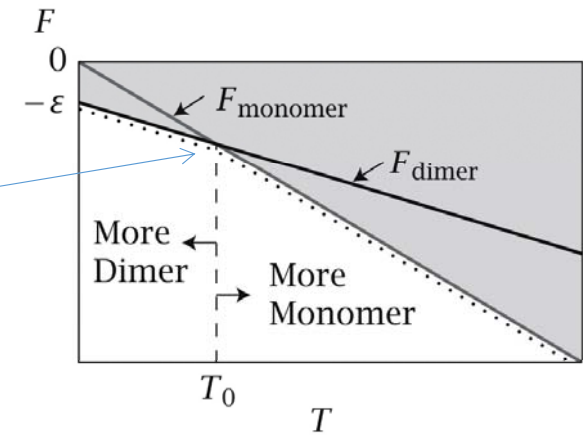


Figure 8.5 Molecular Driving Forces 2/a (© Garland Science 2011)

Model for polymer folding

compact $W_c = 1$, $U = -\varepsilon$

extended $W_e = 4$, $U = 0$

$$F_c = U_c - TS_c = -\varepsilon - kT \ln 1 = -\varepsilon$$

$$F_e = U_e - TS_e = 0 - kT \ln 4$$

low T , polymer is compact

high T , it is extended

collapse \rightarrow heat released. I.e., exothermic (rather than endothermic) process

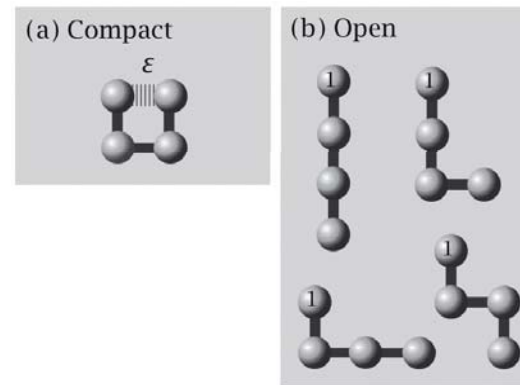


Figure 8.8 Molecular Driving Forces 2a (© Garland Science 2011)

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

$$F = F(T, V, N)$$

$$dF = dU - TdS - SdT$$

$$= -SdT - pdV + \sum \mu_j dN_j$$

$$dF = \left(\frac{\partial F}{\partial T} \right)_{V, N} dT + \left(\frac{\partial F}{\partial V} \right)_{T, N} dV + \sum \left(\frac{\partial F}{\partial N_j} \right)_{T, N, N_{i \neq j}} dN_j$$

gives

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

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

$$\mu_j = \left(\frac{\partial F}{\partial N_j} \right)_{T, N, N_{i \neq j}}$$

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

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

$$F = F(T, V, N) \quad \text{Helmholtz free energy}$$

$$H = H(S, p, N) \quad \text{enthalpy}$$

$$G = G(T, p, N) \quad \text{Gibbs free energy}$$

How do we find the enthalpy?

start with $U(S, V, N)$

write $H = H(S, p, N) = U + pV$

$$dH = dU + pdV + Vdp$$

$$= TdS - pdV + \sum \mu_j dN_j + pdV + Vdp$$

$$= TdS + Vdp + \sum \mu_j dN_j$$

$$G = G(T, p, N)$$

write $G = H - TS$ (or $G = F + pV$)

$$dG = dH - TdS - SdT$$

$$= TdS + Vdp + \sum \mu_j dN_j - TdS - SdT$$

$$= -SdT + Vdp + \sum \mu_j dN_j$$

$$dG = \left(\frac{\partial G}{\partial T} \right)_{p,N} dT + \left(\frac{\partial G}{\partial p} \right)_{T,N} dp + \sum \left(\frac{\partial G}{\partial N_i} \right)_{T,p,N_{j \neq i}} dN_j$$

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

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

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

for equilibrium at fixed T , p , and N , G does not change

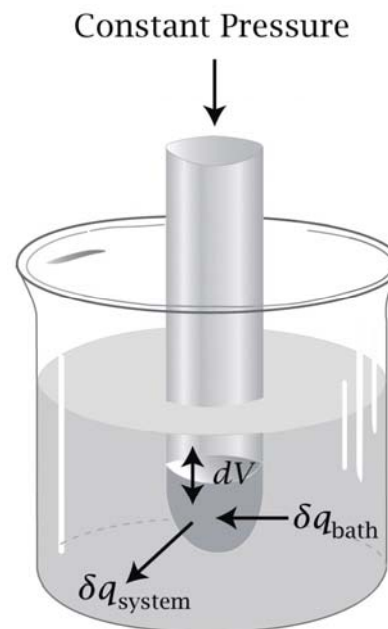


Figure 8.8 Molecular Driving Forces 2/e (© Garland Science 2011)

ice \leftrightarrow water at fixed p_0

G_{solid} } Equilibrium when
 G_{liquid} } they become equal

$$dT = 0, \quad dN_1 = dN_2 \dots = 0, \quad dp = 0$$

$$\Delta G = 0$$

$$\Delta G = \Delta H - T \Delta S$$

$$\Delta H = T_0 \Delta S \quad \text{at a phase change}$$

solid \rightarrow liquid } $\Delta S >$ compensates $\Delta H >$
liquid \rightarrow vapor }

$$U(S, V, N) \quad dU = TdS - pdV + \sum \mu_j dN_j$$

$$S(U, V, N) \quad dS = \frac{1}{T} dU + \frac{p}{T} dV - \sum \mu_j dN_j$$

$$H(S, p, N) \quad dH = TdS + Vdp + \sum \mu_j dN_j \quad H = U + pV$$

$$F(T, V, N) \quad dF = -SdT - pdV + \sum \mu_j dN_j \quad F = U - TS$$

$$G(T, p, N) \quad dG = -SdT + Vdp + \sum \mu_j dN_j \quad G = H - TS = F + pV$$

$$F(T, V, N) = U(T, V, N) - TS(T, V, N)$$

minimizing $U(T, V, N)$ or maximizing $S(T, V, N)$
alone does not give equilibrium

$$G(T, p, N) = H(T, p, N) - TS(T, p, N)$$

The non-fundamental functions are useful in that
they may be easier to measure

$$dH = dU + pdV + Vdp = \delta q + \delta w + pdV + Vdp$$

$$\text{if quasi-static} \quad \delta w = -pdV$$

$$dH = \delta q + Vdp$$

if the process is also const p , $dH = \delta q$

$$C_p = \left(\frac{\delta q}{\delta T} \right)_p = \left(\frac{\partial H}{\partial T} \right)_p = T \left(\frac{\partial S}{\partial T} \right)_p$$

so, from const. p heat capacity measurements can get G

$$(G = H - TS)$$

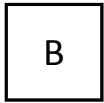
Third law of thermodynamics

$$S(T) = \int_0^T \frac{C_V}{T'} dT' + S(0)$$

third law states $S(0) = 0$ for a perfect crystal



C_p^A



C_p^B

$$T_B > T_A$$

$$\Delta H = \Delta H_A + \Delta H_B = 0 \text{ at equilibrium}$$

$$\Delta H_A = C_A(T - T_A) \quad \Delta H_B = C_B(T - T_B)$$

$$C_A(T - T_A) + C_B(T - T_B) = 0 \Rightarrow T = \frac{C_A T_A + C_B T_B}{C_A + C_B}$$

Standard conditions

$$T = 0^\circ\text{C}, \quad p = 1 \cdot \text{atm}$$

Suppose you want ΔH_{boil} at $T = 0^\circ\text{C}$

$$\left[\begin{array}{l} \Delta H_{\text{boil}}(100^\circ\text{C}) = 540 \text{ cal/g} \\ C_p(\text{steam}) = 0.448 \text{ cal/Kg} \\ C_p(\text{liq}) = 1.00 \text{ cal/Kg} \end{array} \right.$$

$$\Delta H_{\text{liq}} = \int_{100}^0 C_p(\text{liq}) dT = 1.00 \frac{\text{cal}}{\text{Kg}} (-100\text{K}) = -100 \text{ cal/g}$$

$$\Delta H_{\text{steam}} = \int_{100}^0 C_p(\text{steam}) dT = \frac{0.448 \text{ cal}}{\text{Kg}} (-100) = -44.8 \text{ cal/g}$$

$$\begin{aligned} \Delta H_{\text{boil}}(0^\circ\text{C}) &= -\Delta H_{\text{liq}}(100 \rightarrow 0^\circ) + \Delta H_{\text{boil}}(100^\circ\text{C}) + \Delta H_{\text{steam}}(100^\circ \rightarrow 0^\circ\text{C}) \\ &= 100 + 540 - 44.8 = 596.2 \text{ cal/g} \end{aligned}$$

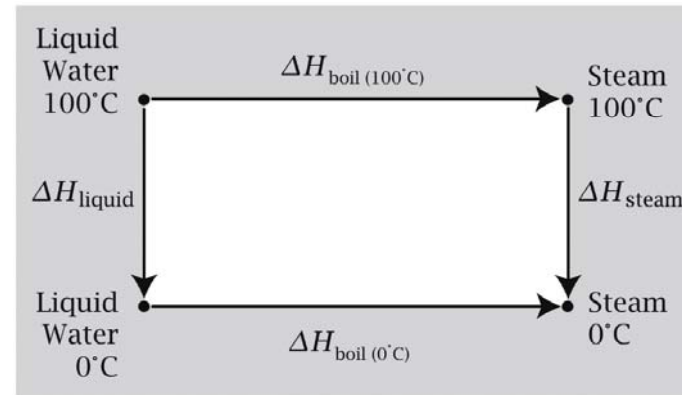
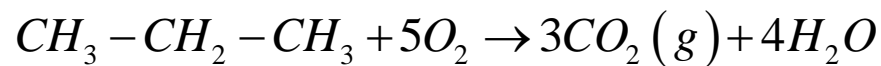


Figure 8.9 Molecular Driving Forces 2/e (© Garland Science 2011)

Chemical Reactions

Enthalpies of molecules $\approx \Sigma$ (bond enthalpies)

| | |
|-------------------------------|-----|
| <i>HH</i> | 436 |
| <i>HO</i> | 460 |
| <i>CH</i> | 414 |
| <i>C = O</i> | 724 |
| <i>C = O (CO₂)</i> | 799 |
| <i>N = N</i> | 941 |
| <i>O = O</i> | 499 |
| <i>C - C</i> | 347 |
| <i>C = C</i> | 619 |



| | | | | | | | |
|-----------|---------|---|-------------|-----------|---------|---|-------------|
| <i>CH</i> | 8 x 414 | → | 3312 | <i>CO</i> | 6 x 699 | → | 4794 |
| <i>CC</i> | 2 x 347 | → | 694 | <i>OH</i> | 8 x 460 | → | <u>3680</u> |
| <i>OO</i> | 5 x 499 | → | <u>2495</u> | | | | <u>8474</u> |
| | | | 6501 | | | | |

$$\Delta H = -[8474] + [6501] = -1973 \text{ kJ / mol}$$