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Course 565/665 Lecture Number _____ Date 3/3/03

Lecturer Dr. Silvia Cavagnero Note Taker Eric Fulmer

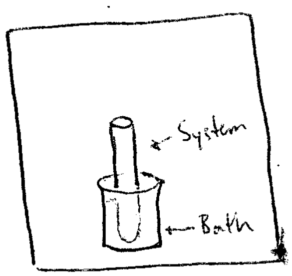
Last Time - Chapter 8 - FREE ENERGY

"W" is difficult to quantify/quantitate in biological systems. The 1st principle may not be straightforward to apply if "W" needs to be explicitly evaluated. Thus, we need new thermodynamic functions.

Constant T, V $\longrightarrow$ Helmoltz Free Energy (F)

Constant T, p $\longrightarrow$ Gibbs Free Energy (G)

Isolated System:



The Test Tube is held at constant T and V. The Test tube plus the bath is the combined system, and it is isolated from its surroundings.

$$dS_{cs} = dS_s + dS_b \qquad \text{(system + bath)}$$

$$dU_{cs} = 0 = dU_s + dU_b$$

$$dS_b = \frac{1}{T}\,dU_b + \cancel{\frac{p}{T}\,dV_b}^{\,0} - \cancel{\frac{\mu}{T}\,dN_b}^{\,0} = \frac{1}{T}\,dU_b$$

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$$dS_b = \frac{dU_b}{T}$$

$$dU_b = -dU_s$$

$$dS_b = -\frac{dU_s}{T}$$

$$\boxed{\begin{aligned} dS_s - \frac{dU_s}{T} &\geq 0 \\ dU_s - TdS_s &\leq 0 \end{aligned}} \qquad (1)$$

For equation (1), the greater than sign (>) is for systems evolving towards equilibrium. When a system has reached equilibrium, these two terms cancel and it is an equality to zero (=).

Define a new function:

$F \equiv U - TS$ where F is the Helmoltz free energy.

$dF = dU - TdS - \cancel{SdT}^{\,0}$ ~~because~~ when T is constant.

$\boxed{dF = dU - TdS}$ at constant T.

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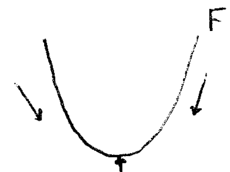
As you approach equilibrium:



$dF < 0$

F decreases as it approaches equilibrium. Once equilibrium is reached,

$dF = 0$ and F is minimized.

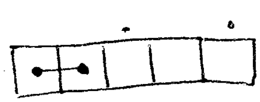
Criteria for equilibrium:

$dS_{sys + surr = universe}$ is maximized.

dF_{sys} is at a minimum at constant T, V, N.

Remember, entropy of the universe is always maximized for any spontaneous process. But this doesn't tell us much about our system. The free energy fills this void.

Example) Study dimer vs. monomer formation.



Could be occupied by

• monomer.

•—• dimer.

2 particles.

V lattice sites

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<u>Dimer</u> - Dimerization energy (if it makes the dimer stable) : $-\varepsilon$ $(\varepsilon < 0)$.

0 — $U_{monomer}$

— U_{dimer}

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

$$U_D = -\varepsilon$$

$$F_D = U_D - T\Delta S_D = -\varepsilon - Tk \ln W_D$$

$$= -\varepsilon - kT \ln (1-V)$$

$$W_M = W_{TOTAL} - W_D = \frac{V!}{2!\,(V-2)!} - (V-1) = \frac{V(V-1)}{2} - V + 1$$

$$= \frac{V^2}{2} - \frac{V}{2} - V + 1 = \frac{V^2}{2} - \frac{3}{2}V + 1$$

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

<u>Note</u>: We define $W_M = W_{TOTAL} - W_D$ because we want all of the states that allow the two monomers to be on the lattice, but not next to each other (that would be then a dimer).

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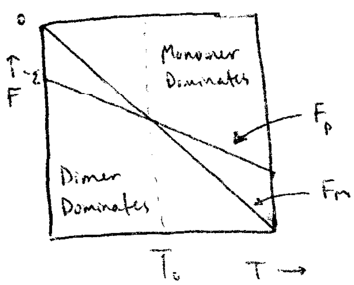
$$F_M = U_M - T S_M = 0 - Tk \ln W_m$$

$$= -kT \ln\left[\left(\frac{V}{2}-1\right)(V-1)\right] = -kT\ln\left(\frac{V}{2}-1\right) - kT\ln(V-1)$$

Plot F vs. T for both F_m, F_P



Lower F ⇒ Dimer is the most stable species or most highly populated species.

⇝ Can Show $T_0 = \dfrac{\varepsilon}{k\ln\left(\frac{V}{2}-1\right)}$

General Example (see phase transitions, protein unfolding)

<u>Example</u> | <u>Polymer Collapse</u>

T, V, N are constant

collapse energy $= -\varepsilon$ $(\varepsilon > 0)$

<u>Compact</u> <u>Open</u>