

Course S6S/66S Lecture Number _____ Date 3/4/03

Lecturer Dr. Silvia Cavagnero Note Taker Eric Fulmer

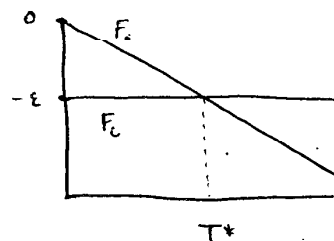
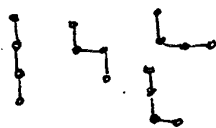
LAST TIME

Example: Polymer Collapse

Compact



Open



$$W_c = 1$$

$$U_c = -\epsilon$$

$$\begin{aligned} F_c &= U_c - TS_c \\ &= -\epsilon - kT \ln 1 \\ &= -\epsilon \end{aligned}$$

$$W_o = 4$$

$$U_o = 0$$

$$\begin{aligned} F_o &= U_o - TS_o \\ &= 0 - kT \ln 4 \\ &= -kT \ln 4 \end{aligned}$$

At the temperature T^* , both open and compact states are present (50% compact, 50% open).

$$\begin{aligned} \text{At } T^*, \quad F_o &= F_c \\ -\epsilon &= -kT^* \ln 4 \\ T^* &= \frac{\epsilon}{k \ln 4} \end{aligned}$$

Above T^* , the open state is more stable. Below T^* , the polymers are more likely to be found in the compact form. T^* can be

thought of as the "melting" or denaturation temperature.

Course 565/1.65 Lecture Number _____ Date 3/4/03Lecturer Cavagnero Note Taker FulmerMore on F:

$$F = U - TS$$

$$dF = dU - TdS - SdT$$

$$dF = \cancel{TdS} - pdV + \mu dN - \cancel{TdS} - SdT$$

$$(\text{since } dU = TdS - pdV + \mu dN)$$

$$dF = -SdT - pdV + \mu dN$$

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

$$dF = \left(\frac{\partial F}{\partial T}\right)_{V,N} dT + \left(\frac{\partial F}{\partial V}\right)_{T,N} dV + \left(\frac{\partial F}{\partial N}\right)_{T,V} dN$$

$$\text{Implying: } \left(\frac{\partial F}{\partial T}\right)_{N,V} = -S, \quad \left(\frac{\partial F}{\partial V}\right)_{T,N} = -P, \quad \left(\frac{\partial F}{\partial N}\right)_{T,V} = \mu$$

Enthalpy (H) (H can be measured by calorimetry)

$$H \equiv U + pV$$

$$dH = dU + pdV + Vdp = TdS - pdV + \mu dN + \cancel{pdV} + Vdp$$

$$dH = TdS + Vdp + \mu dN$$

Course 505/005 Lecture Number _____ Date 3/4/03Lecturer Caragnero Note Taker FulmerGibbs "Free Energy" (G)

$$G \equiv H - TS$$

$$dG = dH - TdS - SdT = \cancel{TdS} + Vdp + \mu dN - \cancel{TdS} - SdT$$

$$dG = -SdT + Vdp + \mu dN$$

KNOW THIS.

dG goes to zero as a system of constant $T, P,$ and N goes to equilibrium. At equilibrium, G reaches a minimum value.

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

$$dG = \left(\frac{\partial G}{\partial T}\right)_{P,N} dT + \left(\frac{\partial G}{\partial P}\right)_{T,N} dP + \left(\frac{\partial G}{\partial N}\right)_{T,P} dN$$

$$\left(\frac{\partial G}{\partial T}\right) = -S, \quad \left(\frac{\partial G}{\partial P}\right) = V, \quad \left(\frac{\partial G}{\partial N}\right) = \mu$$

Work through the phase change section yourself.

Course 565/665 Lecture Number _____ Date 3/4/03Lecturer Cavagnero Note Taker FulmerHeat Capacity

A property of each substance. Essentially, this quantity relates the amount of heat required to raise the temperature of the substance by 1°C .

There are two commonly used heat capacities: C_p and C_v . (Heat capacity at constant pressure or volume).

Constant VConstant P

$$C_v = \left(\frac{\delta q}{\delta T} \right)_v = \left(\frac{\partial U}{\partial T} \right)_v$$

Since for closed systems:

$$dU = TdS - p dV$$

$$dU = TdS \quad \text{at constant } V.$$

And from the 1st Law

$$dU = \delta q + \delta w = \delta q \quad (\delta w = 0 \text{ at constant } V)$$

$$C_v = \left(\frac{\partial U}{\partial T} \right)_v = T \left(\frac{\partial S}{\partial T} \right)_v$$

PRINT NEATLY

USE A BLACK PEN

DO NOT STAPLE

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Heat capacities are T -dependent. However, when the temperature range is small, the heat capacity generally does not change much. Assuming no phase change, one can often approximate the heat capacity as a constant value.

At constant P :

$$\begin{aligned} dH &= dU + p dV + v dp \\ &= T dS - \cancel{p dV} + \cancel{p dV} + v dp \end{aligned}$$

$$dH = T dS = \delta q$$

More tomorrow . . .