Physical Chemistry (Chem 132A)

Lecture 7
Friday, October 13

Homework #2 (WebAssign)
Due Saturday, October 14.

New Homework #3 will be available Saturday evening and due October 21.

Reminder of the Schedule

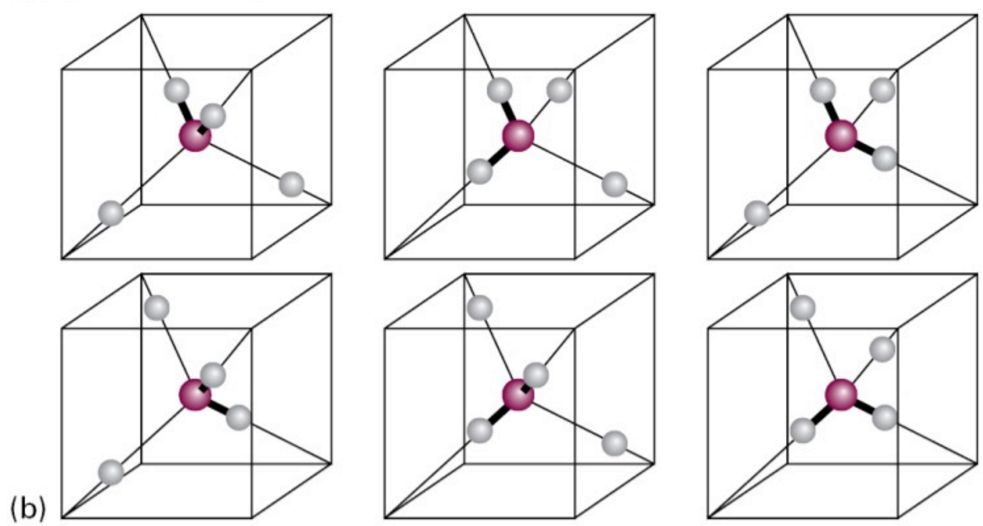
Schedule:

Week	Dates	Topics	Readings
0	Before Sept 28	The Properties of Gases	Chapter 1 A, B, C
1	October 1-7	The First Law of Thermodynamics	Chapter 2
2	October 8-14	The First and Second Laws	Chapter 2, 3
3	Oct 15-Oct 21	Third Law; Physical Transformations	Chapter 3, 4
4	October 22-28	Physical Transformations; Mixtures	Chapter 4, 5
Midterm 1 (Chapters 1-4, 5A), Wednesday, October 25			
5	Oct. 29-Nov. 4	Mixtures; Chemical Equilibrium	Chapter 5, 6
6	Nov. 5-11	Chemical Equilibrium	Chapter 6
7	Nov. 12-18	Molecular Motion	Chapter 19
8	Nov. 19-25	Molecular Motion	Chapter 19
Midterm 2 (Chapters 1-6, 19), November 22			
9	Nov. 26-Dec. 2	Chemical Kinetics	Chapter 20
10	Dec. 3-Dec. 9	Chemical Kinetics, Collision Theory	Chapter 20, 21A
Final Exam (Chapters 1-6, 19, 20, 21A), Friday, Dec. 15, 8:00Am-10:00Am			

Third Law of Thermodynamics

The entropy of all perfect crystalline substances is zero at T=0.

Residual Entropy of Water at 0 K.



Define State Functions A and G

$A = U - TS$ useful for constant V and T

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

For constant V&T ΔA negative is spontaneous

$G = H - TS$ useful for constant P and T

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

For constant P&T ΔG negative is spontaneous

Note: quantities are for the SYSTEM

What happens if ΔS is negative?

We are developing a number of equations for different sets of physical conditions.

The method for developing each set of equations is VERY similar, and depends on what variables you wish to hold constant.

Entropy defines spontaneity. There is no way to avoid The Second Law.

The Free Energies (Helmholtz and Gibbs) account for the entropy by how they have been constructed. A(T,V) and G(T, P)

The Free Energies are in terms of the SYSTEM.

General statements about differentials

Example: dU = TdS – pdV

we've written $$dU = \left(\frac{\partial U}{\partial S}\right)_V dS + \left(\frac{\partial U}{\partial V}\right)_S dV$$

First a Math reminder: for a function F(x,y)

$$\left[\frac{\partial}{\partial y}\left(\frac{\partial F}{\partial x}\right)_y\right]_x = \left[\frac{\partial}{\partial x}\left(\frac{\partial F}{\partial y}\right)_x\right]_y$$

In general is M(x,y)dx + N(x,y)dy an exact differential?

This means does dF exist such that:

dF = M(x,y)dx + N(x,y)dy ?

$$dF(x,y) = \left(\frac{\partial F}{\partial x}\right)_y dx + \left(\frac{\partial F}{\partial y}\right)_x dy$$

Note: in lecture this equation was written incorrectly (dx and dy were omitted on the rhs)

$$M(x,y) = \left(\frac{\partial F}{\partial x}\right)_y \qquad \left(\frac{\partial M}{\partial y}\right)_x = \left[\frac{\partial}{\partial y}\left(\frac{\partial F}{\partial x}\right)_y\right]_x$$

$$N(x,y) = \left(\frac{\partial F}{\partial y}\right)_x \qquad \left(\frac{\partial N}{\partial x}\right)_y = \left[\frac{\partial}{\partial x}\left(\frac{\partial F}{\partial y}\right)_x\right]_y$$

But since we can switch the order of the partial derivatives:

$$\left(\frac{\partial M}{\partial y}\right)_x = \left(\frac{\partial N}{\partial x}\right)_y$$

dF = M(x,y)dx + N(x,y)dy
Means that:

$$\left(\frac{\partial M}{\partial y}\right)_x = \left(\frac{\partial N}{\partial x}\right)_y$$

dU = TdS – pdV means $\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial p}{\partial S}\right)_V$

dH = TdS + Vdp means $\left(\frac{\partial T}{\partial p}\right)_S = \left(\frac{\partial V}{\partial S}\right)_p$

dA = -pdV – SdT means $\left(\frac{\partial p}{\partial T}\right)_V = \left(\frac{\partial S}{\partial V}\right)_T$

dG = Vdp – SdT means $\left(\frac{\partial V}{\partial T}\right)_p = -\left(\frac{\partial S}{\partial p}\right)_T$

Maxwell Relations

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

$$\left(\frac{\partial T}{\partial p}\right)_S = \left(\frac{\partial V}{\partial S}\right)_p$$

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

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

Temperature dependence of G?

dG = Vdp – SdT

$$\left(\frac{\partial G}{\partial T}\right)_p = -S$$

G = H – TS so we have $\left(\frac{\partial G}{\partial T}\right)_p = \frac{G-H}{T}$

$$\left(\frac{\partial G/T}{\partial T}\right)_p = -\frac{H}{T^2}$$

See algebra on pg 144 of text

$$\left(\frac{\partial \Delta G/T}{\partial T}\right)_p = -\frac{\Delta H}{T^2}$$

THE END

SEE YOU Monday