

Week 5 Recitation

Exam 1

Chapter 2 eq: 47-49

Chapter 3 eq: 93-95

Chapter 4 eq: 143-146

Questions?

Midterm Information

- The exam will be held from 7-8:50 pm on Friday 10/2; an extra 10 minutes will be provided to format and upload responses.
- 9/30 (Wed.) is the cut-off date for material covered on the exam.
- Students will upload a single PDF document.
- We will be accepting written or electronic submissions.
- Full credit will require showing work, specifying units, and reporting to the correct number of significant figures.
- The exam is “open book,” but do not seek assistance from others.
- Follow the Code of Conduct, we will be required to refer suspected cases to the Council of Academic Misconduct.

Logistics

- Issues converting notebooks, has to do with symbols?
- Check the posted answer key to compare – will try to submit grades by tomorrow evening!
- Might use Doodle polls more in the future

HW3 Revision: 3.18a and b

a.

We have (symbolically) defined the T and p as constant \therefore

$$\Delta_{\phi} S = \frac{q_{\phi}}{T}, \text{ work depends on volume change, such that } w = -p\Delta V_{\phi,m}$$

$$\text{At constant p, } \Delta_{\phi} H = dq_{\phi}$$

$$\Delta_{\phi} U = q + w = q_{\phi} - p\Delta V_{\phi,m}$$

$$\Delta_{\phi} G = \Delta_{\phi} H - T\Delta_{\phi} S = q_{\phi} - T\frac{q_{\phi}}{T} = 0$$

b.

$$\Delta_{\phi} H(T) = q_{\phi} + (C_{p,B} - C_{p,A})(T - T_{\phi})$$

$$\Delta_{\phi} S(T) = \frac{q_{\phi}}{T} + (C_{p,B} - C_{p,A})R \ln \left(\frac{T}{T_{\phi}} \right)$$

HW3 Revision: 3.18d and e

d.

To calculate the $dH/dS/dG$ at a new temperature, use the following:

$$dH(T2) = dH(T1) + dC_p^*(T2-T1)$$

$$dS(T2) = dS(T1) + dC_p^* \ln(T2/T1)$$

$$dG(T2) = dH(T2) - T2dS(T2)$$

e.

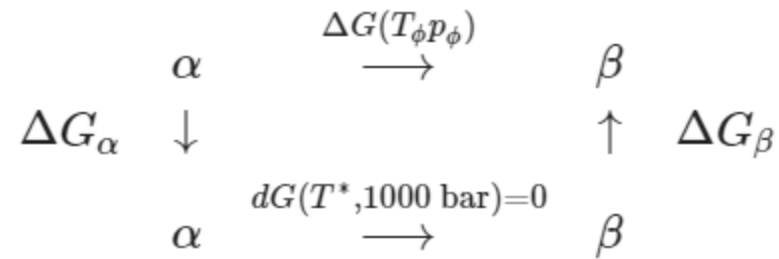
High p favors the side with smaller molar V , phase B sees an increase of +3 mL/mol, thus melting T will increase and phase A will be favored.

HW3 Revision: 3.18f

$$dG_a + dG_b = 0 = dV(p-1000) - dS(T) - dC_p \ln(T_m/T^*)$$

$$dV = V_b - V_a$$

$$dC_p = C_{pb} - C_{pa}$$



HW3 Revision: 3.30

A closed container is at 1 bar/273 K is placed in a -20 deg C freezer. What is the maximum pressure developed at equilibrium? $dH = 333.4$ kJ/kg, $\rho = 0.9172$ (ice) and 1.00 g/mL (water)

Consider the starting conditions:

$$dG_{273K} = 0, dG_{253K} = ?$$

We have an enthalpy of fusion and known temp., use Gibbs-Helmholtz:

$$dG_{253K} = 253 * (dG_{273K}/273 + (1/253 - 1/273) * 333.4 * 10)$$

$$\mathbf{dG_{253K} = -244 \text{ bar} * \text{mL/g}}$$

Use dG_{253K} in the next part...

HW3 Revision: 3.30 cont.

For the second step, recognize that the maximum pressure = constant, T is also defined, so the dG at the end of this process is equal to 0:

$$dG_{253K}(p_2) = 0$$

$$dV = (1.00 - 0.9172) / (1.00 * 0.9172), \text{ units in mL/g}$$

$$dp = (dG_{253K}(p_2) - dG_{253K}) / dV$$

Add initial pressure (1 bar) with dp to get the maximum pressure:

2705 bar, 2.7e3 bar

Ch 2 Review: Definitions of C, H, and U

- Understand the First Law and its implications
- System, surroundings, work (w) done on(+)/by(-), heat flow (q)

Constant pressure

$$dH = q_p = C_p dT$$

$$C_p = C_v + nR$$

Why? System can still do work on surroundings \therefore higher C.

Constant volume

$$dU = q + w, w = -pdV$$

$$dV = 0 \therefore dU = q_v = C_v dT$$

C_v related to degrees of freedom:

- x, y, and z translational modes
- For a diatomic (O=O, O₂), add 2 rotational modes

Ch 2 Review: State vs Path Variables

State variables only depend on the current state of the system:

- p, pressure
- V, volume
- T, temperature

If a variable is a function of state variable, then it is also a description of state:

- $U = 3/2nRT$
- H

Path variables change depending on how the system proceeds:

- w, reversible or irreversible

$$w = -pdV$$

$$w = -nRT\ln(V_2/V_1)$$

- q, reversible or irreversible

Ch 3 Review: Definition of S and Carnot

- Understand the Second Law and its implications
- Spontaneity of reaction, entropy, free energy, Third Law

$dG < 0$, spontaneous

$dS = q/T \therefore$ at constant p and T ,

$dG = 0$

Second Law: Net entropy
(universe) must increase

Third Law: Establishes an entropic
baseline, $S_A(0K) \equiv 0$

1. Isothermal expansion

$$q_1 = -w_1 = nRT_{\text{hot}} \ln(V_2/V_1)$$

2. Adiabatic expansion, $q_2 = 0$

$$dU = nR \ln(V_2/V_3)$$

3. Isothermal compression

$$q_3 = -w_3 = nRT_{\text{cold}} \ln(V_4/V_3)$$

4. Adiabatic compression, $q_4 = 0$

$$dU = nR \ln(V_4/V_1)$$

Ch 4 Review: G, Chemical Potential, K, and a

- Understand the connections between G, K, and mu
- Understand how activities (a) affects G and K

$$G(p, V, T, n_x), \mu_A = \left(\frac{\partial G}{\partial n_A}\right)_{T,P,n_i \neq n_A}$$

$$G = \sum n_i \mu_i$$

$$\mu_A = \mu^\circ_A + RT \ln(a_A)$$

Pure substances:

$$a = 1$$

Debye-Huckel (pg. 145)

Q = reaction quotient

Q > K, move toward r

Q < K, move toward p

Q = K, at equilibrium

pV Work (entropy):

$$\Delta_r G(T_2) - \Delta_r G(T_1) = -(T_2 - T_1) \Delta_r S$$

Gibbs-Helmholtz (enthalpy):

$$\frac{\Delta_r G(T_2)}{T_2} - \frac{\Delta_r G(T_1)}{T_1} = -\Delta_r H \int_{T_1}^{T_2} \frac{1}{T^2} dT = -\Delta_r H \left[\frac{1}{T_2} - \frac{1}{T_1} \right]$$

Questions?