Physical Chemistry (Chem 132A)

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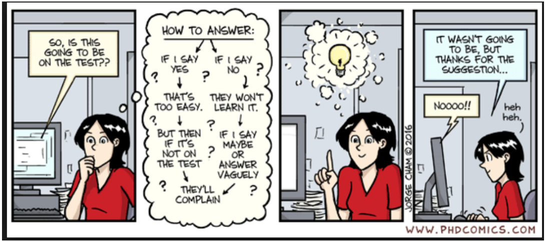


Department of Chemistry, University of California, Irvine, 2208 Natural Sciences II

October 23, 2017

Exam Wednesday (10/25/17)!

- 45 Minute Exam
- Try to be here at 10:50am
- Bring your I.D. and Sit in YOUR seat!
- Do not bring excess 'stuff' to the exam.
- Questions, Comments, Concerns, Raise your hand!
- You CANNOT leave early!
- Bring a calculator (nothing that can access internet, etc).

One 8.5 by 11 (in.) piece of paper with HAND-WRITTEN notes (equations and text). You can use both sides of the paper and write whatever you want!

Everything is on the Exam

- Yes! You should read the book.
- Yes! The lecture material is on the exam.
- Yes! The Webassign is on the exam.
- Yes! The discussion problems are on the exam.
- Yes! Everything covered in Chapters 2, 3, and 4, or topics from discussion and lecture are on the exam.
- STOP! Asking what you should study... I do not know you!
- Stop! Asking for our office/office hours (until after the exam)!
- Consider looking at the Github!

The Story So Far

- Terms: Reversible, Adiabatic, Isochoric, Open, ...
- The Laws of Thermodynamics

The First Law, The Second Law, and The Third Law.

- Thermodynamic Potentials

Internal Energy, Enthalpy, Helmholtz, Gibbs.

- State Functions, Path Functions, Equations of State.
- Total Differentials and Partial Derivatives.

Heat Capacity, Expansion Coefficient, Joule-Thomson Coefficient.

- Deviations from Perfect (Ideal) Behavior.

The Story So Far (Part 2)

Gibbs Free Energy:

- Characteristic variables: G(T,P)
- As a function of Temperature only $\Rightarrow$ Gibbs-Helmholtz Equation.
- As a function of Pressure only $\Rightarrow$ fugacity.
- Chemical Potential!

Phases:

- $\mu \equiv G_m$ (single component system).
- Phase Diagrams!
- solid, liquid, gas, supercritical fluid, triple point, phase line.
- Phase Rule
- First Order Phase Transition
- Second Order Phase Transition
- Clapeyron equation ($\mu(\alpha) = \mu(\beta)$)

Relax!

- Feel Free to attend discussion Tuesday. Come ready to discuss, bring conceptual questions!

- No Discussion Wednesday!

- Thursday and Friday discussions will review the exam.

- Wait until we report back on grades before panicking.

- Come speak to the TAs or Professor Hemminger before taking 'drastic measures'.

Enthalpy

Consider the following chemical reaction.

$$CH_4(g) + O_2(g) \rightleftharpoons CO_2(g) + H_2O(l) \quad (1)$$

Calculate the Enthalpy of Reaction for this reaction using standard Enthalpy of Formation values from the book.

SOLUTION: Start by Balancing The Equation!

$$CH_4(g) + 2\,O_2(g) \rightleftharpoons CO_2(g) + 2\,H_2O(l) \quad (2)$$

Now **Algebraically** solve the question.

$$\Delta H^0_{\mathrm{rxn}}[298] = \quad (3)$$

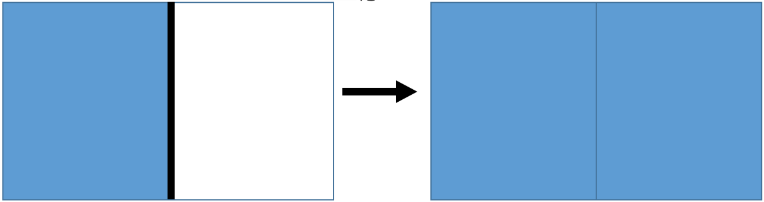
$$\Delta H_f^0(CO_{2,g}) + \Delta 2H_f^0(H_2O_{,l}) - \Delta H_f^0(CH_{4,g}) - \Delta 2H_f^0(O_{2,g}) \quad (4)$$

$$\Delta H^0_{\mathrm{rxn}}[298] = -890.36 \quad \mathrm{kJ/mol} \quad (5)$$

Entropy

Consider the free expansion of one mole of a perfect gas that doubles its volume. Accounting for PV work only, determine the change in Internal Energy, work, heat, and Entropy for this process.

$$\Delta S = ?$$



Entropy Solution:

- ΔU

$$U(T), \Rightarrow \Delta U = 0 \tag{6}$$

- w

w = 0, by definition of Free Expansion.

- q

$$\Delta U = q + w \Rightarrow q = 0 \tag{7}$$

- ΔS

$$S = \frac{q_r}{T} \tag{8}$$

Entropy Solution (Part 2):

Consider: A reversible isothermal expansion, from V_1 to V_2.

$$U = q + w, \Rightarrow q = -w \tag{9}$$

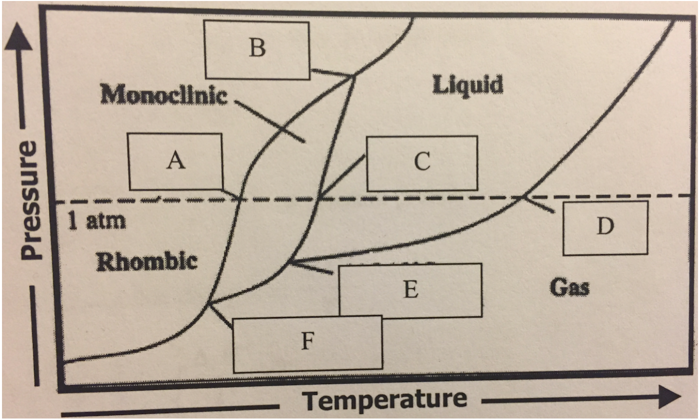
$$\begin{aligned} w &= \int_{V_1}^{V_2} -P_{\text{ext}} dV \\ w &= \int_{V_1}^{V_2} -P_{\text{g}} dV \\ w &= -nRT \int_{V_1}^{V_2} \frac{dV}{V} \\ w &= -RT \ln(2) \end{aligned}$$

$$\Delta S_{\text{univ}} = \Delta S + \Delta S_{\text{surr}} \tag{10}$$

$$\Delta S_{\text{univ}} = \Delta S = R \ln(2) > 0 \tag{11}$$

Sulfur

- Describe the Phase Diagram of Sulfur provided below (be sure to assign each letter).



Sulfur Solution:

Phases:

P-T Phase Diagram with: two solid phases (rhombic, monoclinic), a liquid, and a gas phase (would assume if we keep heating we could get supercritical, but not on graph).

Triple Points:

- F: $\mu_{\text{rhombic}} = \mu_{\text{monoclinic}} = \mu_{\text{gas}}$
- E: $\mu_{\text{liquid}} = \mu_{\text{monoclinic}} = \mu_{\text{gas}}$
- B: $\mu_{\text{rhombic}} = \mu_{\text{monoclinic}} = \mu_{\text{liquid}}$

Transition Points:

- A: $\mu_{\text{rhombic}} = \mu_{\text{monoclinic}}$
- C: $\mu_{\text{monoclinic}} = \mu_{\text{liquid}}$
- D: $\mu_{\text{liquid}} = \mu_{\text{gas}}$

Will an increase in Pressure raise or lower the melting point of sulfur? Raise!

Summary

- Read/Understand the book (hint try Google).
- Try the Discussion Problems (don't use solutions as a crutch).
- Look at Webassign (maybe focus on interesting problems).
- Look online or other books for inspiration.
- Make your 'cheat sheet'!
- Learn where your seat is!