

Chemistry 1A, Spring 2009

KEY

Midterm 3 April 13, 2009

(90 min, closed book)

Name: _____

SID: _____

TA Name: _____

- There are 20 Multiple choice questions worth 3 points each.
- There are 3, multi-part short answer questions.
- For the multiple choice section, fill in the Scantron form AND circle your answer on the exam.
- Put your written answers in the boxes provided. Full credit cannot be gained for answers outside the boxes provided.
- The lecture, homework, chemquizzes, discussion or experiment that each question is based upon is listed after the question e.g. [L3, HW 1.13, CQ 7.3]

Question	Points	Score
Multiple Choice Section	60	
Question 21, K and ΔG	8	
Question 22, Multiple K	13	
Question 23abc, Haber	9	
Question 23defg, Haber	10	
Total	100	

Quantum:

$$E = hv$$

$$\lambda v = c$$

$$\lambda_{\text{deBroglie}} = h / p = h / mv$$

$$E_{\text{kin}}(e^-) = hv - \Phi = hv - hv_0$$

$$E_n = -\frac{Z^2}{n^2} R_\infty$$

$$\Delta x \Delta p \sim h$$

$$p = mv$$

Particle in a box (1-D Quantum):

$$E_n = h^2 n^2 / 8mL^2; n = 1, 2, 3...$$

Vibrational:

$$E_v = (v + 1/2) hA / 2\pi; A = (k/m)^{1/2}$$

Rotational:

$$E_n = n(n + 1) hB; B = h / 8\pi^2 I; I = 2mr^2$$

$$m = m_A m_B / (m_A + m_B)$$

Ideal Gas:

$$PV = nRT$$

Constants:

$$N_0 = 6.02214 \times 10^{23} \text{ mol}^{-1}$$

$$R_\infty = 2.179874 \times 10^{-18} \text{ J}$$

$$R_\infty = 3.28984 \times 10^{15} \text{ Hz}$$

$$k = 1.38066 \times 10^{-23} \text{ J K}^{-1}$$

$$h = 6.62608 \times 10^{-34} \text{ J s}$$

$$m_e = 101939 \times 10^{-31} \text{ kg}$$

$$c = 2.99792 \times 10^8 \text{ m s}^{-1}$$

$$T(\text{K}) = T(\text{C}) + 273.15$$

$$F = 96,485 \text{ C / mol}$$

$$1 \text{ V} = 1 \text{ J / C}$$

Gas Constant:

$$R = 8.31451 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$R = 8.20578 \times 10^{-2} \text{ L atm K}^{-1} \text{ mol}^{-1}$$

$$1 \text{ nm} = 10^{-9} \text{ m}$$

Thermodynamics:

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

$$\Delta H^\circ = \sum \Delta H^\circ_f(\text{products}) - \sum \Delta H^\circ_f(\text{reactants})$$

$$\Delta S^\circ = \sum S^\circ(\text{products}) - \sum S^\circ(\text{reactants})$$

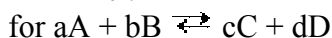
$$\Delta G^\circ = \sum \Delta G^\circ_f(\text{products}) - \sum \Delta G^\circ_f(\text{reactants})$$

$$S = k_B \ln W$$

$$\Delta S = q_{\text{rev}} / T$$

$$\Delta E = q + w$$

$$w = -P_{\text{ext}} \Delta V$$



$$Q = \frac{[C]^c [D]^d}{[A]^a [B]^b} \quad \text{At equilibrium, } Q = K$$

$$\Delta G = \Delta G^\circ + RT \ln Q$$

$$G = G^\circ + RT \ln(a); a = \text{activity} = \gamma P / P^\circ \text{ or } \gamma[A] / [A]^\circ$$

$$\Delta G^\circ = -RT \ln K$$

$$\Delta G^\circ = -nF\Delta E^\circ$$

$$\Delta E = \Delta E^\circ - (RT/nF) \ln Q$$

$$\ln K = -\frac{\Delta H^\circ}{R} \frac{1}{T} + \frac{\Delta S^\circ}{R}$$

$$\Delta T = ik_{b,f} m$$

$$\Pi = iMRT$$

$$P_{\text{total}} = P_A + P_B = X_A P_A^\circ + X_B P_B^\circ$$

Acid Base:

$$\text{pH} = -\log[\text{H}_3\text{O}^+]$$

$$\text{pX} = -\log X$$

$$\text{pH} = \text{p}K_a + \log \frac{[A^-]}{[HA]}$$

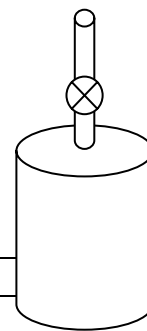
Kinetics:

$$[A]_t = [A]_0 e^{-kt}$$

$$\ln[A]_t = \ln[A]_0 - kt$$

MULTIPLE CHOICE

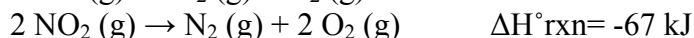
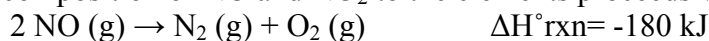
One mole each of gaseous He, CO₂ and NH₃ are placed in a sealed container. The volume of the container is initially 20 L and the temperature is 298K.



- 1) Which gas has the lowest kinetic energy? [CQ 20.1]
A) He B) CO₂ C) NH₃ D) they are all the same
 - 2) Which gas has the most frequent number of collisions with the container walls? [HW 72]
 A) He B) CO₂ C) NH₃ D) they are all the same
 - 3) If the container volume was reduced to 50 mL, which of the gases is most likely to still behave ideally? [L 21]
 A) He B) CO₂ C) NH₃ D) they are all the same
 - 4) The valve on the container is opened and the gases expand adiabatically. The temperature of the gas _____ because _____? [CQ 23.1, HW 6.6]
A) Increases, the gases are traveling faster
B) Increases, the internal energy of the gas is increasing
C) Stays the same, adiabatic means that temperature is constant
D) Decreases, the system loses heat to the surroundings
 E) Decreases, the system does work
-
- 5) A 125.0 g piece of iron is heated to 400 °C and placed in 300.0 g of water at 25 °C. If the specific heat capacities of iron and water are 0.449 J/K•g and 4.184 J/K•g respectively, what will be the final temperature of the water? [Lab 6, HW 6.58]
A) 32 °C
 B) 41 °C
C) 101 °C
D) 383 °C
E) None of the above

- 6) A CD player and its battery together do 500 kJ of work, and the battery also releases 250 kJ of energy as heat and the CD player releases 50 kJ as heat due to friction from spinning. What is the change in internal energy of the system, with the system regarded as the battery and CD player together? [HW 6.52]
- A) +200 kJ B) -700 kJ C) -800 kJ D) -200 kJ E) -750 kJ

The decomposition of NO and NO₂ to the elements proceeds via the following two reactions.



- 7) Calculate the enthalpy change for the reaction: [HW 6.68]
- $$2 \text{NO} (\text{g}) + \text{O}_2 (\text{g}) \rightarrow 2 \text{NO}_2 (\text{g})$$
- A) 247 kJ
B) -247 kJ
 C) -113 kJ
D) -293 kJ
E) None of the above
- 8) Calculate the amount of energy necessary to raise the temperature of 1 cup of water at 23 °C to steam at 105 °C. The specific heat capacity of water is 4.184 J·K⁻¹·g⁻¹ and the specific heat capacity of steam is 4.215 J·K⁻¹·g⁻¹. The density of water can be assumed to be 1.00 g·ml⁻¹. For water, $\Delta H_{\text{vap}} = 40.66 \text{ kJ}\cdot\text{mol}^{-1}$. 1 cup = 0.2366 L [HW 6.38]
- A) 81.2 kJ
B) 122 kJ
C) 534 kJ
 D) 616 kJ
E) None of the above
- 9) At room temperature, an element has a standard state molar entropy that is always _____. [HW 7.24]
- A) negative
B) zero
 C) positive
D) not enough data to answer the question

10) Which of the following equations are true for a system at thermodynamic equilibrium?

[HW 9.2]

A) $\Delta H = T\Delta S$

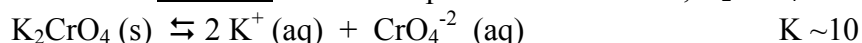
B) $\Delta G = 0$

C) $\Delta H = -T\Delta S$

D) a and b

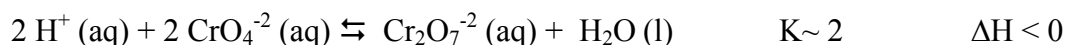
E) b and c

Consider a saturated solution of potassium chromate, K_2CrO_4 .



yellow

yellow



yellow

orange

11) Which of the following will result in a solution of potassium chromate, K_2CrO_4 , turning from yellow to orange? [Lab 7, CQ 28.4]

A) Adding solid potassium chromate, K_2CrO_4

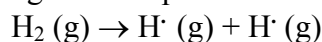
B) Heating the solution

C) Adding KCl

D) Adding a few drops of concentrated NaOH

E) Adding a few drops of concentrated HCl

12) For the following reaction predict the sign of ΔH° and ΔS° :



Under what temperature conditions are the products favored? Explain your reasoning.

[Disc 9]

A) low temperature because the reaction is exothermic

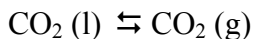
B) low temperature because entropy decreases with decreasing temperature

C) high temperature because the reaction is exothermic

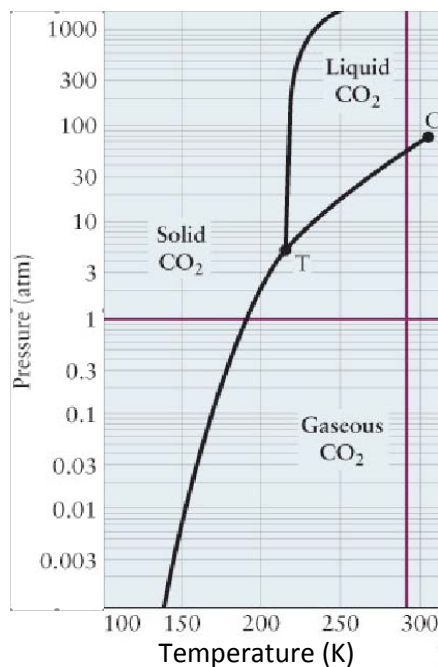
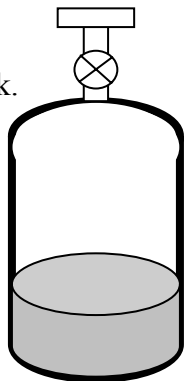
D) high temperature because the entropy term becomes the dominant factor

E) No temperature because enthalpy and entropy terms do not favor products

A CO₂ cylinder for carbonating beverages contains carbon dioxide liquid coexisting at equilibrium with carbon dioxide gas according to the following chemical equation:



The system is the CO₂ inside the tank.



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The phase diagram shown describes how the equilibrium depends on pressure and temperature (the straight lines show 1 atm and 298 K):

13) Using the phase diagram above, estimate the pressure inside the CO₂ cylinder (in atm) at standard temperature (298 K)? [L21]

- A) 1 atm B) 5 atm D) 100 atm

14) At room temperature (298 K) and standard conditions, which is true for the system? [CQ 27.4]

- B) ΔG° = 0 C) ΔG° > 0

15) At room temperature (298 K) and standard conditions, which is true for the system?

- B) Q = K C) Q > K

16) If the tank were cooled to 250K, which is true for the pressure inside the tank?

- A) P₂₉₈ < P₂₅₀ B) P₂₉₈ = P₂₅₀

CO₂ tank, continued

17) If the tank were cooled to 250K, which is true for the equilibrium constant?

A) $K_{298} < K_{250}$

B) $K_{298} = K_{250}$

C) $K_{298} > K_{250}$

The tank valve is opened and some CO₂ gas is released from the system.

18) Which is true for the system immediately after the valve is opened? [HW 9.80]

A) $Q < K$

B) $Q = K$

C) $Q > K$

19) Which is true for the system immediately after the valve is opened for the instantaneous change in free energy (ΔG)? [CQ 30.3]

A) $\Delta G < 0$

B) $\Delta G = 0$

C) $\Delta G > 0$

20) Which is true for the system as the gas is expanding? [HW 7.18]*

A) $\Delta S_{\text{sys}} < 0$


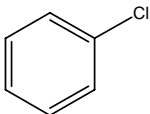
B) $\Delta S_{\text{sys}} = 0$

C) $\Delta S_{\text{sys}} > 0$

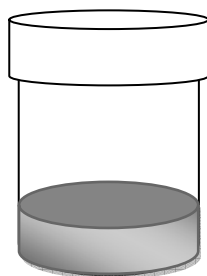
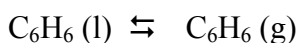
* *Note: All answers were accepted because the question was determined to be too confusing.*

Question 21) Free Energy and the Equilibrium Constant (8 points)

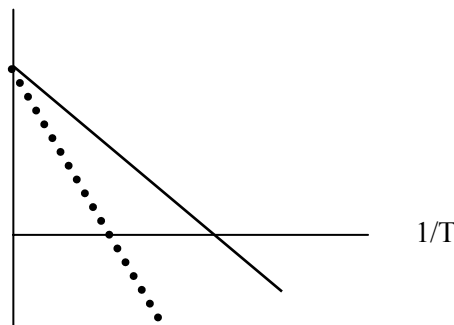
Examine the data below for benzene and chlorobenzene. When placed in a sealed container, the liquid can reach equilibrium with its vapor phase. [CQ 30.2]

Molecule	Formula	Structure	Molar Mass (g/mol)	T _{boiling} (°C)
Benzene	C ₆ H ₆		78.11	80.1
Chlorobenzene	C ₆ H ₅ Cl		112.56	131.8

The graph below shows the relationship between temperature and the equilibrium constant for the vaporization of benzene in a sealed container.



lnK



- a) On the graph above, draw a line corresponding to the vaporization for chlorobenzene.
b) Explain your choice of slope based on the data and the molecular structures.

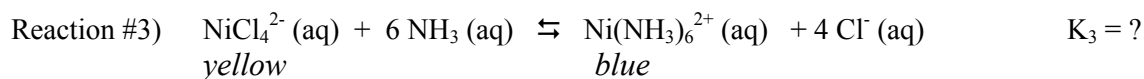
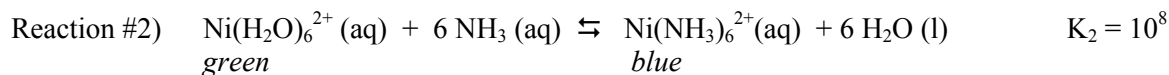
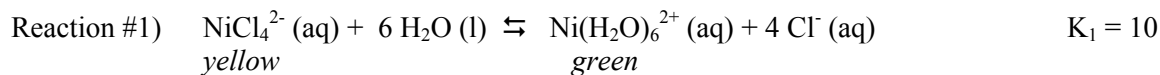
The slope is negative because the reaction is endothermic and the slope = $-\Delta H/R$. The reaction is endothermic because it takes energy to break attractions between molecules in the liquid to evaporate. Chlorobenzene is polar and benzene is nonpolar. The slope for chlorobenzene is steeper than for benzene because the molecules have greater attractive forces.

- c) Explain your choice of y-intercept.

The y-intercept corresponds to $\Delta S/R$. For both molecules this value should be positive because disorder is increasing as you go from a liquid to a gas. The change in entropy for a phase change is similar for similar compounds.

Question 22) Multiple Equilibria [CQ 29.5, HW 9.24] (13 points)

Observing colorful reactions are a great way to study chemical equilibrium. These reactions are similar to a demo done in class.



a) Write the expression for the equilibrium constant (K_3) for Reaction #3.

$$K = \frac{[\text{Ni}(\text{NH}_3)_6^{2+}][\text{Cl}^-]^4}{[\text{NiCl}_4^{2-}][\text{NH}_3]^6}$$

b) What is the value of the equilibrium constant (K_3) for Reaction #3?

$$K_3 = K_1 \times K_2 = 10 \times 10^8 = 10^9$$

A solution is made by mixing 20 mL of 1 M solutions of NiCl_4^{2-} , NH_3 , $\text{Ni}(\text{NH}_3)_6^{2+}$ and Cl^- .

c) What is the value of Q, the reaction quotient for this solution?

When the solutions are mixed, each will have a concentration of $\frac{1}{4}$ M because they dilute each other. $1\text{M} (20\text{mL}/80\text{mL}) = \frac{1}{4}\text{M}$

$$Q = \frac{[\text{Ni}(\text{NH}_3)_6^{2+}][\text{Cl}^-]^4}{[\text{NiCl}_4^{2-}][\text{NH}_3]^6} \quad Q = \frac{[\frac{1}{4}][\frac{1}{4}]^4}{[\frac{1}{4}][\frac{1}{4}]^6} = 16$$

d) What color will this solution be when it reaches equilibrium?

yellow

green

blue

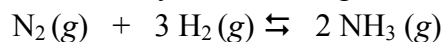
colorless

e) Explain your answer.

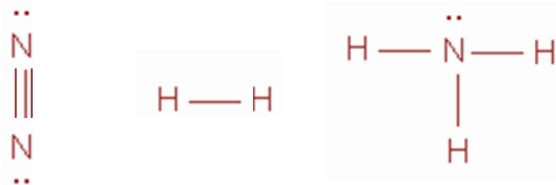
Since K is very large (10^9), at equilibrium the reaction will be very product favored so the solution will be blue.

Question 23) Haber Process [L25, CQ 25.4] (9 points)

Ammonia, NH₃, is an important fertilizer for plants. The Haber process combines atmospheric nitrogen with hydrogen to form ammonia by the following reaction:



- a) Draw the Lewis Structures for N₂, H₂, and NH₃.



- b) Use the following table of bond dissociation energies to calculate the change in enthalpy (ΔH) for the overall balanced reaction.

Bond	Standard Bond Dissociation Energy, BDE (kJ/mol)
N≡N	932
N=N	409
N-N	163
H-H	424
N-H	388

$$\Delta H_{RXN} = \sum BDE_{\text{reactants}} - \sum BDE_{\text{products}}$$

$$\Delta H_{RXN} = [1 \text{ mol}(932 \text{ kJ/mol}) + 3 \text{ mol}(424 \text{ kJ/mol})] - [6 \text{ mol}(388 \text{ kJ/mol})]$$

$$\Delta H_{RXN} = -124 \text{ kJ}$$

$\Delta H = -124 \text{ kJ}$

- c) Use the following table of molar entropies at 298 K to calculate the change in entropy (ΔS) for the overall balanced reaction.

Gas	Molar entropy, S_m° (J/K·mol)
Nitrogen, N ₂ (g)	191.61
Hydrogen, H ₂ (g)	130.68
Ammonia, NH ₃ (g)	192.45

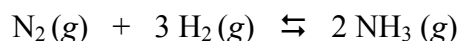
$$\Delta S_{RXN} = \sum S_{\text{products}} - \sum S_{\text{reactants}}$$

$$\Delta S_{RXN} = [2 \text{ mol}(192.45 \text{ J/K}\cdot\text{mol})] - [1 \text{ mol}(191.61 \text{ J/K}\cdot\text{mol}) + 3 \text{ mol}(130.68 \text{ J/K}\cdot\text{mol})]$$

$$\Delta S_{RXN} = -198.75 \text{ J}$$

$\Delta S = -198.75 \text{ J}$

Question 23) Haber Process, continued [L29, HW 9.82] (10 points)



- d) Is the reaction reactant-favored or product-favored at room temperature and standard conditions?

product favored

reactant favored

- e) Explain your reasoning.

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

Since ΔH is negative and ΔS is negative, the ΔG will be negative at low temperatures. If you calculate it ΔG is -64 kJ at room temperature. For systems with a negative ΔG , they are considered product favored.

Some gases can dissolve in water, the extent to which is called molar solubility. Use the following table of molar solubility data to answer the questions below.

Gas	Molar solubility ($\text{mol}\cdot\text{L}^{-1}\cdot\text{atm}^{-1}$)
Nitrogen, N_2 (g)	7.0×10^{-4}
Hydrogen, H_2 (g)	8.5×10^{-4}
Ammonia, NH_3 (g)	1.8×10^{-2}

- f) How would adding water to the bottom of the reaction vessel affect the reaction?

becomes more product favored

becomes more reactant favored

- g) Explain.

Since the molar solubility of Ammonia is 2 orders of magnitude greater than nitrogen and hydrogen, many more moles of ammonia will dissolve into the water as it is produced in the reaction. By removing the product, ammonia gas, as it is formed, the reaction becomes more product driven by Le Chatelier's principle. So, by adding water to the reaction vessel, more ammonia will be produced and drive the reaction more towards favoring products.