Chemistry 112, Spring 2007 Prof. Metz Exam 2 Solutions April 5, 2007
Each question is worth 5 points, unless otherwise indicated

1. A proposed mechanism for the reduction of NO by H_2 is:

$$NO + NO \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} N_2O_2 \qquad \text{fast, equilibrium}$$

$$N_2O_2 + H_2 \xrightarrow{k_2} N_2O + H_2O \qquad \text{slow}$$

The rate law consistent with this mechanism is:
Note: k is a combination of k_1, k_{-1} and k_2

(A) Rate = $k[NO]^2$
(B) Rate = $k[NO][H_2]$
(C) Rate = $k[NO]^2[H_2]$
(D) Rate = $k[N_2O][H_2O]$
(E) Rate = $k[NO]^2[N_2O][H_2O]$

The rate-determining reaction is the second one, so
Rate = $k_2[N_2O_2][H_2]$
However, N_2O_2 is not a reactant or product overall (it's an intermediate), so express $[N_2O_2]$ in terms of reactant concetrations. To do this, use the first reaction. It's an equilibrium, so
Forward reaction rate = reverse reaction rate
$k_1[NO]^2 = k_{-1}[N_2O_2]$
So, $[N_2O_2] = (k_1/k_{-1})[NO]^2$
So, Rate = $k_2[N_2O_2][H_2]$ (from above), then plug in expression for $[N_2O_2]$ to get
Rate = $k_2(k_1/k_{-1})[NO]^2[H_2]$, so Rate = $k\,[NO]^2[H_2]$

Use the following information to answer questions 2 and 3:
A proposed mechanism for the decomposition of hydrogen peroxide by bromide ion is:

$$H_2O_2 + Br^- \rightarrow H_2O + BrO^- \qquad \text{slow}$$
$$H_2O_2 + BrO^- \rightarrow H_2O + O_2 + Br^- \qquad \text{fast}$$

2. A catalyst in this mechanism is:
(A) H_2O_2
(B) H_2O
(C) BrO^-
(D) Br^-
(E) O_2

Br^- is the catalyst. Overall, it is not produced or consumed, but it is added to the reaction and is involved in the rate-limiting step.

3. An intermediate in this mechanism is:
(A) H_2O_2
(B) H_2O
(C) BrO^-
(D) Br^-
(E) O_2

BrO^- is an intermediate. Overall, it's not produced or consumed, and it's not added to the reaction, but is produced by one reaction and consumed by another.

4. A proposed mechanism for the reaction of NO with Br_2 to give BrNO is

$$NO + NO \rightarrow N_2O_2 \qquad \text{slow}$$
$$N_2O_2 + Br_2 \rightarrow 2\,BrNO \qquad \text{fast}$$

The rate law consistent with this mechanism is:

(A) Rate = $k[NO]$
(B) Rate = $k[NO][Br_2]$
(C) Rate = $k[NO]^2$
(D) Rate = $k[N_2O_2][Br_2]$
(E) Rate = $k[NO]^2[Br_2]$

The slow (rate determining) step involves one NO reacting with one NO, so
Rate = $k[NO][NO] = k[NO]^2$

5. Which of the following reaction(s) is/are entropy-favored ($\Delta S_{rxn} > 0$) ?

1. $2\ H_{2\,(g)} + O_{2(g)} \rightarrow 2\ H_2O_{(g)}$
2. $CaCO_{3\,(s)} \rightarrow CaO_{(s)} + CO_{2\,(g)}$
3. $H_2O_{(s)} \rightarrow H_2O_{(liq)}$

(A) 1 only
(B) 2 only
(C) 3 only
(D) 2 and 3 only
(E) 1, 2 and 3

Reaction 1 is not entropy favored because it produces fewer moles of gas than it consumes.
Reaction 2 is entropy favored because it produces more moles of gas than it consumes.
Reaction 3 is also entropy favored because liquid sample of a substance has more entropy than a solid sample of that substance.

6. Egg protein albumin is precipitated when an egg is cooked in boiling water. The activation energy for this reaction is 52 kJ/mol. If this reaction takes 3 minutes (so k = $^1/_{3\ min}$) in Amherst, where water boils at 100 °C, how long does it take at the top of Mt. Washington, where water boils at 90 °C ?

(A) 21 min (B) 16 min (C) 6.5 min *(D) 4.8 min* (E) 3.3 min

$$\ln\left(\frac{k_2}{k_1}\right) = -\frac{E_a}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

T_1 is 100 °C = 373 K, k1 = 1/(3 min) = 0.333 min^{-1}, and T_2 is 90 °C = 363 K.

$$\ln\left(\frac{k_2}{0.333\ \ min^{-1}}\right) = -\frac{52\ \ kJ/mol}{8.314x10^{-3}\ \ kJ/(molK)}\left(\frac{1}{363K} - \frac{1}{373K}\right)$$

$$\ln\left(\frac{k_2}{0.333\ \ min^{-1}}\right) = -6.255x10^3K\left(0.00275482\frac{1}{K} - 0.00268097\frac{1}{K}\right)$$

$$\ln\left(\frac{k_2}{0.333\ \ min^{-1}}\right) = -6.255x10^3K\left(0.00007385\frac{1}{K}\right)$$

$$\ln\left(\frac{k_2}{0.333\ \ min^{-1}}\right) = -0.4619$$

$$\frac{k_2}{0.333\ \ min^{-1}} = e^{-0.4619} = 0.63$$

k_2 = (0.333 min^{-1}) (0.63) = 0.21 min^{-1}
t = 1/k = 1/(0.21 min-1) = 4.8 minutes

For questions 7 and 8 use the thermodynamic data at 298 K given below and the following reaction.

$$Fe_3O_{4\,(s)} + 2\ C_{\,(s)} \rightarrow 3\ Fe_{\,(s)} + 2\ CO_{2\,(g)}$$

	ΔH^o_f (kJ/mol)	ΔG^o_f (kJ/mol)	S^o (J/mol K)
Fe (s)	0	0	27.78
Fe_3O_4 (s)	-1118.4	-1015.4	146.4
C (s)	0	0	5.6
CO_2 (g)	0	-393.5	-394.4
213.74			

7. What is ΔS^o_{rxn} in J/mol K?

(A) 510.82 (B) 427.48 *(C) 353.22* (D) 281.08 (E) 89.52

$$\Delta S^0 = \sum S^0(\text{products}) - \sum S^0(\text{reactants})$$

ΔS^0_{rxn} = 3(27.78) + 2(213.74) – [146.4 + 2(5.6)] = 353.22
Note that ΔS^0_{rxn} is positive, as reaction is entropy favored (consume 0 mol gas, produce 2 moles gas)

8. If magnetite (Fe_3O_4) is placed in 1 atmosphere CO_2 in an isolated system at 298 K:
   (A) a reaction will take place because $\Delta S_{surroundings}$ = 0.
   (B) a reaction will take place because $\Delta S_{universe}$ is positive.
   (C) a reaction will take place because $\Delta G^o_{reaction}$ is positive.
   (D) no reaction will take place because $\Delta S_{universe}$ is negative.
   (E) no reaction will take place because ΔS^o_{rxn} is negative.

This question was poorly worded, so any answer gets full credit. What I was trying to get at is that, although ΔS_{rxn} is positive (entropy of the system), ΔH_{rxn} is also positive, so $\Delta S_{surroundings}$ is negative. Overall, $\Delta S_{universe}$ is negative and the reaction of Fe_3O_4 with C is very reactant favored (ie, Fe_3O_4 really won't react with C at room temperature, as the equilibrium constant favors the reactants)

Thermodynamic values for Problem 9:

Species	**ΔH_f^0(298 K) kJ/mol**	**S^0(298 K) J/(K mol)**	**ΔG_f^0(298 K) kJ/mol**
$C_2H_2(g)$	226.73	200.94	209.20
$C_2H_6(g)$	-83.85	229.2	-31.89
$H_2(g)$	0	130.7	0

9. Use the thermodynamic values above to calculate ΔG_{rxn} in kJ/mol
   at a temperature of 500 K for the reaction
   $C_2H_{2\,(g)} + 2\,H_{2\,(g)} \rightarrow C_2H_{6\,(g)}$

(A) –311 (B) –280 (C) –259 (D) –241 *(E) –194*

$\Delta G = \Delta H - T\Delta S$, so calculate ΔH and ΔS for the reaction using the table, then calculate ΔG. Note that the ΔG values given in the table are at 298 K, so you can't just use them (as ΔG depends on temperature !)
ΔH = -83.85 – [226.73 + (2)(0)] = -310.58 kJ/mol
ΔS = 229.2 – [200.94 + (2)(130.7)] = -233.14 J/mol K
$\Delta G = \Delta H - T\Delta S$
ΔG = -310.58 kJ/mol – (500 K) (-233.14 x 10^{-3} kJ/mol K)
ΔG = -194 kJ/mol
2 pts. partial credit for -241 kJ/mol, which is the value at 298 K (just calculate using ΔG in the table)

10. In class I demonstrated the equilibrium between $Co^{2+}(H_2O)_6$ (pink) and $CoCl_4^{2-}$ (blue):
   $Co^{2+}(H_2O)_{6\,(aq)} + 4\,Cl^-_{(aq)} \rightleftharpoons CoCl_4^{2-}{}_{(aq)} + 6\,H_2O_{(l)}$

The equilibrium constant K for this reaction is

(A) $K = \dfrac{[CoCl_4^{2-}]}{[Co^{2+}(H_2O)_6]}$

(B) $K = \dfrac{[CoCl_4^{2-}][H_2O]}{[Co^{2+}(H_2O)_6][Cl^-]}$

(D) $K = \dfrac{[CoCl_4^{2-}][H_2O]^6}{[Co^{2+}(H_2O)_6][Cl^-]^4}$

(E) $K = \dfrac{[CoCl_4^{2-}]}{[Co^{2+}(H_2O)_6][Cl^-]^4}$

(C) $K = \frac{[CoCl_4^{2-}]}{[Co^{2+}(H_2O)_6][Cl^-]}$

The answer is (E). H_2O is the solvent, so it's not included in the equilibrium constant.

Question 11 refers to the reaction

$$Pb\ (s) + O_2\ (g) \rightarrow PbO_2\ (s)$$

for which ΔH_{rxn} = -277 kJ/mol and ΔS_{rxn} = -201 J/(mol K).

11. What is the temperature in Kelvin above/below which this reaction would have K_p greater than one?

(A) below 726 K
(B) above 726 K
(C) below 1378 K
(D) above 1378 K
(E) There is none

K_p = 1 if ΔG = 0, and K_p > 1 when ΔG is negative. Find T for which ΔG = 0:
$\Delta G = \Delta H - T\Delta S = 0$
$-277\ kJ/mol - T(-201 \times 10^{-3}\ kJ/(mol\ K)) = 0$
$(0.201\ kJ/mol\ K)\ T = 277\ kJ/mol$
$T = (277\ kJ/mol) / (0.201\ kJ/mol\ K) = 1378\ K$
If T is below 1378 K, then ΔG is negative (for example, at T=0 K, ΔG=-277 kJ/mol), and K_p > 1.

12. The reaction

$$H_2\ (g) + I_2\ (g) \rightleftharpoons 2\ HI\ (g)$$

Has K_p = 56 at 298 K. What is ΔG_{rxn} in kJ/mol?

(A) -139 *(B) -10* (C) 10 (D) 33 (E) 139

$\Delta G = -RT \ln(K_p)$
$\Delta G = -(8.314 \times 10^{-3}\ kJ/(mol\ K)\ (298\ K) \ln(56)$
$\Delta G = -9.97\ kJ/mol$

13. The reaction

$$N_{2(g)} + 3\ H_{2(g)} \rightleftharpoons 2\ NH_{3(g)}$$ has K_c=11 at 600 K.

A 1 liter flask is filled with 0.01 moles of N_2, 0.03 moles of H_2 and 0.02 moles of NH_3.
Will any reaction occur ? If so, is NH_3 produced or consumed ?

(A) A reaction will occur; NH_3 will be consumed
(B) A reaction will occur; NH_3 will be produced
(C) No reaction will occur

$$Q = \frac{[NH_3]^2}{[N_2][H_2]^3}$$

$Q = (0.02)^2/[(0.01)(0.03)^3] = 1481$
Q > K_c, so as the reaction proceeds, Q will become smaller (eventually reaching K_c at equilibrium), for Q to decrease, need to make less NH_3, and more N_2 and H_2

14. NOBr dissociates readily:

$$2\ NOBr_{g)} \rightleftharpoons 2\ NO_{(g)} + Br_{2(g)}$$

At equilibrium, the following pressures are found:
P(NOBr) = 0.18 atm, P(NO) = 0.12 atm, P(Br_2) = 0.06 atm.
What is the equilibrium constant K_p for the reaction?

(A) 0.0048
(B) 0.0086
(D) 0.040
(E) 0.22

(C) 0.027

$$K_p = \frac{[NO]^2[Br_2]}{[NOBr]^2}$$ where [NO] means pressure of NO, in atm, etc.

$K_p = (0.12)^2\ (0.06)/(0.18)^2 = 0.0267$

15. A 0.05 M solution of $C_6H_{10}I_2$ is placed in solution and allowed to react via

$C_6H_{10}I_{2\,(aq)} \rightleftharpoons C_6H_{10\,(aq)} + I_{2\,(aq)}$

At equilibrium, $[I_2] = 0.035$ M. What is K for the reaction ?

(A) 2.3 (B) 1.4 (C) 0.70 *(D) 0.082* (E) 0.025

This is a problem that we did in class.

$K_c = [C_6H_{10}][I_2]/[C_6H_{10}I_2]$

	$C_6H_{10}I_2$	C_6H_{10}	I_2
Initial	*0.05*	*0*	*0*
Change	*-x*	*x*	*x*
Equil.	*0.05-x*	*x*	*x*

So, if $[I_2] = 0.035$ M at equilibrium, $x = [I_2] = [C_6H_{10}] = 0.035$ M and $0.05-x = [C_6H_{10}I_2] = 0.015$ M

$K_c = (0.035)(0.035)/0.015 = 0.082$

16. Given the following equilibrium constants:

i) $N_{2(g)} + O_{2(g)} \rightleftharpoons 2\ NO_{(g)}$ $K = 5 \times 10^{-31}$

ii) $N_{2(g)} + 2\ O_{2(g)} \rightleftharpoons 2\ NO_{2(g)}$ $K = 1 \times 10^{-9}$

The equilibrium constant for the reaction

$2\ NO_{(g)} + O_{2(g)} \rightleftharpoons 2\ NO_{2(g)}$ is

(A) 2×10^{21} (D) 5×10^{-22}

(B) 2×10^{12} (E) 5×10^{-40}

(C) 5×10^{-13}

Write the desired reaction in terms of reactions i) and ii):

Reverse of reaction i) has $K= 1/K_i$

-i) $2\ NO_{(g)} \rightleftharpoons N_{2(g)} + O_{2(g)}$ $K=1/K_i = 1/(5 \times 10^{-31})$

+ ii) $N_{2(g)} + 2\ O_{2(g)} \rightleftharpoons 2\ NO_{2(g)}$ $K_{ii} = 1 \times 10^{-9}$

Gives $2\ NO_{(g)} + O_{2(g)} \rightleftharpoons 2\ NO_{2(g)}$ with $K = (1/K_i)\ (K_{ii}) = 2 \times 10^{21}$

17. At 250 °C the reaction

$PCl_{5(g)} \rightleftharpoons PCl_{3(g)} + Cl_{2(g)}$ has $K_p = 1.80$

A 1 liter container is filled with 0.50 atmospheres of PCl_5, what is the PCl_3 pressure (in atmospheres) at equilibrium?

(Note: K_p is fairly large, so a significant amount of the PCl_5 reacts)

(A) 1.34 (D) 0.18

(B) 0.41 (E) 0.092

(C) 0.32

	PCl_5	*PCl_3*	*Cl_2*
Initial	*0.5*	*0*	*0*
Change	*-x*	*x*	*x*
Equil.	*0.5-x*	*x*	*x*

$K_p = [PCl_3][Cl_2]/[PCl_5]$ where [] indicates pressure in atm.

$K_p = (x)(x)/(0.5-x) = 1.80$

Could assume that x is small, but this turns out to be a poor assumption (note that K_p is not small; also, the hint says that a significant amount of PCl_5 reacts, so x isn't small).

So, solve the quadratic equation without approximations:
$x^2 = 1.80\ (0.5 - x)$
$x^2 + 1.8\ x - 0.9 = 0$
$Ax^2 + Bx + C = 0$

$$x = \frac{-B \pm \sqrt{B^2 - 4AC}}{2A}$$

$$x = \frac{-1.8 \pm \sqrt{(1.8)^2 - 4(1)(-0.9)}}{2(1)}$$

$$x = \frac{-1.8 \pm \sqrt{6.84}}{2}$$

x = -2.21, 0.408
The negative root is unphysical, so x = 0.408 atm
$[PCl_3] = x = 0.408$ atm

18. A container is filled with 0.2 atmospheres of NO_2. The following reaction occurs:

$$2\ NO_{2\ (g)} \rightleftharpoons NO_{(g)} + NO_{3\ (g)} \qquad K_p = 3.0 \times 10^{-6}$$

What is the NO_3 pressure (in atmospheres) at equilibrium ?
(Hint: K_p is so small that very little of the NO_2 decomposes)
(A) 7.7×10^{-4}
(B) 3.5×10^{-4}
(C) 1.7×10^{-4}
(D) 3.0×10^{-6}
(E) 6.0×10^{-7}

	NO_2	NO	NO_3
Initial	*0.2*	*0*	*0*
Change	*-2x*	*x*	*x*
Equil.	*0.2-2x*	*x*	*x*

$K_p = [NO][NO_3]/[NO_2]^2$ where [] indicates pressure in atm.
$K_p = (x)(x)/(0.2-2x)^2 = 3.0 \times 10^{-6}$
Because Kp is so small, it's probably a good approximation to assume that x is small (note that that's what the hint says). If x is small, then
0.2 – 2x is approximately 0.2, so
$(x)(x)/(0.2)^2 = 3.0 \times 10^{-6}$
$x^2/0.04 = 3.0 \times 10^{-6}$
$x^2 = 1.20 \times 10^{-7}$
$x = 3.46 \times 10^{-4}$
Note that this is much less than 0.2, so our approximation is good.
Since $[NO_3] = x$, $[NO_3] = 3.46 \times 10^{-4}$ atm

Questions 19 through 21 refer to the following reaction for which
$K_p = 1.4 \times 10^{-9}$ at 1500K and $\Delta H° = 514$ kJ/mol.

$$2\ CO_{2(g)} \rightleftharpoons 2\ CO_{(g)} + O_{2(g)}$$

19. (3 pts) Addition of $CO_{(g)}$ to an equilibrium mixture of the three gases at constant volume and temperature would cause:

(A) K to increase and the amount of $O_{2(g)}$ to increase.
(B) K to decrease and the amount of $O_{2(g)}$ to increase.
(C) K to decrease and the amount of $O_{2(g)}$ to decrease.
(D) no change in K but a decrease in the amount of $O_{2(g)}$.
(E) no change in K but an increase in the amount of $O_{2(g)}$.

Don't change temperature, so don't change K.

Add product, so reaction proceeds in a direction that consumes product (CO and O_2) and produces reactant (CO_2)

20. (3 pts) An equilibrium mixture of the three gases is initially at 1500K. The temperature is increased to 1700K, at constant volume. This would cause:

(A) K to increase and the amount of $O_{2(g)}$ to increase.
(B) K to decrease and the amount of $O_{2(g)}$ to increase.
(C) K to decrease and the amount of $O_{2(g)}$ to decrease.
(D) no change in K but a decrease in the amount of $O_{2(g)}$.
(E) no change in K but an increase in the amount of $O_{2(g)}$.

Change temperature, so change K.
Increase temperature, so reaction proceeds in a direction that uses heat (in the endothermic direction).
Production of CO + O_2 is endothermic, so consume CO_2, producing CO and O_2. Make more product, less reactant, so K increases.

21. (3 pts) Increasing the pressure on an equilibrium mixture by decreasing the volume at constant temperature would cause:

(A) K to increase and the amount of $O_{2(g)}$ to increase.
(B) K to decrease and the amount of $O_{2(g)}$ to increase.
(C) K to decrease and the amount of $O_{2(g)}$ to decrease.
(D) no change in K but a decrease in the amount of $O_{2(g)}$.
(E) no change in K but an increase in the amount of $O_{2(g)}$.

Don't change temperature, so don't change K.
Increase pressure, so reaction proceeds in a direction that decreases pressure, reacting to make fewer moles of gas, so make CO_2 (consuming CO and O_2)

22. (1 pt) You want to make spaghetti for dinner, so you put a pinch of salt (NaCl) into a large pot of boiling water. What happens ?

(A) The NaCl separates into Na and Cl. The sodium reacts violently and explosively with the water, spreading the chlorine gas all over your apartment. You are not happy.
(B) NaCl dissolves endothermically. The water freezes in seconds. You give up and order pizza.
(C) The NaCl dissolves, forming $Na^+_{(aq)}$ and $Cl^-_{(aq)}$. Ten minutes later you are eating yummy pasta and all is right with the world.
(D) NaCl reacts with water, forming a strong acid. It eats through the pot, spills over the oven, and eats through the floor. Your oven falls into the apartment below. You are not happy (nor are your downstairs neighbors)
(E) The sodium in the NaCl has a nuclear reaction with the protons in the water, forming Mg. Incredible amounts of energy are released, forming a microscopic black hole. Soon, the black hole swallows up the water, your kitchen and your apartment. You run out to your car and escape, but your landlord is not happy, and you lose your deposit.

This question is to double-check which version of the exam you had…

Extra Credit (5 pts.)

0.25 atm of N_2 and 0.75 atm of H_2 are placed in a container, which is then sealed. The reaction

$$N_{2(g)} + 3\ H_{2(g)} \rightarrow 2\ NH_{3(g)}$$

is then allowed to proceed until equilibrium is reached. The following pressures of the gases are measured at equilibrium, at two temperatures:

T (K)	$P(N_2)$ (atm)	$P(H_2)$ (atm)	$P(NH_3)$ (atm)
400	0.0118	0.0354	0.4764
700	0.463	1.389	0.074

What are ΔH (in kJ/mol) and ΔS (in J/mol K) for this reaction ?
Assume that the enthalpy and entropy do not change with temperature.
Only answers recorded **on this sheet** will be graded; some partial credit may be awarded for this question, but only for work shown on this sheet.

First, calculate K_p at each temperature:

$$K_p = \frac{[NH_3]^2}{[N_2][H_2]^3}$$ *where [] indicates the pressure of each gas.*

At 400 K, $K_p = (0.4764)^2/[(0.0118)(0.0354)^3] = 4.336 \times 10^5$
At 700 K, $K_p = (0.074)^2/[(0.463)(1.389)^3] = 4.413 \times 10^{-3}$

Then, calculate ΔG at each temperature
$\Delta G = -RT \ln(K_p)$
At 400 K, $\Delta G = -(8.314 \times 10^{-3}$ kJ/mol K) (400 K) ln $(4.336 \times 10^5) = -43.17$ kJ/mol
At 700 K, $\Delta G = -(8.314 \times 10^{-3}$ kJ/mol K) (700 K) ln $(4.413 \times 10^{-3}) = 31.56$ kJ/mol

Finally, find ΔH and ΔS using ΔG = ΔH – TΔS (2 equations and 2 unknowns):
-43.17 kJ/mol = ΔH – (400 K) ΔS
31.56 kJ/mol = ΔH – (700 K) ΔS
Subtract the second from the first to get
-74.73 kJ/mol = (300 K) ΔS
ΔS = -0.249 kJ/mol K = -249 J/mol K
(Note that ΔS is large and negative because there are 2 fewer moles of gas in the products than in the reactants – this isn't the actual value of ΔS for this reaction, but it's pretty close)

Plug the value of ΔS into the first equation above:
-43.17 kJ/mol = ΔH – (400 K) (-0.249 kJ/mol K)
ΔH = -142.77 kJ/mol (again, not the actual ΔH for this reaction, but close)