Chemistry 112, Spring 2007 Prof. Metz Exam 2 Practice

Use the following information to answer questions 1 through 3

A proposed mechanism for the decomposition of hydrogen peroxide by iodide ion is:

$$H_2O_2 + I^- \rightarrow H_2O + OI^- \quad \text{slow}$$
$$H_2O_2 + OI^- \rightarrow H_2O + O_2 + I^- \quad \text{fast}$$

1. The rate law consistent with this mechanism is:

(A) $R = k[H_2O_2]^2$
(B) $R = k[H_2O_2][I^-]$
(C) $R = k[H_2O][OI^-]$
(D) $R = k[H_2O_2]^2[I^-]/[H_2O]$
(E) $R = k[H_2O][OI^-]/[H_2O_2][I^-]$

The rate limiting step is the first reaction, in which one H_2O_2 reacts with one I^-.

2. A catalyst in this mechanism is:

(A) I^-
(B) OI^-
(C) O_2
(D) H_2O
(E) there is none

I^- 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) I^-
(B) OI^-
(C) O_2
(D) H_2O
(E) there is none

OI^- 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. Methanogens are a class of bacteria that metabolize methane. They have an enzyme that allows them to convert methane to methanol. A very simplified mechanism has two steps: First, oxygen binds to the enzyme (E) to produce an enzyme-O_2 complex ($E{\bullet}O_2$), then methane reacts with the $E{\bullet}O_2$ complex to produce methanol:

$$O_2 + E \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} E{\bullet}O_2 \quad \text{fast, equilibrium}$$

$$E{\bullet}O_2 + 2\,CH_4 \xrightarrow{k_2} E + 2\,CH_3OH \quad \text{slow}$$

What is the rate law for this reaction ? (Note: k is a combination of k_1, k_{-1} and k_2)

(A) Rate = $k[O_2][CH_4][E]$
(B) Rate = $k[O_2][CH_4]^2[E]$
(C) Rate = $k[O_2][E]$
(D) Rate = $k[E][CH_4]^2$
(E) Rate = $k[CH_4]^2$

Rate law is determined by rate-limiting (slow) step, so
Rate = $k_2[E{\bullet}O_2][CH_4]^2$
However, $E{\bullet}O_2$ is an intermediate, and it's best to write rate laws in terms of reactants (and products, if necessary), so express $[E{\bullet}O_2]$ in terms of other concentrations. From reaction 1, $k_1[O_2][E] = k_{-1}[E{\bullet}O_2]$, so
$[E{\bullet}O_2] = (k_1/k_{-1})\,[O_2][E]$

Plug this in to the rate equation to get
Rate = $k_2(k_1/k_{-1})$ $[O_2][E][CH_4]^2$

5. A reaction with an activation energy of E_a=100 kJ/mol has a rate constant k=10 s^{-1} at a temperature of 20 °C. What is the rate of this reaction (in s^{-1}) at 50 °C ?

(A) 7.1 (B) 10.0 (C) 14.0 *(D)450* (E) 3300

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

T_1 is 20 °C = 293 K, and T_2 is 50 °C = 323 K.

$$\ln\left(\frac{k_2}{10\ \ s^{-1}}\right) = -\frac{100\ \ kJ/mol}{8.314x10^{-3}\ \ kJ/(molK)}\left(\frac{1}{323K} - \frac{1}{293K}\right)$$

$$\ln\left(\frac{k_2}{10\ \ s^{-1}}\right) = -1.203x10^4 K\left(0.003095975\frac{1}{K} - 0.00341297\frac{1}{K}\right)$$

$$\ln\left(\frac{k_2}{10\ \ s^{-1}}\right) = -1.203x10^4 K\left(-0.00031699\frac{1}{K}\right)$$

$$\ln\left(\frac{k_2}{10\ \ s^{-1}}\right) = 3.8134$$

$$\frac{k_2}{10\ \ s^{-1}} = e^{3.8134} = 45.3$$

$$k_2 = (10\ s^{-1})\ (45.3) = 453\ s^{-1}$$

6. Predict the sign of ΔS^o_{rxn} for the three reactions below:

I. $2NO_2$ (g) → N_2O_4 (liq)
II. NH_4NO_3 (s) → N_2O (g) + $2H_2O$ (g)
III. B (s) + $^3/_2F_2$ (g) → BF_3 (g)

	I	II	III		I	II	III
(A)	+	+	+	(D)	-	-	+
(B)	-	+	-	(E)	+	-	+
(C)	+	+	-				

A reaction that produces more moles of gas than it consumes is entropy favored ($\Delta S>0$), so reactions I and III have $\Delta S<0$, reaction II has $\Delta S>0$

7. Under what circumstances will ΔG for a chemical reaction always be positive?

(A) An endothermic reaction that generates fewer moles of gaseous products than gaseous reactants.

(B) An exothermic reaction that generates solids from liquid reactants.

(C) An exothermic reaction that generates fewer moles of gaseous products than gaseous reactants.

(D) An endothermic reaction that generates more moles of gaseous products than gaseous

reactant.

(E) both (B) and (C) above.

$\Delta G = \Delta H - T\Delta S$
For ΔG to be positive (at all temperatures), ΔH must be positive (endothermic reaction) and $-T\Delta S$ must be positive, so ΔS must be negative (entropy disfavored: generate fewer moles of gas in products than in reactants)

For questions 8 and 9 use the thermodynamic data at 298 K given below and the following reaction.

$$Mg\ (s) + \frac{1}{2} O_2\ (g) \rightarrow MgO\ (s)$$

	ΔH^o_f (kJ/mol)	ΔG^o_f (kJ/mol)	S^o (J/mol K)
Mg (s)	0	0	33
O_2 (g)	0	0	205
MgO (s)	-602	-569	27

8. What is ΔS^o_{rxn} in J/mol K?

(A) -175 (C) -27 *(E) -108*
(B) 27 (D) 108

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

$\Delta S^0_{rxn} = 27 - 33 - (^1/_2)(205) = -108.5$ J/(mol K)
Note that ΔS^0_{rxn} is negative, as reaction is entropy disfavored (consume ½ mol gas, produce 0 moles gas

9. If magnesium metal is ignited in oxygen atmosphere in an isolated system at 300 K:
   (A) no reaction will take place because ΔS^o_{rxn} is negative.
   (B) no reaction will take place because $\Delta S_{surroundings} = 0$.
   (C) a reaction will take place because $\Delta S_{universe}$ is positive.
   (D) no reaction will take place because $\Delta G^o_{reaction}$ is positive.
   (E) a reaction will take place because $\Delta S_{surroundings}$ is negative.

A reaction is spontaneous if $\Delta S_{universe}$ is positive (or equivalently, if $\Delta G^o_{reaction}$ is negative).
Recall that $\Delta S_{universe} = \Delta S_{reaction} + \Delta S_{surroundings}$ and

$$\Delta S_{surroundings} = -\frac{\Delta H_{rxn}}{T}$$

$\Delta H_{rxn} = -602 - (0) - (1/2)(0) = -602$ kJ/mol
$\Delta S_{surroundings} = -(-602$ kJ/mol$)/300$ K $= 2.007$ kJ/(mol K) $= 2007$ J/(mol K)
So, $\Delta S_{universe} = -108$ J/(mol K) $+ 2007$ J/(mol K) $= 1899$ J/(mol K)
The reaction is so exothermic that $\Delta S_{surroundings}$ is very large and positive, completely overwhelming (small, negative) $\Delta S_{universe}$

Questions 10 and 11 refer to the reaction

$$NO\ (g) + \frac{1}{2} O_2\ (g) \rightarrow NO_2\ (g)$$

for which $\Delta H_{rxn} = -57$ kJ/mol and $\Delta S_{rxn} = -73$ J/(mol K) at 298 K.

10. What is ΔG_{rxn} in kJ/mol at 25 °C for this reaction?

(A) -35 (B) -79 (C) -22 (D) 68 (E) 85

$\Delta G = \Delta H - T\Delta S$
$\Delta G = -57$ kJ/mol – (298 K) (-73×10^{-3} kJ/(mol K))
$\Delta G = -35$ kJ/mol

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

(A) below 508 °C
(B) above 508 °C
(C) below 128 °C
(D) above 128 °C
(E) There is none.

$K_p = 1$ if $\Delta G = 0$, and $K_p > 1$ when ΔG is negative. Find T for which $\Delta G = 0$:
$\Delta G = \Delta H - T\Delta S = 0$
-57 kJ/mol – T(-73×10^{-3} kJ/(mol K)) = 0
(0.073 kJ/mol K) T = 57 kJ/mol
T = (57 kJ/mol) / (0.073 kJ/mol K) = 781 K, or 508 °C
If T is below 508 °C, then ΔG is negative (see #10), and $K_p > 1$.

Thermodynamic values for Problems 12 and 13:

Species	ΔH_f^0(298 K) kJ/mol	S^0(298 K) J/(K mol)	ΔG_f^0(298 K) kJ/mol
C(s, graphite)	0	5.6	0
CH_4(g)	-74.87	186.26	-50.8
C_2H_4(g)	52.47	219.36	68.35
C_2H_6(g)	-83.85	229.2	-31.89
CO(g)	-110.53	197.67	-137.17
CO_2(g)	-393.51	213.74	-394.36
H_2(g)	0	130.7	0
H_2O(g)	-241.83	188.84	-228.59
H_2O(l)	-285.83	69.95	-237.15
NO(g)	90.29	210.76	86.58
NO_2(g)	33.1	240.04	51.23
O_2(g)	0	205.07	0

12. Use the thermodynamic values above to calculate ΔG_{rxn} in kJ/mol **at a temperature of 500 K** for the reaction

$$CH_4\,(g) + {}^3/_2\,O_2\,(g) \rightarrow CO\,(g) + 2\,H_2O\,(g)$$

(A) –275 (B) –280 (C) –479 (D) –544 *(E) –560*

$\Delta G = \Delta H - T\Delta S$, 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 = -110.53 + 2(-241.83) – [-74.87 + (3/2)(0)] = -519.32 kJ/mol

ΔS = 197.67 + 2(188.84) – [186.26 + (3/2)(205.07)] = 81.49 J/mol K

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

ΔG = -519.32 kJ/mol – (500 K) (81.49 x 10^{-3} kJ/mol K)

ΔG = -560.1 kJ/mol

13. Use the thermodynamic values at the top of this page to calculate the equilibrium constant K_p at 298 K for the reaction

$$O_2\,(g) + 2\,NO\,(g) \rightarrow 2\,NO_2\,(g)$$

(A) 4.0 x 10^{-13} (B) 6.4 x 10^{-7} (C) 4.8 x 10^{-4} (D) 1.6 x 10^{6} *(E) 2.5 x 10^{12}*

First calculate ΔG for the reaction. Since you want a value at 298 K, can use ΔG^0_f (298 K) values directly:

$$\Delta G^0_{rxn} = \sum G^0_f(\text{products}) - \sum G^0_f(\text{reactants})$$

ΔG_{rxn} = 2(51.23) – [0 + 2(86.58)] = -70.7 kJ/mol

$K_p = e^{-\Delta G/RT}$

$-\Delta G/RT$= -(-70.7 kJ/mol)/[(8.314 x 10^{-3} kJ/mol)(298 K)] = 28.54

So, $K_p = e^{28.54}$ = 2.5 x 10^{12}

Recall that ΔG is negative, so $K_p > 1$.

14. The equilibrium constant K_c for the reaction

$$U_{(s)} + 3\,F_{2(g)} \rightleftharpoons UF_{6(g)} \quad \text{is}$$

(A) $K_c = \dfrac{[UF_6]}{[U][F_2]}$ (D) $K_c = \dfrac{[UF_6]}{[F_2]}$

(B) $K_c = \frac{[UF_6]}{[U][3F_2]}$ (E) $K_c = \frac{[UF_6]}{[F_2]^3}$

(C) $K_c = \frac{[UF_6]}{[U][F_2]^3}$

Don't include U, as it's a solid, so the answer is (E)

15. At a particular temperature, an equilibrium mixture contains the following concentrations of gases:
$[NO_2]$ = 0.32 M, [NO] = 10^{-4} M, $[O_2]$ = 0.045 M. What is the equilibrium constant K_c for the reaction

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

(A) 4.5×10^{-10} (D) 1.4×10^{-5}
(B) 1.4×10^{-9} (E) 4.5×10^{-5}
(C) 4.4×10^{-9}

$$K_c = \frac{[NO]^2[O_2]}{[NO_2]^2}$$

$K_c = (10^{-4})^2\ (0.045)/(0.32)^2 = 4.4 \times 10^{-9}$

16. The reaction

$$H_{2(g)} + I_{2(g)} \rightleftharpoons 2\ HI_{(g)}$$ has K_c=56 at 300 K.

A 1 liter flask is filled with 0.2 moles of H_2, 0.2 moles of I_2 and 0.4 moles of HI.
Will any reaction occur ? If so, is HI produced or consumed ?

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

$$Q = \frac{[HI]^2}{[H_2][I_2]}$$

$Q = (0.4)^2/[(0.2)(0.2)] = 4$
$Q < K_c$, so as the reaction proceeds, Q will become larger (eventually reaching K_c at equilibrium), for Q to increase, need to make more HI product, less H_2 and I_2 reactant

17. 2 moles of $NH_4Cl_{(s)}$ are put into an evacuated 1 liter container at 550 K, and the following reaction occurs:

$$NH_4Cl_{(s)} \rightleftharpoons NH_{3(g)} + HCl_{(g)}$$

At equilibrium, $[NH_{3(g)}] = 2.2 \times 10^{-3}$ M. What is K_c for the reaction ?

(A) 2.2×10^{-3} (B) 2.4×10^{-6} *(C) 4.8×10^{-6}* (D) 9.6×10^{-6} (E) 1.9×10^{-5}

$K_c = [NH_3][HCl]$ (note that NH_4Cl isn't in K_c, as it's a solid).

	NH_4Cl	*NH_3*	*HCl*
Initial	*2*	*0*	*0*
Change	*-x*	*x*	*x*
Equil.	*2-x*	*x*	*x*

So, if $[NH_3] = 2.2 \times 10^{-3}$ M at equilibrium, x = [HCl] = 2.2×10^{-3} M
$K_c = (2.2 \times 10^{-3})(2.2 \times 10^{-3}) = 4.84 \times 10^{-6}$

18. 0.1 moles of $NOCl_{(g)}$ are placed in a 1 liter container at 372 K. The following reaction occurs:

$$2\ NOCl_{(g)} \rightleftharpoons 2\ NO_{(g)} + Cl_{2(g)} \qquad K_c = 1.78 \times 10^{-9}$$

What is the Cl_2 concentration at equilibrium ?
(Hint: K_c is so small that very little of the NOCl decomposes)

(A) 6.67×10^{-6}
(B) 1.33×10^{-5}
(C) 2.66×10^{-5}
(D) 1.64×10^{-4}
(E) 3.28×10^{-4}

	NOCl	*NO*	*Cl_2*
Initial	*0.1*	*0*	*0*
Change	*-2x*	*2x*	*x*
Equil.	*0.1-2x*	*2x*	*x*

$K_c = [NO]^2[Cl_2]/[NOCl]^2$
$K_c = (2x)^2(x)/(0.1-2x)^2 = 1.78 \times 10^{-9}$
Because Kc 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
0.1 – 2x is approximately 0.1, so
$(2x)^2(x)/(0.1)^2 = 1.78 \times 10^{-9}$
$4x^3/0.01 = 1.78 \times 10^{-9}$
$4x^3 = 1.78 \times 10^{-11}$
$x^3 = 4.45 \times 10^{-12}$
$x = 1.64 \times 10^{-4}$
Note that this is much less than 0.1, so our approximation is good.
Since $[Cl_2] = x$, $[Cl_2] = 1.64 \times 10^{-4}$ M

19. At high temperatures, graphite reacts with CO_2 to produce CO:

$$C_{(s)} + CO_{2(g)} \rightleftharpoons 2\ CO_{(g)} \qquad K_c = 0.10$$

If 0.07 moles of CO_2 are placed in a 1 liter container, what is the CO concentration at equilibrium?
(Note: K_c is fairly large, so a significant amount of the CO_2 reacts)

(A) 0.022 M
(B) 0.031 M
(C) 0.043 M
(D) 0.062 M
(E) 0.13 M

	CO_2	*CO*
Initial	*0.07*	*0*
Change	*-x*	*2x*
Equil.	*0.07-x*	*2x*

$K_c = [CO]^2/[CO_2]$ (note that C is a solid, so it's not in K_c)
$K_c = (2x)^2/(0.07 – x) = 0.10$
Could assume that x is small, but this turns out to be a poor assumption (note that K_c is not very small; also, the hint says that a significant amount of CO_2 reacts, so x isn't small).
So, solve the quadratic equation without approximations:
$4x^2 = 0.10\ (0.07 – x)$
$4x^2 + 0.1\ x – 0.007 = 0$
$Ax^2 + Bx + C = 0$

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

$$x = \frac{-0.1 \pm \sqrt{(0.1)^2 - 4(4)(-0.007)}}{2(4)}$$

$$x = \frac{-0.1 \pm \sqrt{0.122}}{8}$$

x = -0.056, 0.0312
The negative root is unphysical, so x = 0.0312 M
[CO] = 2x = 0.0624 M
(I gave partial credit for (B))

Questions 20 through 22 refer to the following gas phase equilibrium for which K_c = 12 at 1100K and
$\Delta H°$ = -198 kJ/mol.

$$2SO_{2(g)} + O_{2(g)} \rightleftharpoons 2SO_{3(g)}$$

20. Increasing the concentration (the pressure) on an equilibrium mixture by decreasing the volume at constant temperature would cause:
   (A) K to decrease and the amount of $O_{2(g)}$ to increase.
   (B) K to decrease and the amount of $O_{2(g)}$ to decrease.
   (C) K to increase and the amount of $O_{2(g)}$ to decrease.
   (D) no change in K but an increase in the amount of $O_{2(g)}$.
   (E) no change in K but a decrease 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 more SO_3 (consuming SO_2 and O_2)

21. Addition of $SO_{3\ (g)}$ to an equilibrium mixture of the three gases at constant volume and temperature
would cause:
   (A) K to decrease and the amount of $O_{2\ (g)}$ to increase.
   (B) K to decrease and the amount of $O_{2\ (g)}$ to decrease.
   (C) K to increase and the amount of $O_{2\ (g)}$ to decrease.
   (D) no change in K but an increase in the amount of $O_{2(g)}$.
   (E) no change in K but a decrease 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 (SO_3), forming more O_2 and SO_2

22. An equilibrium mixture of the three gases is initially at 1100K. The temperature is increased to 1300K, at constant volume. This would cause:
   (A) K to decrease and the amount of $O_{2\ (g)}$ to increase.
   (B) K to decrease and the amount of $O_{2\ (g)}$ to decrease.
   (C) K to increase and the amount of $O_{2\ (g)}$ to decrease.
   (D) no change in K but an increase in the amount of $O_{2(g)}$.
   (E) no change in K but a decrease 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 SO_3 is exothermic, so consume SO_3, producing SO_2 and O_2. Make less product, more reactant, so K decreases.