Chem 116
Test 2 Practice Problems - Solutions

1. Consider the equilibrium $C(s) + CO_2(g) \rightleftharpoons 2CO(g)$ at 1000 °C.

a. Write the expression for K_c.

$$K_c = \frac{[CO]^2}{[CO_2]}$$

b. At 1000 °C, $K_c = 1.603$ mol/L. A mixture of $C(s)$ with 0.750 mol/L $CO(g)$ and 0.500 mol/L $CO_2(g)$ is found at this temperature. Does the system need to **shift right**, **shift left**, or **remain unchanged** to reach equilibrium?

$Q = (0.750)^2/0.500 = 1.12_5 < K_c$ The system must shift right to reach equilibrium.

c. What is the value of K_p at 1000 °C?
$[K_p = K_c(RT)^{\Delta n}$; $R = 0.08206$ L·atm/K·mol = 8.314 J/K·mol; K = °C + 273]

$\Delta n = 2 - 1 = 1 \quad K_p = K_cRT$

$K_p = (1.603 \text{ mol/L})(0.08206 \text{ L atm/K mol})(1273 \text{ K}) = 167.4_5 \text{ atm}$

d. What is the partial pressure of $CO(g)$ in an equilibrium mixture in which the partial pressure of $CO_2(g)$ is 0.100 atm?

$$K_p = \frac{(p_{CO})^2}{p_{CO_2}} = 167.45 \text{ atm} = \frac{(p_{CO})^2}{0.100 \text{ atm}}$$

$$(p_{CO})^2 = 16.74_5 \text{ atm}^2 \qquad p_{CO} = 4.092 \text{ atm}$$

e. If the total pressure on the system at equilibrium is increased, will the equilibrium **shift left**, **shift right**, or **remain unchanged**?

Shift left to make more reactants and lose some product.

f. For the reaction $C(s) + CO_2(g) \rightarrow 2CO(g)$, $\Delta H° = +172.5$ kJ. Would raising the temperature on an equilibrium mixture $C(s) + CO_2(g) \rightleftharpoons 2CO(g)$ favor **$CO(g)$ formation**, **$CO_2(g)$ formation**, or **no change in the equilibrium**?

The forward reaction is endothermic, so higher temperature favors product $CO(g)$ formation.

g. At higher temperature will the value of K_c **increase**, **decrease**, or **remain the same**?

K_c will increase at higher temperature.

2. The reaction $2N_2O_5(g) \rightarrow 4NO_2(g) + O_2(g)$ is first order. The half-life of this reaction at 45 °C is 21.8 min.

a. What is the rate constant, *k*, for this reaction at 45 °C?

$k = 0.693/t_{½} = 0.693/21.8\ \text{min} = 0.0318\ \text{min}^{-1}$

b. A one-liter vessel is filled with 0.500 mol of $N_2O_5(g)$ at 45 °C. How much $N_2O_5(g)$ will remain after 54.5 min.?

elapsed half-lives = $h = t/t_{½} = 54.5\ \text{min}/21.8\ \text{min} = 2.5$

$[N_2O_5] = (0.500\ \text{mol})(½)^{2.5} = (0.500\ \text{mol})(0.177) = 0.0884\ \text{mol}$

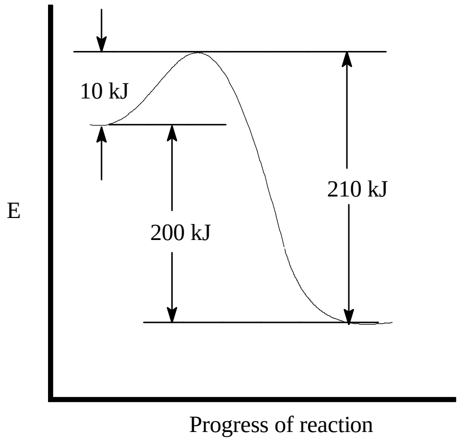
c. A student obtains data for the concentration of $N_2O_5(g)$ over time at 100 °C. How could she use these data to obtain the value of *k* at 100 °C.

Plot ln $[N_2O_5]$ vs. time. The straight line for this plot will have slope equal to $-k$.

d. How could the student use her data to obtain the activation energy for the decomposition of $N_2O_5(g)$? How could she obtain a value for the collision constant, *A*, for the reaction?

Plot ln *k* vs. $1/T$, where *T* is absolute temperature (K). The straight line will have a slope of $-E_a/R$. The *y* intercept will give ln *A*, the logarithm of the collision (Arrhenius) constant. To do this properly, the student should obtain *k* values at more than two temperatures.

3. For the reaction $NO(g) + O_3(g) \rightarrow NO_2(g) + O_2(g)$, $\Delta H° = -200$ kJ. If the activation energy of the forward reaction is 10 kJ, what is the activation energy for the reverse reaction? Sketch a potential energy diagram for the reaction.



$E_a^{\,f} = 10\ \text{kJ} \quad E_a^{\,r} = 210\ \text{kJ} \quad \Delta H = -200\ \text{kJ}$

4. At 750 °C, K_c = 1.30 for the reaction

$$H_2O(g) + CO(g) \rightleftharpoons H_2(g) + CO_2(g)$$

In a one-liter vessel at 750 °C, 1.20 mol of $H_2O(g)$, 1.20 mol of $CO(g)$, 0.100 mol of $H_2(g)$ and 0.100 mol of $CO_2(g)$ are mixed. What will be the concentrations of all species when equilibrium is established?

From the given initial concentrations, calculate Q to see in which direction the reaction runs to reach equilibrium:

$$Q = \frac{[H_2][CO_2]}{[H_2O][CO]} = \frac{(0.100)^2}{(1.20)^2} = 6.9 \times 10^{-3} << K_c = 1.30$$

The reaction must go to the right to reach equilibrium.

$$\begin{array}{ccccccc} H_2O(g) & + & CO(g) & \rightleftharpoons & H_2(g) & + & CO_2(g) \\ 1.20 - x & & 1.20 - x & & 0.100 + x & & 0.100 + x \end{array}$$

$$K_c = 1.30 = \frac{(0.100 + x)^2}{(1.20 - x)^2}$$

Taking the square root of both sides:

$$1.14 = \frac{0.100 + x}{1.20 - x}$$

$$1.36_8 – 1.14x = 0.100 + x$$

$$2.14x = 1.26_8$$

$$x = 0.592_6 = 0.593$$

$$[H_2] = [CO_2] = 0.100 + 0.593 = 0.693 \text{ mol/L}$$

$$[H_2O] = [CO] = 1.20 – 0.593 - 0.60_7 \text{ mol/L} = 0.61 \text{ mol/L}$$

Check: $$Q = \frac{(0.693)^2}{(0.60_7)^2} = 1.3_0 = K_c$$

5. At 425 °C, $K_c = 54.8$ for the equilibrium

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

If 0.500 mol each of $H_2(g)$, $I_2(g)$, and $HI(g)$ are placed in a one-liter vessel, what will be the concentrations of all species when equilibrium is established at 425 °C?

If all reactant and product concentrations are the same, $Q = 1 << K_c = 54.8$. Therefore the reaction must proceed right to reach equilibrium.

$$\begin{array}{ccccc} H_2(g) & + & I_2(g) & \rightleftharpoons & 2HI(g) \\ 0.500 - x & & 0.500 - x & & 0.500 + 2x \end{array}$$

$$K_c = 54.8 = \frac{(0.500 + 2x)^2}{(0.500 - x)^2}$$

Taking the square of both sides:

$$7.40 = \frac{0.500 + 2x}{0.500 - x}$$

$$3.70 - 7.40x = 0.500 + 2x$$

$$9.40x = 3.20$$

$$x = 0.340_4$$

$$[H_2] = [I_2] = 0.500 - 0.340 = 0.160 \text{ mol/L}$$

$$[HI] = 0.500 + (2)(0.340_4) = 1.180_8 \text{ mol/L} = 1.181 \text{ mol/L}$$

Check:

$$Q = \frac{(1.180_8)^2}{(0.160)^2} = 54.4_6 \approx K_c = 54.8$$

6. The reaction $2NO(g) + Cl_2(g) \rightarrow 2NOCl(g)$ might proceed by the following mechanism:

$$NO + Cl_2 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} NOCl_2 \qquad \text{(fast equilibrium)}$$

$$NOCl_2 + NO \xrightarrow{k_2} 2NOCl \qquad \text{(slow)}$$

a. Write the rate law expression ***for the rate-determining step***.

$$rate_2 = k_2[NOCl_2][NO]$$

b. Identify any species that are reaction intermediates.

$$NOCl_2$$

c. Write the equilibrium expression, K_c, ***for the first step***.

$$K_c = \frac{[NOCl_2]}{[NO][Cl_2]}$$

d. Derive the rate law expression that should be observed experimentally if this is the correct mechanism in terms of the observable concentration(s) of [NO] and/or $[Cl_2]$. [Hint: Use your equilibrium expression in part c to write an expression to substitute for an unobservable species that may appear in your *rate* expression for the rate-determining step.]

$$Rate = rate_2 = k_2[NOCl_2][NO]$$

But $NOCl_2$ is a reaction intermediate. We need an expression for $[NOCl_2]$ in terms of observable reactants. Rearranging the K_c expression, we have

$$[NOCl_2] = K_c[NO][Cl_2]$$

Substituting this into the expression for *Rate* gives

$$Rate = k_2\{K_c[NO][Cl_2]\}[NO] = k_{obs}[NO]^2[Cl_2]$$

e. If the observed rate of the reaction is $Rate = k[NO]^2[Cl_2]$, is the proposed mechanism plausible?

Because the derived rate law for the proposed mechanism has the same orders as the observed rate law expression, the mechanism is plausible.

7. Determine the rate law and calculate the value of the rate constant (with the appropriate units) for the reaction

$$A + B \rightarrow \text{products}$$

given the following data:

Exp.	[A]	[B]	Rate, M/s
#1	0.125	0.125	1.04×10^{-4}
#2	0.375	0.125	9.36×10^{-4}
#3	0.375	0.250	9.36×10^{-4}

Comparing #1 and #2, [A] has been tripled and the rate increases by a factor of nine. Because $3^2 = 9$, $\mathit{Rate} \propto [A]^2$

Comparing #2 and #3, [B] has been doubled, but the rate is unchanged. This means the rate law is zero order in [B].

$$\mathit{Rate} = k[A]^2$$

Using data from experiment #1,

$$k = (1.04 \times 10^{-4}\ \mathrm{M\ s^{-1}})/(0.125\ \mathrm{M})^2 = 6.66 \times 10^{-3}\ \mathrm{M^{-1}\ s^{-1}}$$

8. Determine the rate law and calculate the value of the rate constant (with the appropriate units) for the reaction

$$A_2 + B + C \rightarrow AB + AC$$

given the following data:

Exp.	$[A_2]$, M	[B], M	[C], M	Rate, $\mathrm{M \cdot s^{-1}}$
#1	0.125	0.111	0.702	1.07×10^{-3}
#2	0.500	0.111	0.702	2.14×10^{-3}
#3	0.125	0.444	0.702	4.28×10^{-3}
#4	0.125	0.444	0.351	4.28×10^{-3}

From #1 and #2, $[A_2]$ quadruples, but rate increases by only a factor of two. Because $4^{1/2} = 2$, $\mathit{Rate} \propto [A_2]^{1/2}$.

From #1 and #3, [B] doubles, and *Rate* doubles. Therefore, $\mathit{Rate} \propto [B]$.

From #3 and #4, [C] is halved, but there is no effect on *Rate*. Therefore, $\mathit{Rate} \propto [C]^0$.

$$Rate = k[A_2]^{½}\ [B]$$

Using data from experiment #1,

$$k = (1.07 \text{ x } 10^{-3} \text{ M s}^{-1})/(0.125 \text{ M})^{½}(0.111 \text{ M}) = 2.73 \text{ x } 10^{-2} \text{ M}^{-½} \text{ s}^{-1}$$

9. Determine the rate law and calculate the value of the rate constant (with the appropriate units) for the reaction

$$A + B + C \rightarrow \text{products}$$

given the following data:

Exp.	[A], M	[B], M	[C], M	Rate, M·s^{-1}
#1	0.128	0.384	0.702	3.56 x 10^{-3}
#2	0.384	0.384	0.702	1.07 x 10^{-2}
#3	0.128	0.128	0.702	3.56 x 10^{-3}
#4	0.128	0.128	0.351	8.90 x 10^{-4}

From #1 and #2, [A] triples and *Rate* triples. Therefore, $Rate \propto [A]$

From #1 and #3, changing [B] has no effect on the *Rate*. Therefore, $Rate \propto [B]^0$

From #3 and #4, halving [C] make the *Rate* one fourth as fast. Therefore, $Rate \propto [C]^2$

$$Rate = k[A][C]^2$$

Using data from experiment #1,

$$k = (3.56 \text{ x } 10^{-3} \text{ M s}^{-1})/(0.128 \text{ M})(0.702 \text{ M})^2 = 5.64 \text{ x } 10^{-2} \text{ M}^{-2} \text{ s}^{-1}$$