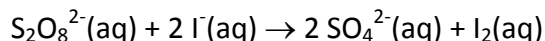Chem1B, General Chemistry II

1.) Peroxodisulfate ($S_2O_8^{2-}$) and iodide (I-) react according to the following **balanced** equation. The data below was collected measuring the rate of the disappearance of $S_2O_8^{2-}$ at 298 K.

$$S_2O_8^{2-}(aq) + 2\ I^-(aq) \rightarrow 2\ SO_4^{2-}(aq) + I_2(aq)$$

Experiment	[$S_2O_8^{2-}$], initial	[I^-], initial	Rate, M/s
1	1.0×10^{-4} M	0.010	1.09
2	2.1×10^{-4} M	0.010	2.18
3	2.1×10^{-4} M	0.0049	1.11

a.) Derive the complete **rate law** for the above reaction.

For $S_2O_8^{2-}$, use Exp. 1 and 2:

$$\left(\frac{1.0 \times 10^{-4}}{2.1 \times 10^{-4}}\right)^x = \frac{1.09}{2.18}$$

$(0.476)^x = 0.5 \rightarrow x = 1$, first order in $S_2O_8^{2-}$

For I-, use Exp. 2 and 3:

$$\left(\frac{0.010}{0.0049}\right)^x = \frac{2.18}{1.11}$$

$(2.040)^x = 1.963 \rightarrow x = 1$, first order in I^-

rate = k[$S_2O_8^{2-}$][I^-]

b.) Calculate the **average rate constant** for all three trials, including units. Express it to three significant figures.

For Exp. 1: 1.09 M/s = k (1.0×10^{-4} M)(0.010 M) $\rightarrow$ k = 1.09×10^6 M^{-1} s^{-1}
For Exp. 2: 2.18 M/s = k (2.1×10^{-4} M)(0.010 M) $\rightarrow$ k = 1.038×10^6 M^{-1} s^{-1}
For Exp. 3: 1.11 M/s = k (2.1×10^{-4} M)(0.0049 M) $\rightarrow$ k = 1.078×10^6 M^{-1} s^{-1}
Average: (1.09×10^6 M^{-1} s^{-1} + 1.038×10^6 M^{-1} s^{-1} + 1.078×10^6 M^{-1} s^{-1})/3
k = $1.068 \times 10^6 \rightarrow$ **1.07×10^6 M^{-1} s^{-1}**

c.) Calculate the rate constant at 315 K, given that the activation energy for this reaction is 51.8 kJ/mol.

Use Arrhenius's Equation (ratio).
$\ln(k_1/1.07 \times 10^6)$ = - (51.8×10^3 J/mol)/(8.314 J/mol * K)[(1/315 K) – (1/298 K)]
$\ln(k_1/1.07 \times 10^6)$ = (- 6230 K)(-0.000181**1** K^{-1})
$\ln(k_1/1.07 \times 10^6)$ = 1.1**2**8
$(k_1/1.07 \times 10^6)$ = $e^{1.128}$ = 3.0**9**0
k_1 = (3.0**9**0)(1.07 × 10^6) = 330**6**874 $\rightarrow$ **3.31×10^6 M^{-1} s^{-1}**

2.) Calculate the half life ($t_{1/2}$) for a second-order reaction that has a rate constant of 3.18×10^{-4} M^{-2} s^{-1} and an initial concentration of 0.0561 M.

Use the half-life equation for the second order reaction.
$t_{1/2}$ = 1/(k · [A]$_0$) = 1/(3.18×10^{-4} M^{-2} s^{-1} · 0.0561 M) = 1/(1.7**84** $\times 10^{-5}$) = 56**0**54 $\rightarrow$ **5.61×10^4 s**

Chem1B, General Chemistry II

3.) Consider the following equilibrium.

$$CO(g) + 3 H_2(g) \rightleftharpoons CH_4(g) + H_2O(g) \qquad \Delta H = -230 \text{ kJ/mol, } K_c = 190 \text{ at } 1000 \text{ K}$$

a.) At 1000 K, does the reaction favor reactants or products? Explain.

**Products**. K_c is larger than one (190 > 1), so the numerator ([products]) is larger.

b.) In which direction will this reaction shift (to reactants or to products) at 200 K? Explain.

Products. The negative enthalpy indicates that the reaction is exothermic; therefore, heat is a *product*. Lowering the temperature will lower the heat, thus forcing the equilibrium to favor the forward reaction to produce more.

c.) In which direction will this reaction shift (to reactants or products) if the volume of the container is *lowered*? Explain.

Products. Lowering the volume will increase the pressure. There are four moles of gas total on the reactants side and two on the products, the equilibrium will favor the forward reaction to reduce the pressure.

d.) Calculate K_p for the above equilibrium.

Use $K_p = K_c(RT)^{\Delta n}$
$K_p = (190)[(0.0821 \text{ L·atm·mol}^{-1} \text{ K}^{-1})(1000 \text{ K})]^{-2}$
$K_p = (190)(0.000\underline{1}48) = 0.0\underline{2}8 \rightarrow \textbf{0.03}$

4.) A 1.00 mole sample of $NaHCO_3(s)$ is put in an evacuated (empty) 2.50 L flask at 373.15 K. Calculate the partial pressures of $CO_2(g)$ and $H_2O(g)$, in atm.

$$2 \text{ NaHCO}_3(s) \rightleftharpoons Na_2CO_3(s) + CO_2(g) + H_2O(g) \qquad K_p = 0.23$$
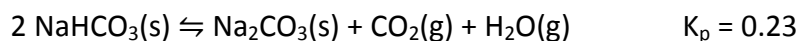
$K_p = (P_{CO2})(P_{H2O})$, pure solids do NOT appear in the equilibrium constant expression.

	CO₂	H₂O
Initial	0	0
Change	+ x	+ x
Equilibrium	x	x

$0.23 = (x)(x) \rightarrow x = \sqrt{0.23} = 0.4\underline{7}9 \rightarrow 0.48 \text{ atm}$
For $CO_2(g)$: **0.48 atm**
For $H_2O(g)$: **0.48 atm**
Total pressure: 0.48 atm + 0.48 atm = 0.96 atm

5.) Consider the following equilibrium.

$$Ag^+(aq) + Fe^{2+}(aq) \leftrightarrows Ag(s) + Fe^{3+}(aq) \qquad K_c = 2.98$$
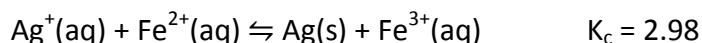
Initially, the solutions are prepared with excess Ag(s), $[Ag^+] = [Fe^{2+}] = 0.200$ M, and $[Fe^{3+}] = 0.350$ M. Calculate the concentrations of **each** ion at equilibrium.

Calculate Q to compare to K_c.

$Q = \dfrac{(0.350 \text{ M})}{(0.200 \text{ M})(0.200 \text{ M})} = 8.75 > K_c$, therefore <u>backwards</u> reaction will occur.

	Ag^+	Fe^{2+}	Fe^{3+}
Initial	0.200	0.200	0.350
Change	+ x	+ x	- x
Equilibrium	0.200 + x	0.200 + x	0.350 - x

$2.98 = \dfrac{(0.350-x)}{(0.200+x)(0.200+x)} = \dfrac{0.350-x}{0.04+0.400x+x^2}$

$(2.98)(0.04 + 0.400x + x^2) = 0.350 - x$

$2.98x^2 + 1.192x + 0.1192 = 0.350 - x$

$2.98x^2 + 2.192x - 0.2308 = 0$

$x = \dfrac{-2.192 \pm \sqrt{2.192^2 - (4)(2.98)(-0.2308)}}{(2)(2.98)}$

$x = (-2.192 \pm 2.7488)/5.96$, must be + to avoid negative concentration

$x = (-2.192 + 2.7488)/5.96 = (0.5568)/6.06 = 0.09\underline{342}$

$[Ag^+] = 0.200$ M + 0.09342 M = **0.293 M**

$[Fe^{2+}] = 0.200$ M + 0.09342 M = **0.293 M**

$[Fe^{3+}] = 0.350$ M − 0.09342 M = **0.257 M**

6.) The following reaction has an experimentally-derived rate law as given.

$$2\ NO + 2\ H_2 \rightarrow N_2 + 2\ H_2O \qquad \text{rate} = k[NO]^2[H_2]$$

Show that this is consistent with the following three-step mechanism.

  (1) $2\ NO \leftrightarrows N_2O_2$ (forward k_1; backward k_2), *fast*
  (2) $N_2O_2 + H_2 \rightarrow N_2O + H_2O$ (k_3), *slow*
  (3) $N_2O + H_2 \rightarrow N_2 + H_2O$ (k_4), *fast*

Rate-determining step: $N_2O_2 + H_2 \rightarrow N_2O + H_2O$, rate $= k_3[N_2O_2][H_2]$
From (1): $k_1[NO]^2 = k_2[N_2O_2]$, so $[N_2O_2] = (k_1[NO]^2)/k_2$
Therefore,
rate $= k_3(k_1[NO]^2/k_2)[H_2] = (k_3k_1/k_2)[NO]^2[H_2]$