Exam 2 Review Key

1. Reaction Rate

   (a) How is the rate at which ozone disappears related to the rate at which oxygen appears in the reaction $2\,O_3(g) \longrightarrow 3\,O_2(g)$? If the rate at which O2 appears is 6.0×10^{-5} M/s at a particular instant, what is the rate of disappearance of O_3 at the same time?
   Ignoring the sign difference between disappearance and appearance and using the equation rate of $X = \frac{\nu_x}{\nu_y}$ rate of Y, where ν represents the stoichiometric coefficient of X or Y, we get the answer:
   rate of disappeareance of ozone $= \frac{2}{3}$ rate of appearance of oxygen
   $\implies$ rate of disappearance of ozone $= 4.0\times10^{-5}$ M/s

   (b) At a certain time in a reaction, substance A is disappearing at a rate of 4.0×10^{-1} M/s, substance B is appearing at a rate of 2.0×10^{-2} M/s and substance C is appearing at a rate of 6.0×10^{-2} M/s. What is the stoichiometry of the reaction? Write out the reaction with the proper coefficients.
   Assigning a coefficient of 1 to the substance with the lowest rate and assigning the others in terms of this gives $2\,A \longrightarrow B + 3\,C$

   (c) If the rate of decomposition of N_2O_5 in the reaction $2\,N_2O_5 \longrightarrow 4\,NO_2 + O_2$ at a particular instant is 4.2×10^{-7} M/s, what are the rates of appearance for NO_2 and O_2, and what is the rate of reaction?
   rate $NO_2 = \frac{4}{2}$ rate $N_2O_5 = 8.4\times10^{-7}$ M/s
   rate $O_2 = \frac{1}{2}$ rate $N_2O_5 = 2.1\times10^{-7}$ M/s
   The rate of reaction is the same as the rate for the substance with a coefficient of 1, so it is also 2.1×10^{-7}

2. Rate Laws

   (a) Sketch on a graph of concentration vs time the difference between an average rate and an instantaneous rate. What is special about an instantaneous rate?
   As you can see, the instantaneous rate is exactly the rate at a given point, whereas the average
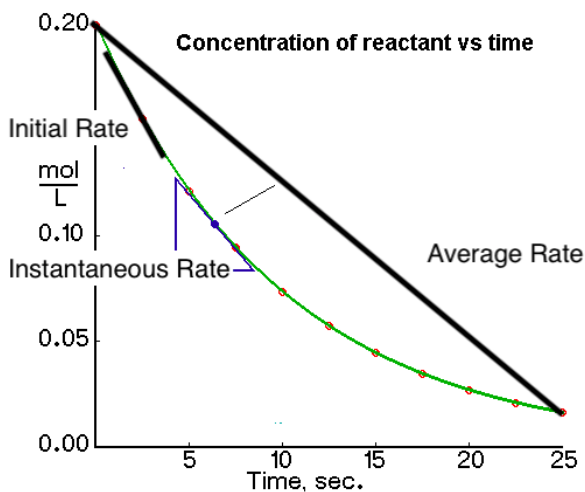
   rate corresponds to the instantaenous rate only if the average is over a short area. The initial rate is special because the graph is approximately linear very close to the beginning, allowing an average rate that can be determined experimentally to give a good approximation of the instantaneous rate.

   (b) Use the data in the table below to determine the rate law for the reaction $A+B+C \longrightarrow$ products, the rate constant (with proper units), and the rate of reaction when all the reactants are at 0.100 M concentrations. (You will probably need the back of the page for this one.)

Run	$[A]_0$	$[B]_0$	$[C]_0$	Initial Rate (M/s)
1	0.151	0.213	0.398	0.480
2	0.251	0.105	0.325	0.356
3	0.151	0.213	0.525	1.102
4	0.151	0.250	0.480	0.988

Recall the method of initial rates begins by taking the ratio of two rate law expressions that for this reaction are of the form rate = $k[A]^x[B]^y[C]^z$. Usually, we find pairs of reactions in which only the initial rate and the concentration of one reactant changes, so we can cancel the rest of the terms. This works for reactant C in this case, using runs 1 and 3:

$$\frac{rate_3}{rate_1} = \frac{k\cancel{[A_3]^x}\cancel{[B_3]^y}[C_3]^z}{k\cancel{[A_1]^x}\cancel{[B_1]^y}[C_1]^z} = \left(\frac{[C_3]}{[C_1]}\right)^z$$

From here, you can take either the log or ln of both sides, which allows you to bring the exponent down in front, and dividing both sides by the logarithm of the concentrations gives

$$\frac{\ln \frac{rate_3}{rate_1}}{\ln \frac{[C_3]}{[C_1]}} = z$$

Plugging in the relevant numbers gives z = 3. Now, we go back to the table and look for a pair of runs where only the initial rate, C and one of the others is changing because while C will not cancel with itself, we can plug in the numbers and the order, z, and still calculate another order. Between runs 1 and 4, A is constant but B and C change, so we will use that pair to calculate y. Start the same way, but this time only k and the A terms will cancel:

$$\frac{rate_4}{rate_1} = \frac{k\cancel{[A_4]^x}[B_4]^y[C_4]^z}{k\cancel{[A_1]^x}[B_1]^y[C_1]^z} = \left(\frac{[B_4]}{[B_1]}\right)^y\left(\frac{[C_4]}{[C_1]}\right)^z$$

At this point, you can choose to plug in numbers and isolate the numeric values to the left side before taking the logarithm, but I prefer to use properties of logarithms to rearrange symbolically:

$$\ln\frac{rate_4}{rate_1} = \ln\left[\left(\frac{[B_4]}{[B_1]}\right)^y\left(\frac{[C_4]}{[C_1]}\right)^z\right] = \ln\left(\frac{[B_4]}{[B_1]}\right)^y + \ln\left(\frac{[C_4]}{[C_1]}\right)^z = y\ln\left(\frac{[B_4]}{[B_1]}\right) + z\ln\left(\frac{[C_4]}{[C_1]}\right)$$

Then, subtract over the C term and divide by the B term to isolate y and find that y = 1:

$$\frac{\ln\frac{rate_4}{rate_1} - z\ln\left(\frac{[C_4]}{[C_1]}\right)}{\ln\frac{[B_4]}{[B_1]}} = y$$

The calculation of x is very similar, but only k will cancel, so the math is slightly more difficult, but you should get x = 2. From there, you have most of the rate law, rate = $k[A]^2[B][C]^3$ and can solve for k by plugging in the values from any of the runs. Using run 1,

$$0.480 = k \times 0.151^2 \times 0.213 \times 0.398^3 \implies k = 0.480/0.151^2 \times 0.213 \times 0.398^3 = 1567$$

But k is not finished without proper units, so use the formula $M^{1-z}\ s^{-1}$, where z is the overall order of the reaction to get k = 1567 $M^{-5}\ s^{-1}$. The overall order is just the sum of the individual orders so z in this case is 3 + 2 + 1 = 6. The rate law is now rate = $1567[A]^2[B][C]^3$ and the rate when the concentration of all reactants is 0.100 M is rate = 1567 $\times 0.100^2 \times 0.100 \times 0.100^3 = 1567 \times 0.100^6 = 1567 \times 10^{-6} = 1.567 \times 10^{-3}$ M/s

(c) The decomposition of dimethyl ether at 510°C has a rate constant of 6.8×10^{-4}. If it has an initial pressure of 135 torr, what is its pressure after 1420 s, assuming it follows zero-order kinetics? What about first-order? Second-order?

Zero-order integrated rate law: $[A] = (A)_0 - kt$
First-order: $\ln[A] = \ln(A)_0 - kt$
Second-order: $1/[A] = 1/(A)_0 + kt$
Just plug in the given values to each of these equations and get 134 torr for zero-order, 51 torr for first-order, and 1 torr for second-order.

(d) Calculate the rate constant for the decay of tritium given the fact that it follows first order kinetics and has a half-life of 12.32 years.

   Using the first-order rate law from above, and plugging in $[A] = 1$ and $(A)_0 = 2$ because there will be half of what you started with after one half life, you get $\ln(1) - \ln(2) = \ln(1/2) = -kt \implies k = \ln(2)/t$ from the fact that a negative logarithm is the same as inverting its argument. This gives $k = 0.056$ years^{-1}.

3. Equilibrium

   (a) What is the defining characteristic of equilibrium?
   rate of the forward reaction = rate of reverse reaction

   (b) Write the equilibrium constant expression for the reactions $2\,SO_2(g) + O_2(g) \rightleftharpoons 2\,SO_3(g)$, $2\,SO_2(s) + O_2(g) \rightleftharpoons 2\,SO_3(g)$, and $2\,SO_2(g) + O_2(l) \rightleftharpoons 2\,SO_3(g)$.
   Pure liquids and solids are left out of the equilibrium constant expression so we get $K_c = \frac{[SO_3]^2}{[O_2][SO_2]^2}$, $\frac{[SO_3]^2}{[O_2]}$, and $\frac{[SO_3]^2}{[SO_2]^2}$

4. K vs Q

   (a) At $448°$ C, the equilibrium concentrations for the reaction $H_2(g) + I_2(g) \rightleftharpoons 2\,HI(g)$ are $[H_2]$ = 0.20 M, $[I_2]$ = 0.10 M, and $[HI]$ = 1.00 M. Calculate the equilibrium constant, K_c for this reaction. In which direction will the reaction proceed if we start with 2.0×10^{-2} moles of HI, 1.0×10^{-2} moles of H_2, and 3.0×10^{-2} moles of I_2 in a 2.00-L container?
   First calculate K_c using the given equilibrium concentrations to be 50. Then, calculate Q_c at the given concentrations and use its relation to K_c to determine the direction of the reaction. $Q_c = 1.33 < K_c$ so the reaction proceeds toward the products.

   (b) For the exothermic reaction $N_2(g) + 3\,H_2(g) \rightleftharpoons 2\,NH_3(g)$, known as the Haber process, use Le Chatelier's Principle to predict how the reaction will respond to

   i. Increasing the temperature For exothermic reactions, treat heat as a product, so adding products shifts the equilibrium toward the reactants
   ii. Removing some ammonia Decreasing products shifts toward products
   iii. Adding more nitrogen Adding reactants shifts toward prodcuts

   (c) Given the reactions $HF\,(aq) \rightleftharpoons H^+(aq) + F^-(aq)$ and $H_2C_2O_4(aq) \rightleftharpoons 2\,H^+(aq) + C_2O_4{}^{2-}$ and the respective equilibrium constants, $K_c = 6.8 \times 10^{-4}$ and $K_c = 3.8 \times 10^{-6}$, determine the value of K_c for the reaction $2\,HF\,(aq) + C_2O_4{}^{2-}(aq) \rightleftharpoons 2\,F^-(aq) + H_2C_2O_4(aq)$.

$$HF \rightleftharpoons H^+ + F^- \tag{1}$$
$$H_2C_2O_4 \rightleftharpoons 2\,H^+ + C_2O_4{}^{2-} \tag{2}$$
$$2\,HF + C_2O_4{}^{2-} \rightleftharpoons 2\,F^- + H_2C_2O_4 \tag{3}$$
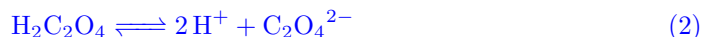
   The sum of equations 1 and 2 does not make equation 3, so some rearrangement is necessary. First, we need to double equation 1, which leads to a squaring of its K_c. We also need the reactants in equation 2 to be the products in equation 3, so we have to reverse equation 2 and take the inverse of its K_c. This gives the system

$$2\,HF \rightleftharpoons 2\,H^+ + 2\,F^- \tag{4}$$
$$2\,H^+ + C_2O_4{}^{2-} \rightleftharpoons H_2C_2O_4 \tag{5}$$
$$2\,HF + C_2O_4{}^{2-} \rightleftharpoons 2\,F^- + H_2C_2O_4 \tag{6}$$

   Now the equations do add up to the desired equation, and the desired K_c is the product of the K_c values for equations 4 and 5, which are the squared K_c of equation 1 and the inverse K_c of equation 2: $K_c = (6.8 \times 10^{-4})^2 \times (3.8 \times 10^{-6})^{-1} = 0.122$.

3

(d) At $800°$ C, the reaction $C(s) + H_2O(g) \rightleftharpoons CO(g) + H_2(g)$ has an equilibrium constant of 14.1. What are the equilibrium concentrations of H_2O, CO and H_2 if we start with 0.100 moles of water in a 1.00-L vessel? Also, what is the minimum amount of carbon needed to achieve equilibrium?
First of all, I edited this question to ask for the equilibrium concentrations of each species instead of partial pressures because for K_c you need to use molar concentrations, so assuming we are using a K_c like we have seen before, this is just a straightforward RICE table calculation.

(R)	$C +$	$H_2O \rightleftharpoons$	$CO +$	H_2
I	–	0.100	0	0
C	–	$-x$	$+x$	$+x$
E	–	$0.100-x$	x	x

Setting K_c equal to the resulting expression and solving for x gives the equilibrium concentrations of CO and H_2, and subtracting x from 0.100 gives the equilibrium concentration of H_2O. Carbon is not included in the equilibrium because it is a pure solid. $K_c = 14.1 = \frac{x^2}{0.100-x} \implies x = 0.0993$, which gives $[CO] = [H_2] = 0.0993$, and $[H_2O] = 0.0007$. Because the stoichiometry of the reaction is 1:1 $C:H_2O$, this is also the same amount of carbon necessary to achieve equilibrium.

5. Acid Base

 (a) When CH_3COOH is dissolved in water, it is called acetic acid. Write the equilibrium for its reaction with water and identify the conjugate acid-base pairs.
 $CH_3COOH + H_2O \rightleftharpoons CH_3COO^- + H_3O^+$
 Water and acetate are the conjugate bases, while acetic acid and hydronium are the conjugate acids.

 (b) Write the equilibrium for the dissociation of hydrochloric acid in liquid ammonia and identify the conjugate pairs.
 $HCl + NH_3 \rightleftharpoons Cl^- + NH_4^+$
 Ammonia and chloride are the conjugate bases while hydrochloric acid and ammonium are the conjugate acids.

 (c) Write the acid-dissociation constant expressions for the previous two problems.
 $K_{a1} = \frac{[H_3O^+][CH_3COO^-]}{[CH_3COOH]}$
 $K_{a2} = \frac{[Cl^-][NH_4^+]}{[HCl]}$

 (d) The K_a for acetic acid is 1.8×10^{-5} and the K_b for formate is 5.6×10^{-11}. Is acetic or formic acid stronger?
 It is easiest to compare these if they are both in terms of K_a so divide K_w by the given K_b to get a K_a for formic acid of 1.8×10^{-4}. From here, recall that the higher the K_a the stronger the acid, so formic acid is stronger.

6. Ionization

 (a) Hydrofluoric acid is a weak acid used in the builiding industry to etch patterns into glass for elegant windows. Because it dissolves glass, it is the only inorganic acid that must be stored in plastic containers. A 0.1 M solution of HF has a pH of 2.1. Calculate $[H_3O^+]$ and $[OH^-]$ for this solution.
 $pH = -\log[H_3O^+]$, so $10^{-pH} = [H_3O^+]$. Additionally, $[H_3O^+] \times [OH^-] = K_w = 1.0 \times 10^{-14}$, so $K_w / [H_3O^+] = [OH^-]$. Using this, $[H_3O^+] = 7.9 \times 10^{-3}$ and $[OH^-] = 1.3 \times 10^{-12}$.

 (b) The pH of a 0.129 M solution of a weak acid, HB, is 2.34. What is the K_a of the weak acid?
 This is a RICE problem, but we have everything we need to calculate the change because we can calculate the equilibrium hydronium concentration just like in the problem above: $[H_3O^+] = 10^{-2.34} = 4.57 \times 10^{-3}$ M

(R)	$HB +$	$H_2O \rightleftharpoons$	$H_3O^+ +$	B^-
I	0.129	–	0	0
C	$-x$	–	$+x$	$+x$
E	$0.129 -x$	–	4.5×10^{-3}	4.5×10^{-3}

This gives $K_a = \frac{(4.5\times10^{-3})^2}{0.129-4.5\times10^{-3}} = 1.6\times10^{-4}$

(c) How many moles of HB must be dissolved in 1.00 liter of aqueous solution to produce a solution with a pH of 2.00?

Like last problem, we are given pH and need to calculate $[H_3O^+]$ using it: $[H_3O^+] = 10^{-2} = 0.01$ M. Then, it is just a simple RICE problem.

(R)	HB + H₂O ⇌ H₃O⁺ + B⁻			
I	x	−	0	0
C	−0.01	−	+0.01	+0.01
E	x − 0.01	−	0.01	0.01

Using the K_a from the previous problem, we get $1.6\times10^{-4} = \frac{0.01^2}{x-0.01}$, and solving this gives x = 0.635 moles, which makes sense at least insofar as it is greater than the number of moles that gave a higher pH in the previous problem.

(d) Find the pH of a 0.115 M solution of ammonia, given the K_a of ammonium is 5.6×10^{-10}.

This is another RICE table, but I tried to trick you by giving you the K_a of the conjugate acid instead of the K_b of ammonia. Converting to K_a and the RICE table are left as an exercise for the reader. Solving for x yields x = 0.00142. Care is required here because this is $[OH^-]$, not $[H_3O^+]$ like we get for acid dissociation, so you can either calculate pOH and get pH by subtracting from 14 or you can convert to $[H_3O^+]$ using K_w as we did previously. If you use the first method, pOH = 2.85, and the corresponding pH is $14 - 2.85 = 11.15$.

(e) Morphine, an opiate derived from the opium poppy (genus *Papaver*), has the molecular formula $C_7H_{19}NO_3$. It is a weakly basic amine, with a K_b of 1.6×10^{-6}. What is the pH of a 0.0045 M solution of morphine?

This is exactly the same as the idea from the previous problem, but I gave you K_b instead. Set up the RICE table and solve for x to get $[OH^-] = 8.4\times10^{-5}$ and pOH = 4.08, which corresponds to a pH of 9.92.

7. BONUS: Sulfur dioxide can be generated by the reaction of sodium hydrogen sulfite ($NaHSO_3$) with hydrochloric acid. Write the balanced chemical equation for the reaction, given that the other products are sodium chloride and water. If 1.9 g of sodium hydrogen sulfite is reacted with excess HCl, what mass of SO_2 is produced? If the gas generated is in a 100 mL vessel at 25° C, and 0.05 mol of O_2 is introduced equilibrium between SO_2, O_2 and SO_3 will be established as shown by $SO_2 + \frac{1}{2}O_2 \rightleftharpoons SO_3$, with a K_c of 2.6×10^{12}. Calculate the equilibrium concentration of each species.