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### QUESTIONS ABOUT MEASURING REACTION RATES

$$1. \quad \text{rate} = \frac{-\Delta[\text{H}_2]}{\Delta \text{time}} \quad \text{rate} = \frac{-\Delta[\text{I}_2]}{\Delta \text{time}} \quad \text{rate} = \frac{\Delta[\text{HI}]}{\Delta \text{time}}$$

These rates are not equal. Since the stoichiometry of the reaction shows that there are 2 moles of HI produced for each  $\text{H}_2$  and  $\text{I}_2$  consumed, then the rate as measured as a function of  $[\text{HI}]$  is twice the rate as measured as a function of  $[\text{H}_2]$  or  $[\text{I}_2]$ . Therefore, the rate of consumption of  $\text{H}_2$  and  $\text{I}_2$  are equal to one-half the rate of production of HI.

$$\text{rate} = \frac{-\Delta[\text{H}_2]}{\Delta \text{time}} = \frac{-\Delta[\text{I}_2]}{\Delta \text{time}} = \frac{1}{2} \times \frac{\Delta[\text{HI}]}{\Delta \text{time}}$$

$$2. \quad \text{a) } \text{rate} = \frac{1}{2} \times \frac{-\Delta[\text{A}]}{\Delta \text{time}} = \frac{-\Delta[\text{B}]}{\Delta \text{time}} = \frac{\Delta[\text{C}]}{\Delta \text{time}} = \frac{1}{3} \times \frac{\Delta[\text{D}]}{\Delta \text{time}}$$

$$\therefore \frac{-\Delta[\text{B}]}{\Delta \text{time}} = \frac{1}{2} \times \frac{-\Delta[\text{A}]}{\Delta \text{time}} = \frac{1}{2} \times (2.8 \times 10^{-3} \text{ Ms}^{-1}) = 1.4 \times 10^{-3} \text{ Ms}^{-1}$$

$$\text{b) } \frac{1}{2} \times \frac{-\Delta[\text{A}]}{\Delta \text{time}} = \frac{1}{3} \times \frac{\Delta[\text{D}]}{\Delta \text{time}} \quad \text{or} \quad \frac{\Delta[\text{D}]}{\Delta \text{time}} = \frac{3}{2} \times \frac{-\Delta[\text{A}]}{\Delta \text{time}} = \frac{3}{2} \times 2.8 \times 10^{-3} \text{ Ms}^{-1} = 4.2 \times 10^{-3} \text{ Ms}^{-1}$$

$$3. \quad \text{a) } \frac{-\Delta[\text{A}]}{\Delta \text{time}} = \frac{-(0.9689 \text{ M} - 0.9986 \text{ M})}{15.00 \text{ min} \times \frac{60 \text{ s}}{1 \text{ min}}} = \frac{0.0297 \text{ M}}{900.0 \text{ s}} = 3.30 \times 10^{-5} \text{ Ms}^{-1}$$

$$\text{b) } \text{rate} = \frac{-\Delta[\text{A}]}{\Delta \text{time}} = \frac{1}{3} \times \frac{-\Delta[\text{B}]}{\Delta \text{time}} = \frac{1}{2} \times \frac{\Delta[\text{C}]}{\Delta \text{time}} = \frac{1}{2} \times \frac{\Delta[\text{D}]}{\Delta \text{time}}$$

$$\frac{-\Delta[\text{A}]}{\Delta \text{time}} = \frac{1}{3} \times \frac{-\Delta[\text{B}]}{\Delta \text{time}} \quad \therefore \quad \frac{\Delta[\text{B}]}{\Delta \text{time}} = 3 \times \frac{-\Delta[\text{A}]}{\Delta \text{time}} = 3 \times 3.30 \times 10^{-5} \text{ Ms}^{-1} = 9.90 \times 10^{-5} \text{ Ms}^{-1}$$

$$\text{c) } \frac{-\Delta[\text{A}]}{\Delta \text{time}} = \frac{1}{2} \times \frac{\Delta[\text{C}]}{\Delta \text{time}} \quad \therefore \quad \frac{\Delta[\text{C}]}{\Delta \text{time}} = 2 \times \frac{-\Delta[\text{A}]}{\Delta \text{time}} = 2 \times 3.30 \times 10^{-5} \text{ Ms}^{-1} = 6.60 \times 10^{-5} \text{ Ms}^{-1}$$

$$\& \quad \frac{-\Delta[\text{A}]}{\Delta \text{time}} = \frac{1}{2} \times \frac{\Delta[\text{D}]}{\Delta \text{time}} \quad \therefore \quad \frac{\Delta[\text{D}]}{\Delta \text{time}} = 2 \times \frac{-\Delta[\text{A}]}{\Delta \text{time}} = 2 \times 3.30 \times 10^{-5} \text{ Ms}^{-1} = 6.60 \times 10^{-5} \text{ Ms}^{-1}$$

4. a) One could follow this reaction by measuring the intensity of the yellow color of the  $\text{Cl}_2$  using a spectrometer like the one used to measure the intensity of the dye in lab. This is probably the easiest method.

One could also follow this reaction by measuring the pressure since the reaction involves 2 moles of gas being converted into 1 mole of gas. Thus, the pressure drop will be proportional to the moles of  $\text{Cl}_2$  or  $\text{C}_2\text{H}_4$  consumed or to the moles of product.

- b) Again, one could also follow this reaction by measuring the pressure since the reaction involves the formation of a gas from a liquid solution. This time, the pressure increase will be proportional to the moles of  $\text{O}_2$  produced.

One could also simply collect and measure the volume of gas produced. This is probably the easiest.

- c) This time, the only likely method would be to measure the pressure drop since the reaction involves the formation of 3 moles of gas from 4 moles of gas.
- d) One could measure the amount of  $\text{OH}^-$  remaining in the solution. This can be done by titration (if the reaction is sufficiently slow that a negligible amount of  $\text{OH}^-$  reacts during the time of the titration itself) or one could use a pH meter to measure the  $[\text{OH}^-]$  directly.

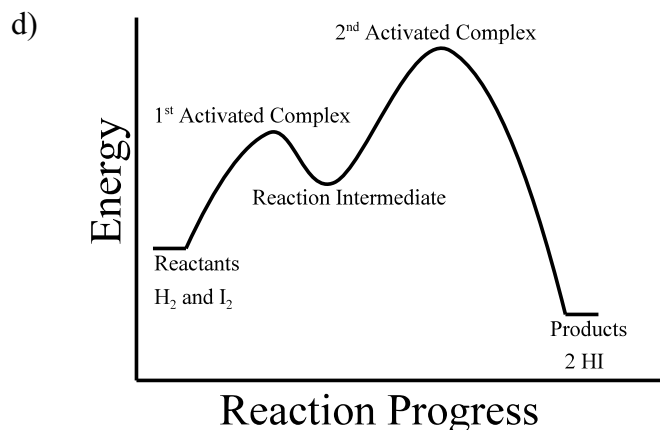
### QUESTIONS ABOUT THE FACTORS THAT AFFECT REACTION RATES

5. The collision frequency is the number of collisions between the different particles involved in the reaction. It doesn't take into consideration the collision energetics. Not all collisions are of sufficient force to cause the desired reaction. Many collisions merely result in the particles recoiling away from one another unchanged. The molecules involved must possess a certain minimum K.E. in order to collide with sufficient force to react. In the Arrhenius equation this energy factor is considered in the exponential term.

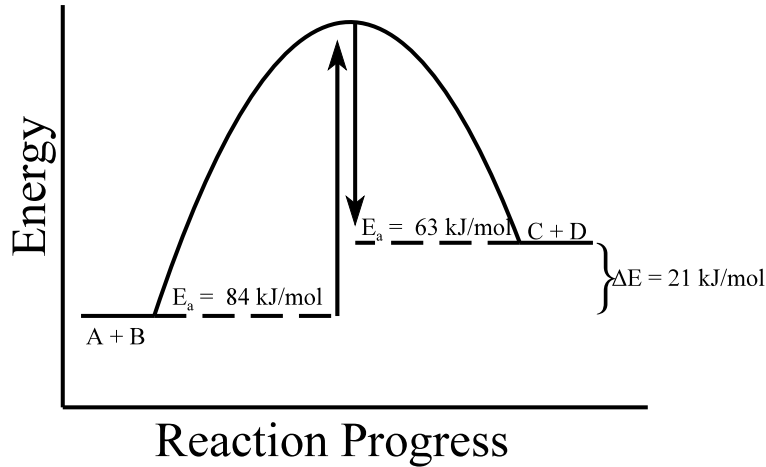
I.e.,  $e^{-E_a/RT} \propto$  fraction of molecules with the minimum K.E.

6. Increasing the pressure on a gas results in smaller distances between the molecules. If the distance is reduced then there will be more collisions between the molecules per unit time (greater collision frequency) and thus a faster reaction rate.
7. Temperature effects the rate in two ways. First, an increase in the temperature means the average K.E. of the molecules increases and thus the speed of the molecules increases. If the molecules travel faster then they will collide with each other more frequently (increases the collision frequency). Secondly and more importantly, an increase in the temperature increases the number of molecules with K.E. above the minimum needed to react. This increase is an exponential increase ( $e^{-E_a/RT}$ ) and therefore a small increase in temperature produces a large change in the number of molecules which are able to react.

8. a) Replacing  $I_2$  with  $Br_2$  would be expected to slow the reaction rate. The bond strength of  $Br_2$  (193 kJ/mol) is greater than the bond strength of  $I_2$  (151 kJ/mol). Therefore at the same temperature fewer molecules of  $Br_2$  would have sufficient energy to dissociate than in a sample of  $I_2$ .
- b) Replacing  $I_2$  with  $N_2$  would also be expected to slow the reaction rate. The bond strength of  $N_2$  (946 kJ/mol) is greater than the bond strength of  $I_2$  (151 kJ/mol). Therefore at the same temperature fewer molecules of  $N_2$  would have sufficient energy to dissociate than in a sample of  $I_2$ . In fact, the mechanism must be different for the reaction of  $N_2$  from the mechanism involving  $I_2$  since the bond strength of  $N_2$  now exceeds the bond strength of  $H_2$ . The dissociation of  $N_2$  can no longer be the first step since the degree of dissociation of  $N_2$  is much less than the degree of dissociation of  $H_2$ .
9. A catalyst change the rate by providing a new reaction pathway (mechanism) that has a lower activation energy.
10. a) There are two elementary step in the mechanism as indicated by the two "humps" in the graph.
- b) The second step is the rate determining step (RDS) in the mechanism as indicated by the fact that the second "hump" is higher or more energy requiring step.
- c) The reaction overall is exothermic as indicated by the fact that the reactants (the beginning plateau) is higher than the products (the final plateau) indicating that energy was released in the overall process. One can also tell that the first step is endothermic since the reaction intermediate (the first "valley") is above the reactants.



11. a)



b) The activation energy is 63 kJ/mol ( $E_a$  forward -  $E_a$  reverse =  $\Delta E$ ).

$$12. a) \quad \frac{R_2}{R_1} = \frac{k \cdot [S_2O_8^{2-}]_2^x [I^-]_2^y}{k \cdot [S_2O_8^{2-}]_1^x [I^-]_1^y} \quad \text{or substituting the values} \quad \frac{2.8 \times 10^{-5} \text{ M}\cdot\text{s}^{-1}}{1.4 \times 10^{-5} \text{ M}\cdot\text{s}^{-1}} = \frac{[0.076]_2^x [0.060]_2^y}{[0.038]_1^x [0.060]_1^y}$$

$$2.0 = 2.0^x \quad \text{therefore} \quad x = 1$$

$$\frac{R_3}{R_1} = \frac{k \cdot [S_2O_8^{2-}]_3^1 [I^-]_3^y}{k \cdot [S_2O_8^{2-}]_1^1 [I^-]_1^y} \quad \text{or substituting the values} \quad \frac{4.4 \times 10^{-5} \text{ M}\cdot\text{s}^{-1}}{1.4 \times 10^{-5} \text{ M}\cdot\text{s}^{-1}} = \frac{[0.060]_3^1 [0.120]_3^y}{[0.038]_1^1 [0.060]_1^y}$$

$$3.1_4 = 1.5_7 \times 2.0^y \quad \text{or} \quad 2.0 = 2.0^y \quad \text{therefore} \quad y = 1$$

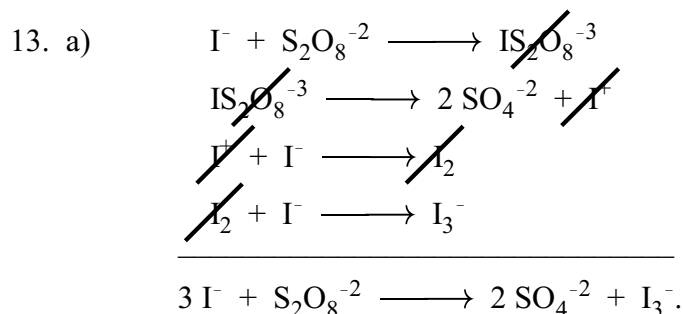
Therefore the reaction is first order in  $S_2O_8^{2-}$ , first order in  $I^-$ , and second order overall.

$$b) \text{ Using the first reaction} \quad R_1 = k \cdot [S_2O_8^{2-}]_1^1 [I^-]_1^1 \quad k = \frac{R_1}{[S_2O_8^{2-}]_1^1 [I^-]_1^1} \text{ or}$$

therefore after substituting in the concentrations and the rate

$$k = \frac{1.4 \times 10^{-5} \text{ M}\cdot\text{s}^{-1}}{(0.038 \text{ M}) (0.060 \text{ M})} = 6.1 \times 10^{-3} \text{ M}^{-1}\cdot\text{s}^{-1}$$

$$c) \text{ rate} = 6.1 \times 10^{-3} \text{ M}^{-1}\cdot\text{s}^{-1} \cdot [S_2O_8^{2-}] [I^-]$$



b) The rate of the reaction is equal to the rate of the slowest step which in this case is the first step.

Therefore, the rate =  $k \cdot [\text{S}_2\text{O}_8^{-2}] [\text{I}^-]$ .

Step one might be expected to be the slowest step because it involves the reaction of two negatively charged ions. The electrostatic repulsion between the two ions would produce a high activation energy thus making it a slow step.

14. a)  $\frac{R_2}{R_1} = \frac{k \cdot [\text{O}_2]_2^x [\text{NO}]_2^y}{k \cdot [\text{O}_2]_1^x [\text{NO}]_1^y}$  or substituting the values  $\frac{6.40 \times 10^{-3} \text{ M}\cdot\text{s}^{-1}}{3.20 \times 10^{-1} \text{ M}\cdot\text{s}^{-1}} = \frac{k \cdot [0.0220]_2^x [0.0130]_2^y}{k \cdot [0.0110]_1^x [0.0130]_1^y}$

$2.00 = 2.00^x$  therefore  $x = 1$

$\frac{R_3}{R_1} = \frac{k \cdot [\text{O}_2]_3^1 [\text{NO}]_3^y}{k \cdot [\text{O}_2]_1^1 [\text{NO}]_1^y}$  or substituting the values  $\frac{1.28 \times 10^{-2} \text{ M}\cdot\text{s}^{-1}}{3.20 \times 10^{-3} \text{ M}\cdot\text{s}^{-1}} = \frac{k \cdot [0.0110]_3^1 [0.0260]_3^y}{k \cdot [0.0110]_1^1 [0.0130]_1^y}$

$4.00 = 2.00^y$  therefore  $y = 2$

Therefore, the reaction is first order in  $\text{O}_2$ , second order in  $\text{NO}$ , and third order overall.

Using the first reaction  $R_1 = k \cdot [\text{O}_2]_1^1 [\text{NO}]_1^2$   $k = \frac{R_1}{[\text{O}_2]_1^1 [\text{NO}]_1^2}$  or

therefore after substituting in the concentrations and the rate

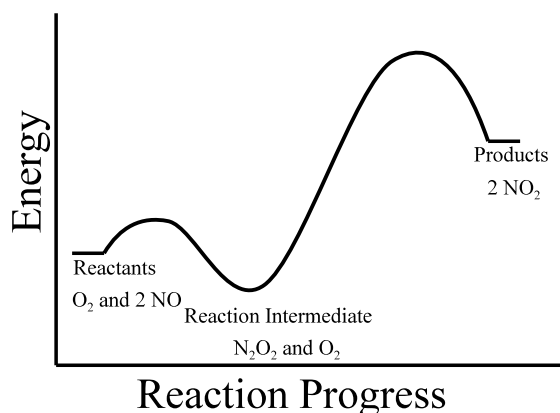
$k = \frac{3.20 \times 10^{-3} \text{ M}\cdot\text{s}^{-1}}{(0.0110 \text{ M}) (0.0130 \text{ M})^2} = 1.72 \times 10^3 \text{ M}^{-2}\cdot\text{s}^{-1}$  (Actually, this should be done for each experiment and the results averaged to get a better value for k.)

The rate equation is; rate =  $1.72 \times 10^3 \text{ M}^{-2}\cdot\text{s}^{-1} \cdot [\text{O}_2] [\text{NO}]^2$

b) Although it is possible for this reaction to occur as a single step since the overall stoichiometry in one mole of  $\text{O}_2$  to 2 mole of  $\text{NO}$  which would give a rate equation equal to the observed rate equation, it probably does not occur in a single step. A single step mechanism would require all three particles to collide at the same instant with the correction orientation for all three molecules which is a highly unlikely event. More likely, this reaction occurs in a multistep mechanism with each step having a molecularity of either one or two.

- c) No, bond breaking is highly unlikely to be the first (or any) step since this would require the breaking of the bonds in either  $O_2$  or  $NO$ . The bond strength of  $O_2$  is 498 kJ/mol and the bond strength of  $NO$  is even higher. (Look them up in your text. This is a homework assignment!) With bond energies this high the activation energy would result in an amazingly slow (imperceptibly slow) reaction.
- d) The most likely first step is the same one presented in class, i.e.,  $2 NO \rightleftharpoons N_2O_2$ .
- e) This step involves bond making and thus is exothermic.
- f) The second step might be  $N_2O_2 + O_2 \longrightarrow 2 NO_2$ . This would make it only a two step mechanism.
- g) Since the first step is exothermic while the overall process is endothermic, the second step must be endothermic to an extent greater than the first step is exothermic.

h)



$$15. a) \frac{R_2}{R_3} = \frac{k \cdot [OCl^-]_2^x [I^-]_2^y [OH^-]_2^z}{k \cdot [OCl^-]_3^x [I^-]_3^y [OH^-]_3^z} \text{ or } \frac{5.0 \times 10^{-4} M \cdot s^{-1}}{2.4 \times 10^{-4} M \cdot s^{-1}} = \frac{k \cdot [0.0020]_2^x [0.0040]_2^y [1.00]_2^z}{k \cdot [0.0020]_3^x [0.0020]_3^y [1.00]_3^z}$$

$$2.1 = 2.0^y \quad \text{therefore} \quad y = 1.1 \sim 1$$

$$\frac{R_1}{R_3} = \frac{k \cdot [OCl^-]_1^x [I^-]_1^y [OH^-]_1^z}{k \cdot [OCl^-]_3^x [I^-]_3^y [OH^-]_3^z} \text{ or } \frac{4.8 \times 10^{-4} M \cdot s^{-1}}{2.4 \times 10^{-4} M \cdot s^{-1}} = \frac{k \cdot [0.0040]_1^x [0.0020]_1^y [1.00]_1^z}{k \cdot [0.0020]_3^x [0.0020]_3^y [1.00]_3^z}$$

$$2.0 = 2.0^x \quad \text{therefore} \quad x = 1$$

$$\frac{R_3}{R_4} = \frac{k \cdot [OCl^-]_3^x [I^-]_3^y [OH^-]_3^z}{k \cdot [OCl^-]_4^x [I^-]_4^y [OH^-]_4^z} \text{ or } \frac{2.4 \times 10^{-4} M \cdot s^{-1}}{4.6 \times 10^{-4} M \cdot s^{-1}} = \frac{k \cdot [0.0020]_3^x [0.0020]_3^y [1.00]_3^z}{k \cdot [0.0020]_4^x [0.0020]_4^y [0.50]_4^z}$$

$$0.52 = 2.0^z \quad \text{therefore} \quad z = -0.94 \sim -1$$

Therefore, the reaction is first order in  $OCl^-$ , first order in  $I^-$ , negative first order in  $OH^-$  and third order overall.

b) The overall rate expression is:

$$R = \frac{k \cdot [\text{OCl}^-]^1 [\text{I}^-]^1}{[\text{OH}^-]^1}$$

Using the first reaction  $R_1 = \frac{k \cdot [\text{OCl}^-]^1_1 [\text{I}^-]^1_1}{[\text{OH}^-]^1_1}$   $k = \frac{R_1 \cdot [\text{OH}^-]^1_1}{[\text{OCl}^-]^1_1 [\text{I}^-]^1_1}$  or

therefore after substituting in the concentrations and the rate

$$k = \frac{4.8 \times 10^{-4} \text{ M} \cdot \text{s}^{-1} \cdot [1.00]_1^1}{[0.0040]_1^1 [0.0020]_1^1} = 60 \text{ s}^{-1} \quad (\text{Actually, } k \text{ should be calculated for each run and then averaged to get the best value for } k. \text{ The average value is } 60 \text{ s}^{-1}.)$$

The rate equation is;  $\text{rate} = \frac{60 \text{ s}^{-1} \cdot [\text{OCl}^-]^1 [\text{I}^-]^1}{[\text{OH}^-]^1}$

c) The RDS is the second step in the mechanism. Thus the rate of the reaction is equal to the rate for this step. I.e.,

$\text{Rate} = k_2 \cdot [\text{I}^-] [\text{HOCl}]$  Note that HOCl is NOT one of the original reactants.

Also note that the first step is an equilibrium, i.e.,  $\text{OCl}^- + \text{H}_2\text{O} \rightleftharpoons \text{HOCl} + \text{OH}^-$  and therefore the forward rate for this step is equal to the reverse rate for this step.

$$\text{Rate}_{\text{forward}} = k_{1f} \cdot [\text{OCl}^-]^1 [\text{H}_2\text{O}]^1 = k_{1f} \cdot [\text{OCl}^-]^1 = \text{Rate}_{\text{reverse}} = k_{1r} \cdot [\text{HOCl}]^1 [\text{OH}^-]^1$$

(Remember that the  $[\text{H}_2\text{O}]$  is so large that it doesn't change during the course of the reaction. Therefore, it is included into the rate constant)

This relationship can be solved for  $[\text{HOCl}]^1$ ;  $[\text{HOCl}]^1 = \frac{k_{1f} \cdot [\text{OCl}^-]^1}{k_{1r} \cdot [\text{OH}^-]^1}$

When the right hand side of this equation is substituted for  $[\text{HOCl}]$  in the rate equation the following is obtained;

$$\text{rate} = \frac{k_{1f} \cdot k_2 \cdot [\text{OCl}^-]^1 [\text{I}^-]^1}{k_{1r} \cdot [\text{OH}^-]^1} = \frac{k_{\text{obs}} \cdot [\text{OCl}^-]^1 [\text{I}^-]^1}{[\text{OH}^-]^1}$$

d) Step one is an equilibrium:  $\text{OH}^- + \text{H}_3\text{O}^+ \rightleftharpoons 2 \text{H}_2\text{O}$  (FAST).

Therefore, the forward rate is equal to the reverse rate.

$$\text{Rate}_{\text{forward}} = k_{1f} \cdot [\text{OH}^-]^1 [\text{H}_3\text{O}^+]^1 = \text{Rate}_{\text{reverse}} = k_{1r} \cdot [\text{H}_2\text{O}]^2 = k_{1r} = \text{constant}$$

(Remember that the  $[\text{H}_2\text{O}]$  is so large that it doesn't change during the course of the reaction. Therefore, it is included into the rate constant)

This relationship can be solved for  $[\text{OH}^-]^1$ ;  $[\text{OH}^-]^1 = \frac{k_{1r}}{k_{1f} \cdot [\text{H}_3\text{O}^+]^1}$

When the right hand side of this equation is substituted for  $[\text{OH}^-]$  in the rate equation the following is obtained;

$$\text{rate} = \frac{k_{1f} \cdot k_{2f} \cdot k_3 \cdot [\text{OCl}^-]^1 [\text{I}^-]^1 [\text{H}_3\text{O}^+]^1}{k_{1r} \cdot k_{2r}} = k \cdot [\text{OCl}^-]^1 [\text{I}^-]^1 [\text{H}_3\text{O}^+]^1$$

e) Since the rate is proportional to the  $[\text{H}_3\text{O}^+]$ , then increasing the  $[\text{H}_3\text{O}^+]$  increases the rate.

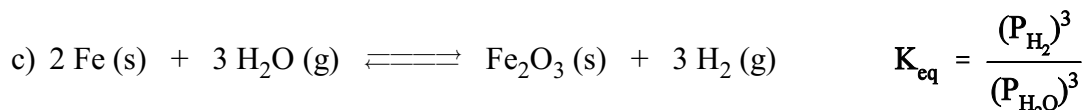
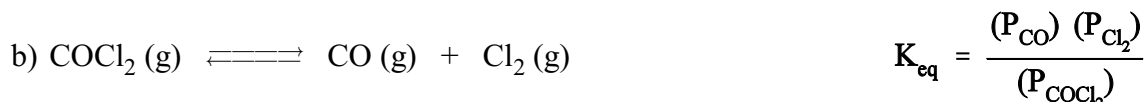
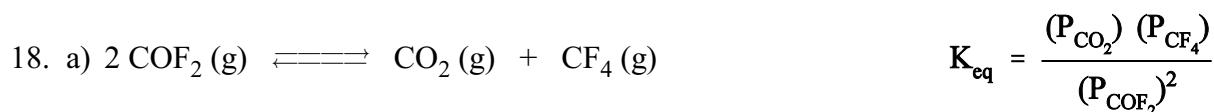
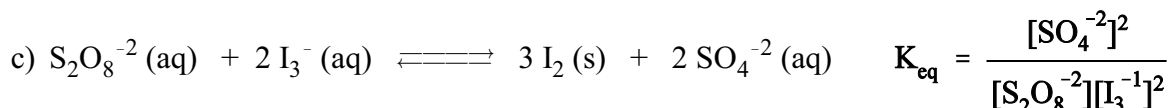
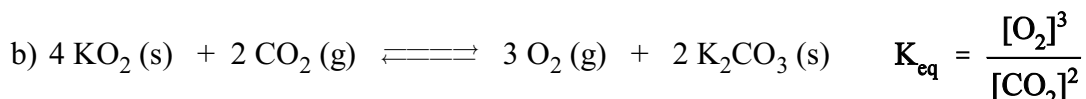
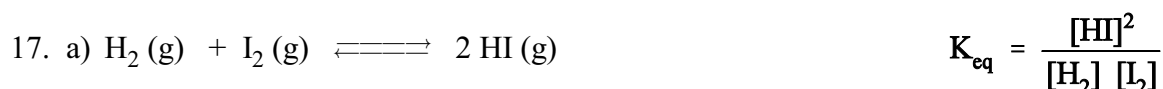
f) Yes, adding 6M HCl (a source of  $\text{H}_3\text{O}^+$ ) caused the rate to increase. It would suggest that a mechanism similar to that above (where [dye] replaces  $[\text{I}^-]$ ) might be the correct mechanism for the dye/bleach reaction.

### QUESTIONS ABOUT EQUILIBRIUM CONSTANTS EXPRESSIONS

16. a)  $K_{\text{eq}} = \frac{[\text{H}_2\text{S}]^3}{[\text{H}_2]^3}$

b)  $K_{\text{eq}} = \frac{[\text{SO}_2][\text{Cl}_2]}{[\text{SO}_2\text{Cl}_2]}$

c)  $K_{\text{eq}} = [\text{CO}_2]$



19.  $K_p = K_c \cdot (RT)^{\Delta n}$  where  $\Delta n = \text{\#moles of product} - \text{\#moles of reactants}$ .

a)  $\Delta n = 0$  Therefore,  $(RT)^{\Delta n} = (RT)^0 = 1$  Thus,  $K_p = K_c = 50.2$

b)  $\Delta n = 1$  Therefore,  $(RT)^{\Delta n} = (RT)^1 = (0.082058 \text{ L}\cdot\text{atm/mol}\cdot\text{K}) \cdot (298.15 \text{ K}) = 24.47 \text{ L}\cdot\text{atm/mol}$

Thus,  $K_p = K_c \cdot 24.47 \text{ L}\cdot\text{atm/mol}$  **OR**  $K_c = K_p / 24.47 \text{ L}\cdot\text{atm/mol} = 28.5 \text{ atm} / 24.47 \text{ L}\cdot\text{atm/mol}$

$K_c = 1.16 \text{ mol/L} = 1.16 \text{ M}$

c)  $\Delta n = 0$  Therefore,  $(RT)^{\Delta n} = (RT)^0 = 1$  Thus,  $K_p = K_c = 2.00$

d)  $\Delta n = 1$  Therefore,  $(RT)^{\Delta n} = (RT)^1 = (0.082058 \text{ L}\cdot\text{atm/mol}\cdot\text{K}) \cdot (941.15 \text{ K}) = 77.23 \text{ L}\cdot\text{atm/mol}$

Thus,  $K_p = K_c \cdot 77.23 \text{ L}\cdot\text{atm/mol}$  **OR**  $K_c = K_p / 77.23 \text{ L}\cdot\text{atm/mol} = 22.5 \text{ atm} / 77.23 \text{ L}\cdot\text{atm/mol}$

$K_c = 0.291 \text{ mol/L} = 0.291 \text{ M}$

20. If the reaction went 100% (it doesn't since it is an equilibrium) then the 1 mol of  $\text{I}_2$  would be consumed as would 1 mol of  $\text{H}_2$  to make 2 mol of HI. Since the reaction doesn't actually go 100% then the only thing that can be said is that the amount of HI must be less than 2 mol or answer d).

### QUESTIONS ABOUT EVALUATING THE EQUILIBRIUM CONSTANT

$$21. \text{ a) } K_c = \frac{[\text{CO}] [\text{H}_2\text{O}]}{[\text{H}_2] [\text{CO}_2]} = \frac{\frac{\text{mol CO}}{V} \times \frac{\text{mol H}_2\text{O}}{V}}{\frac{\text{mol H}_2}{V} \times \frac{\text{mol CO}_2}{V}} = \frac{\text{mol CO} \times \text{mol H}_2\text{O}}{\text{mol H}_2 \times \text{mol CO}_2}$$

Thus  $K_c$  is not dependent on the volume of the container.

$$\text{b) } K_c = \frac{\text{mol CO} \times \text{mol H}_2\text{O}}{\text{mol H}_2 \times \text{mol CO}_2} = \frac{0.224 \text{ mol CO} \times 0.224 \text{ mol H}_2\text{O}}{0.276 \text{ mol H}_2 \times 0.276 \text{ mol CO}_2} = 0.659$$

$$22. \quad K_c = \frac{[\text{PCl}_5]}{[\text{PCl}_3] [\text{Cl}_2]} = \frac{\frac{\text{mol PCl}_5}{V}}{\frac{\text{mol PCl}_3}{V} \times \frac{\text{mol Cl}_2}{V}} = \frac{\text{mol PCl}_5 \times V}{\text{mol PCl}_3 \times \text{mol Cl}_2}$$

$$K_c = \frac{\text{mol PCl}_5 \times V}{\text{mol PCl}_3 \times \text{mol Cl}_2} = \frac{\frac{\text{g PCl}_5}{\text{MM PCl}_5} \times V}{\frac{\text{g PCl}_3}{\text{MM PCl}_3} \times \frac{\text{g Cl}_2}{\text{MM Cl}_2}}$$

$$K_c = \frac{\frac{0.105 \text{ g PCl}_5}{208.239 \text{ g/mol PCl}_5} \times 2.50 \text{ L}}{\frac{0.220 \text{ g PCl}_3}{137.333 \text{ g/mol PCl}_3} \times \frac{2.12 \text{ g Cl}_2}{70.906 \text{ g/mol Cl}_2}} = 26.3_2 \text{ L/mol}$$

For this reaction  $\Delta n = -1$ .

$$K_p = K_c \cdot (RT)^{\Delta n} \quad \text{or} \quad K_p = K_c \times (RT)^{\Delta n} = \frac{K_c}{(RT)}$$

$$K_p = \frac{26.3_2 \text{ L/mol}}{(0.082058 \text{ L}\cdot\text{atm/mol}\cdot\text{K})(523.15\text{K})} = 0.613 \text{ atm}^{-1}$$

23. The equilibrium constant expression for the original equilibrium is:

$$K_c(\text{original}) = \frac{[\text{H}_2] [\text{CO}_2]}{[\text{CO}] [\text{H}_2\text{O}]} = 23.2$$

a) The equilibrium constant expression for this equilibrium is the INVERSE of the original expression.

$$K_c(\text{new}) = \frac{[\text{CO}] [\text{H}_2\text{O}]}{[\text{H}_2] [\text{CO}_2]} = \frac{1}{\frac{[\text{H}_2] [\text{CO}_2]}{[\text{CO}] [\text{H}_2\text{O}]}} = \frac{1}{K_c(\text{Orig})} = \frac{1}{23.2} = 0.0431$$

**Note:** that when an equilibrium is written in the REVERSE direction then the new  $K_{eq}$  is the INVERSE of the original  $K_{eq}$ .

b) The equilibrium constant expression for this equilibrium is the SQUARE of the original expression.

$$K_c(\text{new}) = \frac{[\text{H}_2]^2 [\text{CO}_2]^2}{[\text{CO}]^2 [\text{H}_2\text{O}]^2} = [K_c(\text{orig})]^2 = (23.2)^2 = 538$$

**Note: that when an equilibrium is written with TWICE the original coefficients then the new  $K_{\text{eq}}$  is the SQUARE of the original  $K_{\text{eq}}$ .**

c) The equilibrium constant expression for this equilibrium is the SQUARE ROOT of the original expression.

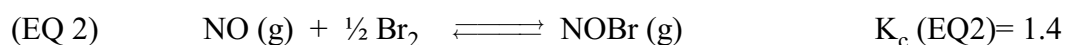
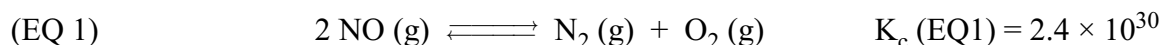
$$K_c(\text{new}) = \frac{[\text{H}_2]^{1/2} [\text{CO}_2]^{1/2}}{[\text{CO}]^{1/2} [\text{H}_2\text{O}]^{1/2}} = [K_c(\text{Orig})]^{1/2} = (23.2)^{1/2} = 4.82$$

**Note: that when an equilibrium is written with HALF the original coefficients then the new  $K_{\text{eq}}$  is the SQUARE ROOT of the original  $K_{\text{eq}}$ .**

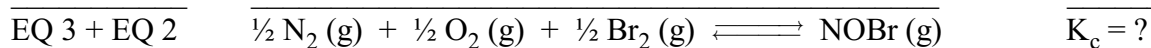
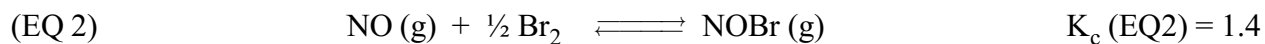
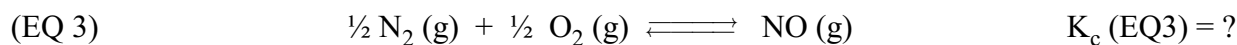
24. The equilibrium constant expression for :  $\frac{1}{2} \text{N}_2 (\text{g}) + \frac{1}{2} \text{O}_2 (\text{g}) + \frac{1}{2} \text{Br}_2 (\text{g}) \rightleftharpoons \text{NOBr} (\text{g})$

$$\text{is } K_c(\text{final}) = \frac{[\text{NOBr}]}{[\text{N}_2]^{1/2} [\text{O}_2]^{1/2} [\text{Br}_2]^{1/2}}$$

You are given two equations with their respective equilibrium constants.



Note that the original equilibrium CAN be rewritten as the sum of two equilibria (TRICKY, HEH!). Why would anyone wish to do that? Be patient!



Note that EQ 3 is the reverse of EQ 1 but with half of the coefficients. Therefore the equilibrium constant for EQ 3 must be INVERSE SQUARE ROOT of the constant for EQ 1. Thus

$$K_c(\text{EQ3}) = \frac{1}{[K_c(\text{EQ1})]^{1/2}} = \frac{1}{[2.4 \times 10^{30}]^{1/2}} = 6.4_5 \times 10^{-16}$$

When EQ 2 and EQ 3 are added we get the original equilibrium. When the equilibrium constant expression for EQ 2 is multiplied by the constant expression for EQ 3 we get the original equilibrium constant expression. That is:

$$K_c(\text{final}) = \frac{[\text{NOBr}]}{[\text{Br}_2]^{1/2} [\text{NO}]} \times \frac{[\text{NO}]}{[\text{N}_2]^{1/2} [\text{O}_2]^{1/2}} = \frac{[\text{NOBr}]}{[\text{N}_2]^{1/2} [\text{O}_2]^{1/2} [\text{Br}_2]^{1/2}}$$

$$\underbrace{\frac{[\text{NOBr}]}{[\text{Br}_2]^{1/2} [\text{NO}]}_{K_c(\text{EQ2})} \times \underbrace{\frac{[\text{NO}]}{[\text{N}_2]^{1/2} [\text{O}_2]^{1/2}}}_{K_c(\text{EQ3})} = \underbrace{\frac{[\text{NOBr}]}{[\text{N}_2]^{1/2} [\text{O}_2]^{1/2} [\text{Br}_2]^{1/2}}}_{K_c(\text{final})}$$

Therefore,  $K_c(\text{final}) = K_c(\text{EQ2}) \times K_c(\text{EQ3}) = (1.4) \times (6.45 \times 10^{-16}) = 9.0 \times 10^{-16}$

**Note: that when two equilibria are ADDED then the new  $K_{eq}$  is the PRODUCT of the two original  $K_{eq}$ 's.**

### SIMPLE CALCULATIONS INVOLVING THE EQUILIBRIUM CONSTANT

$$25. \quad K_c = \frac{[\text{NO}]^2}{[\text{N}_2\text{O}_4]} = 4.61 \times 10^{-3} \text{ M} \quad \text{or} \quad [\text{NO}] = \sqrt{4.61 \times 10^{-3} \text{ M} \times [\text{N}_2\text{O}_4]}$$

Therefore,  $[\text{NO}] = \sqrt{4.61 \times 10^{-3} \text{ M} \times [\text{N}_2\text{O}_4]} = \sqrt{4.61 \times 10^{-3} \text{ M} \times 0.0277 \text{ M}} = 0.0113 \text{ M}$

26. For the reaction;  $\text{PCl}_5 (\text{g}) \rightleftharpoons \text{PCl}_3 (\text{g}) + \text{Cl}_2 (\text{g})$

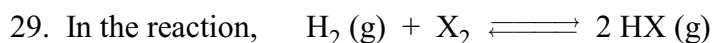
a) If the final concentration of  $\text{PCl}_5$  is 0.0420 M and the volume of the container is 1.00L then there must be 0.0420 moles of  $\text{PCl}_5$  left. Thus the amount of  $\text{PCl}_5$  that decomposed is 0.0820 moles minus 0.0420 moles or 0.0400 moles. When the 0.0400 moles of  $\text{PCl}_5$  decomposed it created 0.0400 moles of  $\text{PCl}_3$  and 0.0400 moles of  $\text{Cl}_2$ . Again, the container has a volume of 1.00 L thus the  $[\text{PCl}_3] = 0.0400 \text{ M}$  and the  $[\text{Cl}_2] = 0.0400 \text{ M}$ .

$$b) \quad K_c = \frac{[\text{PCl}_3][\text{Cl}_2]}{[\text{PCl}_5]} = \frac{(0.0400 \text{ M})(0.0400 \text{ M})}{(0.0420 \text{ M})} = 0.0381 \text{ M}$$

### FACTORS THAT MAY AFFECT THE EQUILIBRIUM CONSTANT

27. If a reaction is highly exothermic then the reaction is favorable and the equilibrium lies very far to the right hand side (i.e., there exists a lot of products with little reactant left at equilibrium). Thus, the equilibrium constant has a large numerator and a small denominator which would produce a large value for the equilibrium constant.

28. a) The term “more energetically stable” refers to those chemicals having a lower heat content. As energy is released in a chemical reaction (an exothermic process) the chemicals lose some of their heat content and the products become “more energetically stable”. For an endothermic process (one that absorbs energy) the products become “less energetically stable” than the reactants. In this case the reactants are more energetically stable than the products.
- b) Bond breaking is endothermic and bond making is exothermic. In going from the reactants, A and B, to the products, C and D, some bonds must be broken in A and B and new bonds must form to make the new products, C and D. If the bonds broken in A and B are stronger than those made in C and D then more energy is required to break bonds than is produced in C and D.
- c) In the diagram the products are higher in energy than the reactants which means that the reactants are favored. That means that at equilibrium there is a larger amount of reactants than the amount of products. This will produce an equilibrium constant with a small numerator and a large denominator. I.e., it will produce a small  $K_{eq}$ .
- d) If the bonds inside of C and D were stronger than those of A and B this would be an exothermic process. This would mean that the products were favored and that there would be a larger amount of products than the amount of reactants which would produce a very large  $K_{eq}$ .



The bonds in  $H_2$  and in  $X_2$  must be broken while two H-X bonds must be created. Therefore, the overall heat change ( $\Delta H_{rxn}$ ) is equal to the DIFFERENCE of the energies for these two steps.

$$\text{I.E., } \Delta H_{RXN} = BE_{H_2} + BE_{X_2} - 2 \times BE_{HX}$$

When  $X_2$  is fluorine,

$$\Delta H_{RXN} = BE_{H_2} + BE_{F_2} - 2 \times BE_{HF} = 432 \text{ kJ/mol} + 159 \text{ kJ/mol} - 2 \times 565 \text{ kJ/mol} = -539 \text{ kJ/mol}$$

When  $X_2$  is chlorine,

$$\Delta H_{RXN} = BE_{H_2} + BE_{Cl_2} - 2 \times BE_{HCl} = 432 \text{ kJ/mol} + 243 \text{ kJ/mol} - 2 \times 427 \text{ kJ/mol} = -179 \text{ kJ/mol}$$

When  $X_2$  is bromine,

$$\Delta H_{RXN} = BE_{H_2} + BE_{Br_2} - 2 \times BE_{HBr} = 432 \text{ kJ/mol} + 193 \text{ kJ/mol} - 2 \times 363 \text{ kJ/mol} = -101 \text{ kJ/mol}$$

When  $X_2$  is iodine,

$$\Delta H_{RXN} = BE_{H_2} + BE_{I_2} - 2 \times BE_{HI} = 432 \text{ kJ/mol} + 151 \text{ kJ/mol} - 2 \times 295 \text{ kJ/mol} = -7 \text{ kJ/mol}$$

In changing from  $F_2$  to  $Cl_2$  to  $Br_2$  to  $I_2$  the reactions progressively become LESS favorable. Thus the value of  $K_{eq}$  will become progressively smaller in the series.

30. a) The increase in the concentration of one of the reactants will cause the equilibrium to shift to the right to lower that reactant's concentration. Since this shift is due to a change in concentration of one of the reactants and NOT due to a change in the forward rate constant then the ratio of  $k_f/k_r$  (which is equal to  $K_{eq}$ ) will not change.
- b) The decrease in volume will result in an increase in the pressures of all gasses. The equilibrium will shift in a direction which will lower the pressure of the system. To do this fewer moles of gas will produce a lower pressure. Therefore the system will move in the direction of the side with fewer moles of gas. Since this shift is caused by a change in concentration and not on a change in the value of the rate constants then the ratio of  $k_f/k_r$  (which is equal to  $K_{eq}$ ) will not change.
- c) The change in temperature will not cause any change in concentration. But, since the rate constant,  $k$  does depend on temperature. I.e.,

$$k = A \cdot e^{-E_a/RT}$$

Then changing the temperature will change both  $k_f$  and  $k_r$  and therefore the ratio of  $k_f/k_r$  and therefore change the value of  $K_{eq}$ .

31. a) The equilibrium,  $2 \text{NO}_2(\text{g}) \rightleftharpoons \text{N}_2\text{O}_4(\text{g})$  obviously involves bond making in going from left to right. Since bond making releases energy this must be an exothermic process.  
(Actually,  $\Delta H_{rxn} = -57.24 \text{ kJ}$ )

- b) Since the reaction is exothermic then the products are more stable than the reactants and therefore the right side of the equilibrium is favored. Thus, at equilibrium there will be more products than reactants and therefore a large value for the equilibrium constant.

$$\text{c) } K_p = 8.87 \text{ atm}^{-1} = \frac{P_{\text{N}_2\text{O}_4}}{(P_{\text{NO}_2})^2} \text{ or } P_{\text{N}_2\text{O}_4} = K_p \times (P_{\text{NO}_2})^2 = 8.87 \text{ atm}^{-1} \times (1.00 \text{ atm})^2 = 8.87 \text{ atm}$$

Under these conditions ( $P_{\text{total}} = 9.87 \text{ atm}$ ) therefore there is actually more  $\text{N}_2\text{O}_4$  (8.87 times as much) at equilibrium than there is  $\text{NO}_2$ ! (Even at a total pressure of 1 atm there will still be 2.52 times as much  $\text{N}_2\text{O}_4$  as there will be  $\text{NO}_2$ .)

- d) It does seem strange to refer to this mixture as nitrogen dioxide since it is the minor component. If one "had" to use the name of one of the components as a name for this mixture then a better name for the mixture would be dinitrogen tetroxide as it is the major component.