

Name \_\_\_\_\_ KEY \_\_\_\_\_ Rec. TA/time \_\_\_\_\_

1. (5 pts) A reaction with activation energy of 123 kJ/mol is originally at 38.0 °C. At what **temperature**, in °C, will its rate constant be double that at 38.0 °C?

Use Arrhenius equation in its two point form.

$$\ln\left(\frac{k_2}{k_1}\right) = \frac{E_a}{R} \left(\frac{1}{T_1} - \frac{1}{T_2}\right) \quad T \text{ in KELVIN, } R = 8.314 \text{ J/mol}\cdot\text{K}$$

$$\begin{array}{l} k_1 \\ k_2 = 2 k_1 \end{array} \quad \begin{array}{l} T_1 = 38.0^\circ\text{C} = 311.\underline{15} \text{ K} \quad (\text{using } 273.15 \text{ to convert to kelvin}) \\ T_2 = ? \end{array}$$

$$E_a = 123 \text{ kJ/mol} = 123 \times 10^3 \text{ J/mol} \quad (\text{units for } E_a \text{ must agree with those of } R)$$

$$\ln\left(\frac{2k_1}{k_1}\right) = \frac{123 \times 10^3 \text{ J/mol}}{8.314 \text{ J/mol}\cdot\text{K}} \left(\frac{1}{311.\underline{15} \text{ K}} - \frac{1}{T_2}\right) \quad \text{Note: don't need numerical values for } k_1 \text{ \& } k_2 \text{ just some relationship between them.}$$

$$0.693 = 1.4794 \times 10^4 \text{ K} \left(\frac{1}{311.\underline{15} \text{ K}} - \frac{1}{T_2}\right)$$

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$$4.6852 \times 10^{-5} \text{ K}^{-1} = \frac{1}{311.\underline{15} \text{ K}} - \frac{1}{T_2}$$

$$3.16703 \times 10^{-3} \text{ K}^{-1} = 1/T_2$$

$$T_2 = 315.753 \text{ K}; \quad T_2 = 315.6 \text{ K} - 273.15 = 42.603 \text{ }^\circ\text{C} = 42.6 \text{ }^\circ\text{C}$$

2. (9 pts) Consider the following hypothetical reaction and the established rate law. Select an acceptable mechanism.



The rate law is written based on the slow (rate determining) step

a) 2<sup>nd</sup> step is the slow step



$r = k_2 [B_2] [A]$  A is an intermediate - try to replace it using conc. of reactants &/or product

Use 1<sup>st</sup> fast equilibrium step to determine [A]

$$r_{\text{forward},1} = r_{\text{reverse},1}$$

$$k_1 [A_2] = k_{-1} [A]^2$$

$$[A] = \left(\frac{k_1}{k_{-1}}\right)^{1/2} \cdot [A_2]^{1/2} \quad \text{substitute this expression for [A] into r from step 2}$$

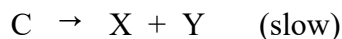
$$r = k_2 [B_2] [A]$$

$$r = k_2 [B_2] \left\{ \left(\frac{k_1}{k_{-1}}\right)^{1/2} \cdot [A_2]^{1/2} \right\}$$

$$r = k_2 \left(\frac{k_1}{k_{-1}}\right)^{1/2} [B_2] [A_2]^{1/2} = k [B_2] [A_2]^{1/2}$$

This does not agree w. exp. rate law given - NOT the proper mechanism

b) 2<sup>nd</sup> step is the slow step



$r = k_2 [C]$  C is an intermediate - try to replace it using conc. of reactants &/or product

Use 1<sup>st</sup> fast equilibrium step to determine [C]

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7. (Cont.)

$$r_1 = r_{-1}$$

$$k_1 [A_2] [B_2] = k_{-1} [C]$$

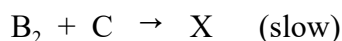
$$[C] = \left(\frac{k_1}{k_{-1}}\right) [A_2] [B_2] \quad \text{substitute this expression for [A] into r from step 2}$$

$$r = k_2 [C]$$

$$r = k_2 \left\{ \left(\frac{k_1}{k_{-1}}\right) [A_2] [B_2] \right\} = \left(\frac{k_2 k_1}{k_{-1}}\right) [A_2] [B_2] = k [A_2] [B_2]$$

This does not agree w. exp. rate law given - NOT the proper mechanism

c) 2<sup>nd</sup> step is the slow step



$r = k_2 [B_2] [C]$       C is an intermediate - try to replace it using conc. of reactants &/or product

Use 1<sup>st</sup> fast equilibrium step to determine [C]

$$r_1 = r_{-1}$$

$$k_1 [A_2] = k_{-1} [C] [Y]$$

$$[C] = \frac{k_1}{k_{-1}} \cdot \frac{[A_2]}{[Y]} \quad \text{substitute this expression for [C] into r from step 2}$$

$r = k_2 [B_2] [C]$       -      rate law from above

$$r = k_2 [B_2] \left\{ \frac{k_1}{k_{-1}} \cdot \frac{[A_2]}{[Y]} \right\}$$

$$r = \left\{ \frac{k_2 k_1}{k_{-1}} \right\} \cdot \frac{[B_2] [A_2]}{[Y]}$$

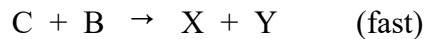
$$r = k \frac{[B_2] [A_2]}{[Y]}$$

This agrees w. exp. rate law given - It **IS** the proper mechanism

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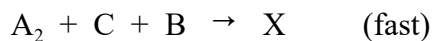
7. (Cont.)

d) 1st step is the slow step



$r = k_1 [\text{B}_2]$  This does not agree w. exp. rate law given - NOT the proper mechanism

e) 2<sup>nd</sup> step is the slow step



$r = k_2 [\text{B}]$  B is an intermediate - try to replace it using conc. of reactants &/or product

Use 1<sup>st</sup> fast equilibrium step to determine [B]

$$r_1 = r_{-1}$$

$$k_1 [\text{B}_2] = k_{-1} [\text{B}]^2$$

$$[\text{B}] = \left(\frac{k_1}{k_{-1}}\right)^{1/2} \cdot [\text{B}_2]^{1/2} \quad \text{substitute this expression for [B] into r from step 2}$$

$$r = k_2 [\text{B}]$$

$$r = k_2 \left\{ \left(\frac{k_1}{k_{-1}}\right)^{1/2} \cdot [\text{B}_2]^{1/2} \right\}$$

$$r = k_2 \left(\frac{k_1}{k_{-1}}\right)^{1/2} [\text{B}_2]^{1/2} = k [\text{B}_2]^{1/2}$$

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7. (Cont.)

**Note:** Anything that appears in the rate law must appear as a **reactant** in the **slow step** or as a **reactant** and/or **product** in the **fast equilibrium steps** which **precede** the **slow step**.

The fast steps which follow the slow step have no effect on the rate law. They are only there to make sure all steps add up to the balanced equation.

This brings up a good point that makes this type of problem easier to approach.

First look at mech. w. slow step 1 - easy to determine these rate laws (only the reactants in this step will appear in the rate law).

Then look at remaining mech.

To get a rate law with a  $\frac{1}{2}$  power (e.g.  $[A_2]^{1/2}$ ) there would need to be the following type of elementary step as a fast step preceding the slow step.

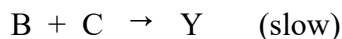
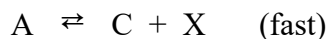


$$r_{\text{forward},1} = r_{\text{reverse},1}$$

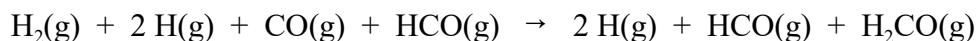
$$k_1 [A_2] = k_{-1} [A]^2$$

$$[A] = \left(\frac{k_1}{k_{-1}}\right)^{1/2} \cdot [A_2]^{1/2}$$

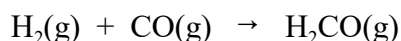
Also, look at the following mechanism: Get C in the rate law based on step 2. Then if you look at step 1 you will get something for [C] involving A and X (a product). X will appear in the denominator in the rate law. You really shouldn't have to go through the math to see you will wind up with X in the rate law. In order to get a product in the rate law the first step can't be the rate determining step.



3. (9 pts) The following mechanism has been proposed for the gas phase reaction between H<sub>2</sub> and CO.



- (a) What is the overall reaction? (cancel things that appear on both sides)



- (b) What are the **intermediates** in the mechanism?

H(g) & HCO(g) Things that don't appear in overall eqn., but appear in mechanism are either intermediates or catalysts. Intermediates appear for the first time as a product and used in following step(s) as a reactant.

- (c) What is the **molecularity** of each elementary step? # reactant molecules in a step

Step 1  
**unimolecular**  
(1 reactant molecule)

Step 2  
**bimolecular**  
(2 reactant molecules)

- (d) What is the **rate-determining step** (explain why)?

Step 2 - **slowest step** rate for entire rxn can **NOT** be **faster** than **SLOWEST step** in mech.

- (e) What is the **rate law** predicted by this mechanism?

$$r = k_2 [\text{H}] [\text{CO}] \quad \text{based on reactants in step 2 (slowest, rate-determining step)}$$

Can't have intermediate, H, in the rate law - use step 1 (fast equilibrium step) to find [H]

For step 1

$$\text{rate}_{\text{forward 1}} = \text{rate}_{\text{reverse 1}}$$

Write rate law for each rate

$$k_1 [\text{H}_2] = k_{-1} [\text{H}]^2$$

solve for [H]

$$[\text{H}] = \left\{ \frac{k_1}{k_{-1}} [\text{H}_2] \right\}^{1/2}$$

Substitute this into rate eqn base on step 2

$$r = k_2 [\text{H}] [\text{CO}]$$

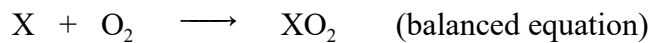
$$r = k_2 \left\{ \frac{k_1}{k_{-1}} [\text{H}_2] \right\}^{1/2} [\text{CO}]$$

$$r = k_2 \left( \frac{k_1}{k_{-1}} \right)^{1/2} [\text{H}_2]^{1/2} [\text{CO}]$$

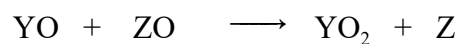
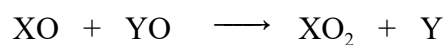
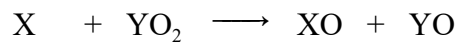
$$r = k [\text{H}_2]^{1/2} [\text{CO}]$$

$$\text{where, } k = k_2 \left( \frac{k_1}{k_{-1}} \right)^{1/2}$$

4. (3 pts) Given the following mechanism, which answer below contains all species which may be classified as **catalyst(s)** in the formation of  $XO_2$  from X and  $O_2$  ( $X + O_2 \rightarrow XO_2$ )?



Mechanism below:



intermediates: XO, YO, Y, ZO

Appear for the **first time** as a **product** and **used** in **subsequent step** as a **reactant**.

**catalysts:**  $YO_2$ , Z

Appear for the **first time** as **reactant** and **reproduced** in **subsequent step** as a **product**.

5. (3 pts) Which response contains all the following statements that are **TRUE** and no false statements?
- From the Arrhenius equation one can say that the **rate constant** always **decreases** as **temperature rises**.
  - The activation energy,  $E_a$ , for a reaction generally does **not** change as temperature changes (i.e.  $E_a$  is treated as a constant).
  - The activation energy,  $E_a$ , is usually about the **same** as  $\Delta H$  (or  $\Delta E$ ) for a reaction.
  - A **catalyst increases** the **rate** of a reaction by **lowering** the **activation energy**,  $E_a$ .
  - A **catalyst increases** the **kinetic energy** of the **reactants**.
- a) 5                      b) 1, 3                      c) 3, 5                      d)\* 2, 4                      e) 3, 4, 5

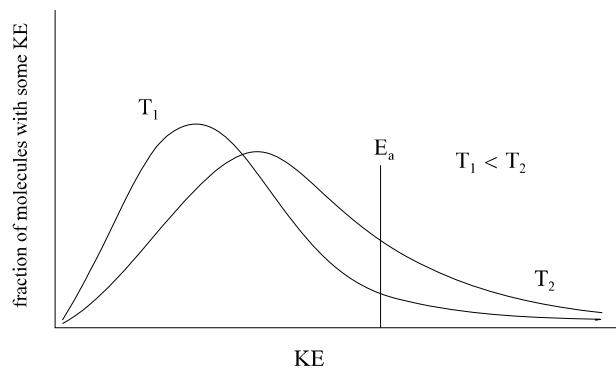
The true statements are bolded and the false statements have been corrected.

**D** (2 & 4 are both correct)

1) F:  $k = A e^{-(E_a/RT)}$                       Arrhenius eqn.

As **T inc.**,  $E_a/RT$  dec,  $e^{-(E_a/RT)}$  inc., **k inc.**, **rate inc** ( $r \propto k$ )  
**T dec.**,  $E_a/RT$  inc,  $e^{-(E_a/RT)}$  dec., **k dec.**, **rate dec** ( $r \propto k$ )

An inc. in T causes an inc. in K.E. so more molecules have  $KE > E_a$  and may therefore react



- 2) **T**:  $E_a$  is treated as a constant w. temp changes (generally does not change appreciably w. temp and is treated as being constant).
- 3) **F**: There is no direct relationship between size of  $E_a$  and  $\Delta H$  ( $\Delta E$ ) other than  $\Delta E = E_{a_{for}} - E_{a_{rev}}$

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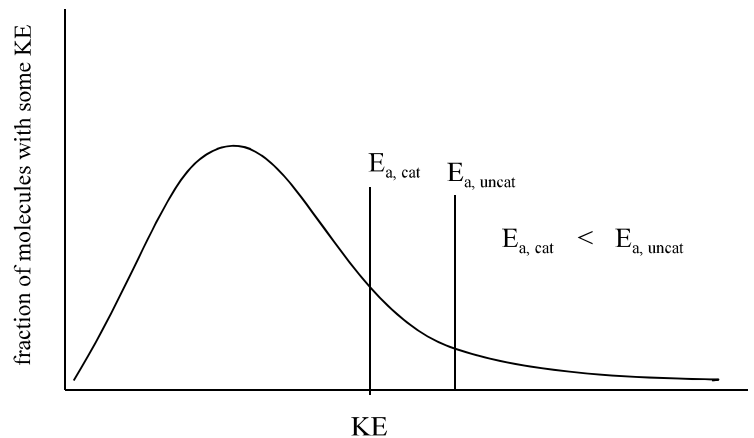
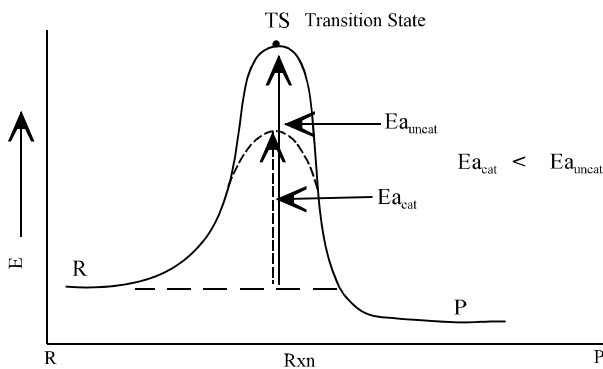
5. (cont.)

4) T: **Catalyst inc rxn rate** by **lowering  $E_a$**  so that at the same temp more molecules have  $KE > E_a$ . A catalyst lowers the “hill” (rxn barrier) so it takes less energy to get over (through the transition state, TS).

Catalysts do not shift the equilibrium toward products. **Catalysts speed up the rate** at which equilibrium is reached but do **not effect the position of equilibrium** (i.e. Amounts of reactant and product at equilibrium). **Catalyst inc rxn rate** by **lowering  $E_a$**  so that at the same temp more molecules have  $KE > E_a$ . A catalyst lowers the “hill” (rxn barrier) so it takes less energy to get over (through the transition state, TS). Can use the Arrhenius eqn to see this.

$$k = A e^{-(E_a/RT)} \quad \text{Arrhenius eqn.}$$

As  $E_a$  **inc.**,  $E_a/RT$  inc.,  $e^{-(E_a/RT)}$  dec., **k dec.**, **rate dec** ( $r \propto k$ )  
 $E_a$  **dec.**,  $E_a/RT$  dec.,  $e^{-(E_a/RT)}$  inc., **k inc.**, **rate inc** ( $r \propto k$ )

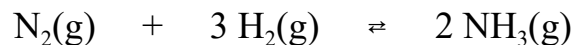


The **rate** of a reaction depends **ONLY** on  $E_a$  and not whether a reaction is exothermic or endothermic or how exothermic or endothermic the reaction is. An endothermic reaction will be faster than an exothermic reaction if the  $E_a$  for the endothermic reaction is smaller than the  $E_a$  for the exothermic reaction.

Reaction 1	Reaction 2
-----	-----
$\Delta H = -30 \text{ kJ}$	$\Delta H = 20 \text{ kJ}$
$E_a = 20 \text{ kJ}$	$E_a = 10 \text{ kJ}$
	faster

5) F: A catalyst does not necessarily inc. the KE of the reactants. As a matter of fact, in heterogeneous catalysis when a solid catalyst is involved the reactants adsorb to the surface of the solid catalyst and likely will actually **slow down**, so **KE** would **dec.**

6. (3 pts) The equilibrium constant for the following reaction is 70 at 350°C. A system at equilibrium has  $[\text{N}_2] = 0.200 \text{ M}$  and  $[\text{NH}_3] = 0.118 \text{ M}$ . What is the  $[\text{H}_2]$ ?



$$K_c = \frac{[\text{NH}_3]^2}{[\text{N}_2] [\text{H}_2]^3} = 70$$

$$[\text{H}_2] = \left( \frac{[\text{NH}_3]^2}{K_c [\text{N}_2]} \right)^{1/3}$$

$$[\text{H}_2] = \left( \frac{(0.118)^2}{(70)(0.200)} \right)^{1/3}$$

$$= 0.0998 \text{ M}$$

$$= 0.10 \text{ M}$$

7. (3 pts) The properly written heterogeneous  $K_c$  expression for the following reaction as written is:



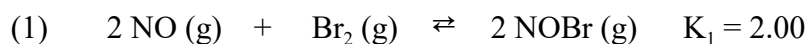
Pure **solids** and **liquids** do **NOT** appear in the equilibrium constant expression (or in Q).

$$K_c = \frac{[\text{Ni}^{2+}] [\text{CO}_2]}{[\text{H}^+]^2}$$

$\text{NiCO}_3(\text{s})$  &  $\text{H}_2\text{O}(\text{l})$  do **NOT** appear in K

- gases & solutes in solution do appear in the expression for K.

8. (5 pts) Given the following two equilibrium reactions,

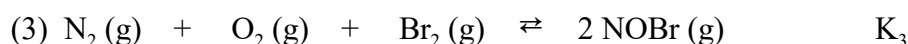


$$K_1 = \frac{[\text{NOBr}]^2}{[\text{NO}]^2 [\text{Br}_2]}$$



$$K_2 = \frac{[\text{N}_2]^{1/2} [\text{O}_2]^{1/2}}{[\text{NO}]}$$

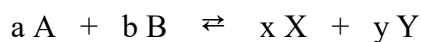
What is the equilibrium constant,  $K_3$ , for the reaction below,



$K_{\text{rev}}$  for rev. rx is  $1/K_{\text{for}}$  (reciprocal of  $K_{\text{for}}$  for the forward rx)

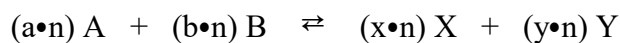
Also, when multiply a rxn by some factor the  $K$  for the new rxn is equal to original  $K$  raised to the factor the rxn was multiplied by (multiplying by -1 reverses the rxn)

### Proof



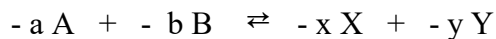
$$K_1 = \frac{[\text{X}]^x [\text{Y}]^y}{[\text{A}]^a [\text{B}]^b}$$

Multiply by  $n$

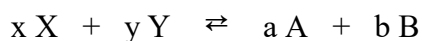


$$K_2 = \frac{[\text{X}]^{xn} [\text{Y}]^{yn}}{[\text{A}]^{an} [\text{B}]^{bn}} = \left( \frac{[\text{X}]^x [\text{Y}]^y}{[\text{A}]^a [\text{B}]^b} \right)^n = K_1^n$$

Multiply by -1 reverses rxn.



want (+) coeff - like in math switch reactants & products to other sides



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## 8. (cont.)

When you add reactions together to get another reaction the K for the overall reaction equals the K's from the added reactions multiplied together.

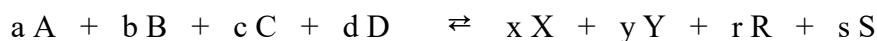


$$K_1 * K_2 = K_3$$

**Proof**

$$K_1 = \frac{[X]^x [Y]^y}{[A]^a [B]^b} \quad K_2 = \frac{[R]^r [S]^s}{[C]^c [D]^d}$$

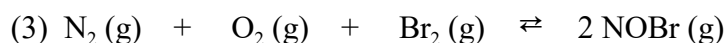
Add the two equations (reactions) to get a third equation (reaction)



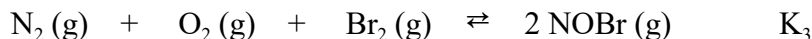
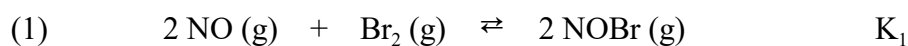
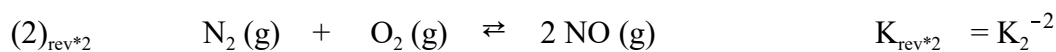
$$K_3 = \frac{[X]^x [Y]^y [R]^r [S]^s}{[A]^a [B]^b [C]^c [D]^d} = \left( \frac{[X]^x [Y]^y}{[A]^a [B]^b} \right) * \left( \frac{[R]^r [S]^s}{[C]^c [D]^d} \right)$$

$$K_3 = K_1 * K_2$$

To get reaction 3 for this question,

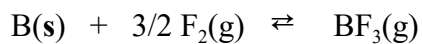


must first reverse rx 2 and multiply it by 2 and then add it to rxn 1



$$K_3 = K_1 * K_{\text{rev}*2} = K_1 * K_2^{-2} = (2.00)(1.45 \times 10^{15})^{-2} = 9.51 \times 10^{-31}$$

9. (4 pts) The equilibrium constant  $K_c$  for the following reaction at  $1100^\circ\text{C}$  is  $6.80 \times 10^{51}$ . What is  $K_p$ ?



use  $K_p = K_c (RT)^{\Delta n}$  ( $\Delta n =$  change in moles of **gas**)

$$\Delta n = 1 - 3/2 = -1/2$$

Do **NOT** include the **solid** (if you do then  $\Delta n = -3/2$ )

$$K_c = \frac{[\text{BF}_3]}{[\text{F}_2]^{3/2}}$$

$$K_p = \frac{P_{\text{BF}_3}}{(P_{\text{F}_2})^{3/2}}$$

$R = 0.08206 \text{ L}\cdot\text{atm}/\text{mol}\cdot\text{K}$  **NOT**  $8.314 \text{ J}/\text{mol}\cdot\text{K}$

$T = 1100^\circ\text{C} + 273 = 1373 \text{ K}$  (**must** be in **kelvin**)

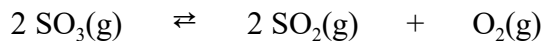
$$K_c = 6.80 \times 10^{51}$$

$$K_p = K_c (RT)^{-1/2}$$

$$= (6.80 \times 10^{51}) \{(0.08206)(1373)\}^{-1/2}$$

$$K_p = 6.40 \times 10^{50}$$

10. (5 pts) The following reaction is started with 2.000 moles of  $\text{SO}_3$  in a 2.000-L container. When equilibrium is reached there are 1.645 moles of  $\text{SO}_3$  in the container. What is the value of the equilibrium constant,  $K_C$ ? (Show the ICE table. You can use numbers or variables in your ICE table.)



$$K_C = \frac{[\text{SO}_2]^2 \cdot [\text{O}_2]}{[\text{SO}_3]^2}$$

Concentration of **Products** in **Numerator**

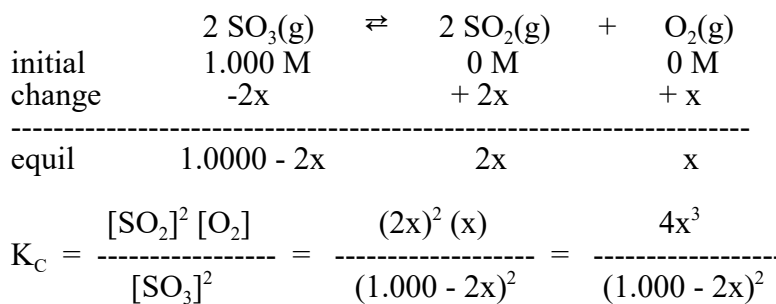
Concentration of **Reactants** in **Denominator**

Use **coefficients** in **balanced equation** as the **exponents** of the concentrations.

Pure solids (s) and liquids (l) do not appear in the expression for K or Q.

The solution to the actual problem given is:

**Use ICE (equil.) table** (in Molarity when dealing w.  $K_C$ )



you know rxn must proceed to right (in forward direction) since starting with no  $\text{SO}_2$  or  $\text{O}_2$ . Conc. of  $\text{SO}_3$  is 1.000 M since you have 2 mol/2 L. Must use Molarity in ICE table.

Can solve for x from the information given for the equilibrium concentration of  $\text{SO}_3$ .

$$(1.000 - 2x) \approx 1.645 \text{ mol}/2.000 \text{ L} = 0.8225 \text{ M}$$

$$x = 0.08875 \text{ M}$$

$$K_C = \frac{4x^3}{(1.000 - 2x)^2} = \frac{4 (0.08875)^3}{\{1.000 - 2(0.08875)\}^2} = 4.1333 \times 10^{-3} = 4.13 \times 10^{-3} \quad (3 \text{ s.f.})$$

11. (3 pts) A plot of  $\ln(r)$  vs.  $\ln[A]$  has a slope of -2.5 and an intercept of -10.55. Determine the **rate constant** and **order** of the reaction for the rate law,  $r = k[A]^n$ .

$$r = k [A]^n \quad k = \text{rate constant} \quad n = \text{order}$$

Convert this to a linear equation.

Take the log of both sides, use the rules of logarithms and rearrange to make it look like an equation for a straight line. You can use either log or ln.

$$\log(r) = \log\{k[A]^n\} = \log(k) + \log\{[A]^n\} = \log(k) + n \log[A]$$

$$\log(r) = n \cdot \log[A] + \log(k) \quad \text{or} \quad \ln(r) = n \cdot \ln[A] + \ln(k)$$

$$y = m \cdot x + b$$

Using the equation from (a) how do you graphically obtain k and n (i.e. what do you plot as x and y and what are n and k related to on the graph)?

The data you have is concentration,  $[A]$ , and the corresponding rate. You take the log of each and plot  $\log(r)$  vs  $\log[A]$  (i.e.  $\log(r)$  is on the y axis and  $\log[A]$  is on the x axis) or  $\ln(r)$  and  $\ln[A]$ .

$$\text{if using log: } \log(k) = \text{y-intercept} \quad k = 10^{(\text{y-int})}$$

$$\text{if using ln: } \ln(k) = \text{y-intercept} \quad k = e^{(\text{y-int})}$$

$$n = \text{slope} \quad (\text{The slope can be either positive or negative depending on the order.})$$

$$n = -2.5 \quad \ln(k) = -10.55 \quad k = e^{-10.55} = 2.6 \times 10^{-5} \text{ M}^{3.5} \cdot \text{s}^{-1}$$

(Assuming molarity and seconds for units.)

This was the problem I presented in lecture and told everyone to do and ask the TAs or me whether you did it correctly. Only a few people asked.