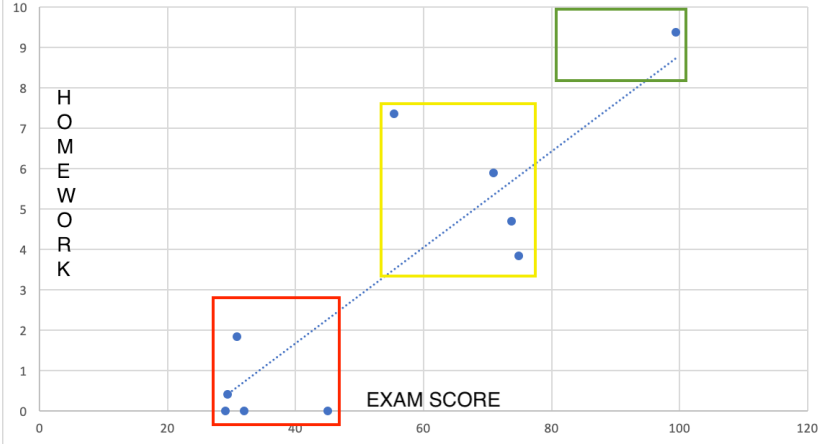


1412 - E2
CH 13 - Equilibrium
Notes

13

Exam 1: Bonus vs. Exam Score



CHAPTER 13 CHEMICAL EQUILIBRIA

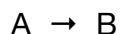
Introduction [13.1]

Basic idea of this chapter is to set up equations which all one to calculate the concentrations of reactants and products after a reaction has “run it’s course” (after the rate is no longer changing)

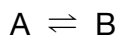
One-way versus Equilibrium Reactions

- For some reactions virually all reactants are converted to product (“one way”)
- For other reactions, only part of the reactants are converted to products (“equilibrium”)

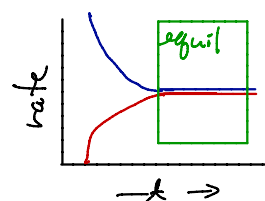
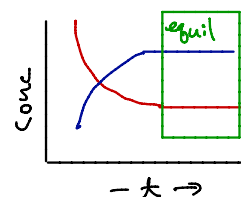
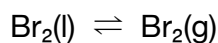
One-way



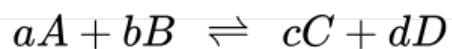
Dynamic Equilibrium



e.g., PHASE CHANGES are often in equilibrium



Reaction Quotients & Equilibrium Constants [13.2]



molar
concentrations

$$\text{reaction quotient} = Q_c = \frac{[C]^c [D]^d}{[A]^a [B]^b} \qquad Q_c = \frac{[\text{PRODUCTS}]^p}{[\text{REACTANTS}]^r}$$

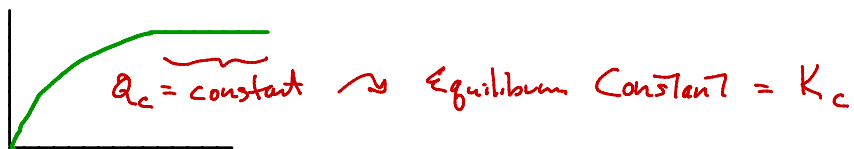
... for example...



$$Q_c = \frac{[\text{NO}_2]^4 [\text{H}_2\text{O}]^6}{[\text{NH}_3]^4 [\text{O}_2]^7}$$

Reaction Quotient vs. Equilibrium Constant

- At equilibrium, the 'REACTION QUOTIENT' is referred to as the EQUILIBRIUM CONSTANT, which is assigned the variable "Kc" (rather than Qc)

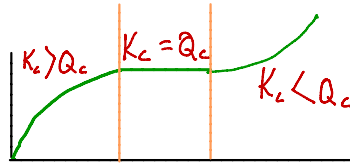


Caveat!!!

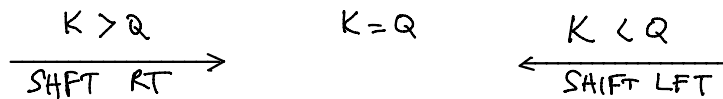
Kc changes with temperature

Shifting toward Equilibrium: K_c vs. Q_c

- One way to know if a reaction is at equilibrium is to compare its calculated Q_c value to the reactions known K_c value (this assumes K_c is known)
 - ↳ if $K_c > Q_c$, then the reaction will shift to the right (the measured situation does not have enough product)
 - ↳ if $K_c < Q_c$, then the reaction will shift to the left (the measured situation has too much product)
- Remember, Q_c will change until it equals K_c ; that is, the reaction will keep working toward equilibrium

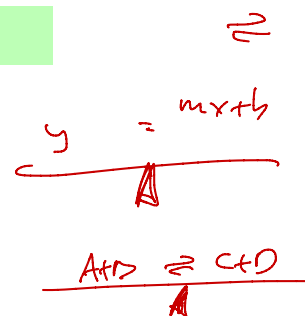
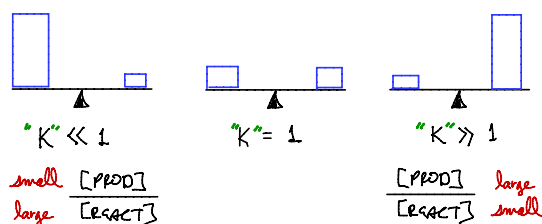


memory device



Visual aid: Relative Sizes of "K"

- ↳ If $K = 1$, then $[\text{PRODUCTS}]^p$ is equal to $[\text{REACTANTS}]^r$
- ↳ If $K < 1$, then $[\text{PRODUCTS}]^p$ is less than $[\text{REACTANTS}]^r$
- ↳ If $K > 1$, then $[\text{PRODUCTS}]^p$ is more than $[\text{REACTANTS}]^r$



- In industry, companies tend to want to make product, and so desire reactions for which K is as large as possible, which means little reactant is left over (unreacted). This translates to more product to sell and less waste.

(EX) K_c vs. Q – Reaction Shift

¿If K_c for a reaction is 65.0, but the current concentrations of reactant and products give $Q = 38.1$, what will happen to the reaction mixture: it will shift to the right; it will shift to the left; or it will remain as it is?

$$K_c > Q \quad \therefore \text{Shift rxn to right}$$

$$65.0 > 38.1$$

– Need to know next three sections to be able to write expressions for “K” –

Activity vs. Concentration

- Activity and Concentration are related, but they are not exactly the same...
- ACTIVITY is the “effective concentration” at specified conditions
 - ↳ activities are dimensionless
 - ↳ for DILUTE SOLUTIONS, activity \sim [conc]
 - ↳ for PURE SOLIDS AND LIQUIDS (consensed phases), activity = 1
 - ↳ for BULK SOLVENTS, assume activity = 1

NOTE:

recognizing the above unity activity situations can greatly simplify some of the calculations to come... factors of “1” can oft be ignored, simplifying many equations which would otherwise be more complicated

Homogeneous Equilibria

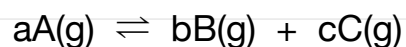
- All reactants and products are present in the same phase
- Two types
 - ↳ all liquid solution
 - ↳ all gas solution
- Review
 - ↳ (s) = solid, activity = 1
 - ↳ (l) = liquid, activity = 1
 - ↳ (g) = gas
 - ↳ (aq) = aqueous, activity = [conc] if dilute

Partial Pressure vs. Concentration

- Because Partial Pressure is proportional to [CONC], equilibrium constants for solutions containing gases can be derived using pressure

$$PV = nRT \quad \rightarrow \quad P = \frac{n}{V} RT \quad \rightarrow \quad PV = MRT \quad \rightarrow \quad P \propto M$$

Generic expressions: Can write GAS solutions in terms of Partial Pressure or Concentration



$$K_p = \frac{(P_B)^b (P_C)^c}{(P_A)^a}$$

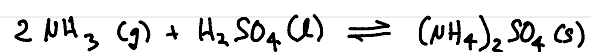
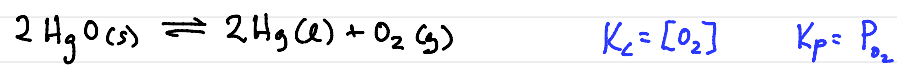
$$K_c = \frac{[B]^b [C]^c}{[A]^a}$$

Caveat!!!

$$K_p \neq K_c$$

(EX) Expressions for K

¿Write expressions for K_c and/or K_p for the following reactions?



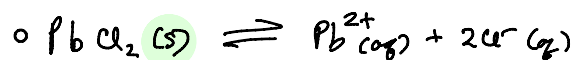
$$K_c = \frac{1}{[\text{NH}_3]^2} = [\text{NH}_3]^{-2}$$

$$K_p = \frac{1}{(P_{\text{NH}_3})^2} = (P_{\text{NH}_3})^{-2}$$

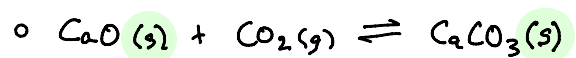
(EX) Expressions for K

Write expressions for K_c and/or K_p for the following reactions?

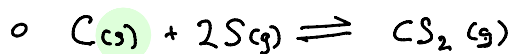
In Openstax ...



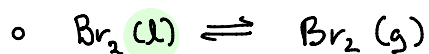
$$K_c = [\text{Pb}^{2+}][\text{Cl}^{-}]^2$$



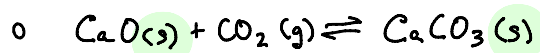
$$K_c = 1/[\text{CO}_2]$$



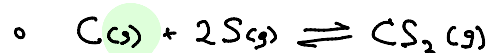
$$K_c = [\text{CS}_2]/[\text{S}]^2$$



$$K_c = [\text{Br}_2]$$



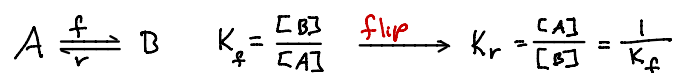
$$K_p = 1/P_{\text{CO}_2}$$



$$K_p = P_{\text{CS}_2}/(P_{\text{S}})^2$$

Converting Kp-to-Kc, and vice versa

Kc(forward) vs. Kc(reverse)



$$K_{c,reverse} = \frac{1}{K_{c,forward}}$$

Kc vs. Kp

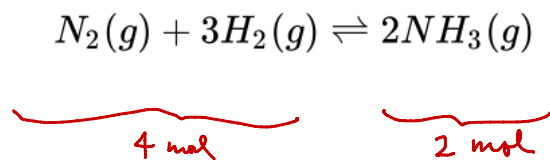
$$K_p = K_c (RT)^{\left(\begin{array}{l} \text{total moles} \\ \text{PROD side} - \text{REACT side} \end{array} \right)}$$

← BCE coefficients

$$K_p = K_c (RT)^{\Delta n}$$

(EX) Calculate K_p from K_c

¿The equilibrium constant for the Haber Process at 500 °C is 0.286. What is K_p ??



$$K_c = 0.286$$

$$K_p = K_c (RT)^{\Delta n}$$

$$K_p = K_c (RT)^{\Delta n} = (0.286) \left[(0.0821)(773) \right]^{(2-4)} = 7.10 \times 10^{-5}$$

How K_c changes with a Coefficient Change

$$K_{p, \text{original}} = K_{p, \text{new}}^n \quad n = \text{multiplier factor}$$

orig \times n = new

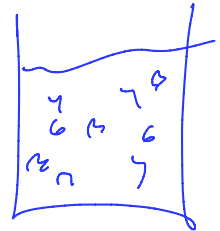
e.g. $2A \rightleftharpoons 2B + C \quad K_c = \frac{(3)^2 \cdot 4}{(2)^2} = 9$

$\downarrow \times \frac{1}{2}$

$$A \rightleftharpoons B + \frac{1}{2}C \quad K_c = \frac{3 \cdot (4)^{1/2}}{2} = 3$$

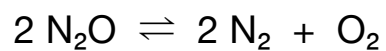
concentrations don't change b/c chemist uses different coeff.

K_c changes so [conc] can stay the same



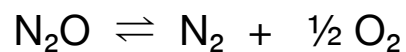
(EX) cont'd

In a previous example, K was determined to be 24.5,



$$K_c = 24.5$$

¿What is Kc for the reaction...



The multiplication factor is $\frac{1}{2}$. Don't start over and perform RICE. Rather...

$$K_{\text{new}} = (K_{\text{orig}})^{n\text{-factor}} = (24.5)^{\frac{1}{2}}$$

$$K_{\text{new}} = 4.95$$

(EX) Calculate K_c from RICE

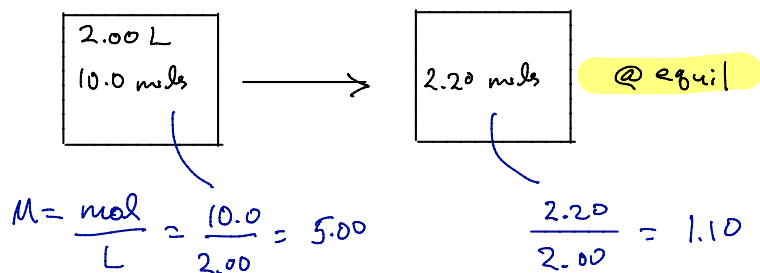
10.0 moles of N_2O are placed into a 2.00 L container, where it decomposes. At equilibrium, 2.20 moles of N_2O remain. What is K_c ?





(EX) Calculate K_c from RICE

¿ 10.0 moles of N_2O are placed into a 2.00 L container, where it decomposes. At equilibrium, 2.20 moles of N_2O remain. What is K_c ?



FAST

R	$2 N_2O \rightleftharpoons 2 N_2 + O_2$		
I	5.00	0	0
C	-3.90	+3.90	$\frac{1}{2}(3.90)$
Σ	1.10	3.90	1.95

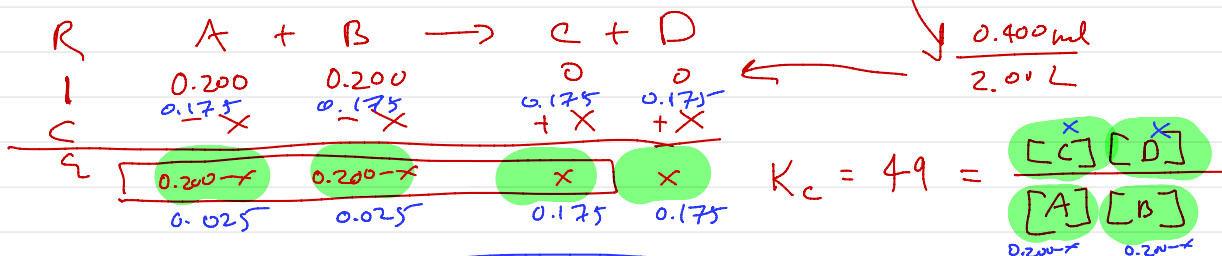
← EQ ← K
 ← X K
 ← X K

$$K_c = \frac{[N_2]^2 [O_2]}{[N_2O]^2} = \frac{(3.90)^2 | 1.95}{(1.10)^2} = 24.5 \text{ unitless}$$

Wed, Oct 2

(EX) Calc EQ concentration from K_c

What are the equilibrium concentrations for A, B, C, D if one started with 0.400 mol of A & B in a 2.00 L container, and knowing $K_c = 49$?



$$K_c = 49 = \frac{x \cdot x}{(0.200-x)(0.200-x)} \Rightarrow \frac{(x)^2}{(0.200-x)^2} = 49$$

$$x = 7(0.200 - x)$$

$$x = 1.400 - 7x$$

$$8x = 1.400$$

$$x = 0.175$$

$$\Leftrightarrow \frac{x}{0.200-x} = 7$$





(EX) Calc EQ concentration from K_c

¿What are the equilibrium concentrations for A,B,C,D if one started with 0.400 mol of A & B in a 2.00 L container, and knowing $K_c = 49$?

$$M_A = M_B = 0.400 \text{ mol} / 2.00 \text{ L} = 0.200$$

R	A	+	B	→	C	+	D	
I	0.200		0.200		0		0	
C	-x		-x		+x		+x	
E	0.2-x		0.2-x		x		x	$K_c = 49$



$$K_c = 49 = \frac{(x)(x)}{(0.2-x)(0.2-x)} = \frac{x^2}{(0.2-x)^2}$$

$$\sqrt{49} = \sqrt{\frac{x^2}{(0.2-x)^2}} \xrightarrow[\text{square}]{\text{perfect}} 7 = \frac{x}{0.2-x}$$

$A = 0.200 - 0.175 = 0.025 \text{ M}$
 $B = \quad \quad \quad = 0.025 \text{ M}$
 $C = x = 0.175$
 $D = x = 0.175$

$$\begin{aligned}
 7(0.2-x) &= x \\
 1.4 - 7x &= x \\
 1.4 &= 8x \\
 \boxed{0.175 = x}
 \end{aligned}$$

The Quadratic Equation

for $ax^2 + bx + c = 0$

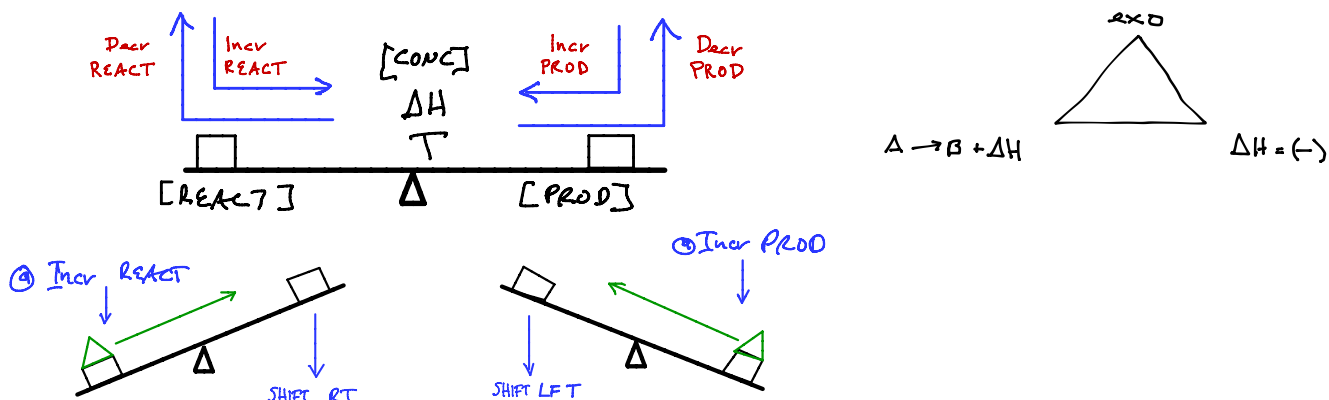
$$X = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

Shifting Equilibria [13.3]

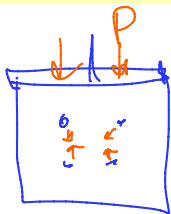
$$K_c = \frac{[\text{PRODUCTS}]^p}{[\text{REACTANTS}]^r}$$

← If any one changes, another must too...
 ... to RESTORE K

Rock-the-Boat: LeChatlier's Principle



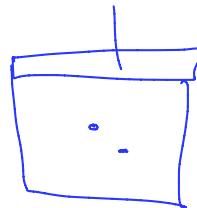
Gases



$$P = \left(\frac{n}{V}\right) RT \quad \leftarrow \text{[conc]}$$

↓ PV affects both sides ↓

$$\frac{[\text{REACT}]}{\Delta} [\text{PROD}]$$



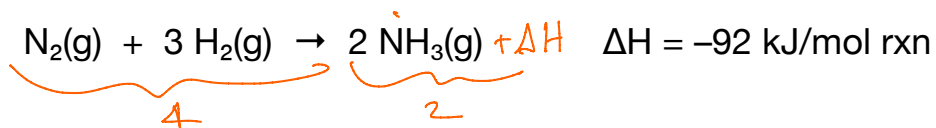
- o sys wants to keep same amount of "CROWDEDNESS"
 - Ⓐ $\uparrow P, \downarrow V \rightarrow$ more crowded \rightarrow SHIFT to side that gives SMALLER # particles
 - Ⓑ $\downarrow P, \uparrow V \rightarrow$ less crowded \rightarrow SHIFT to side that gives LARGER # particles

Catalyst

No effect on K

(EX) Predict Shift

In a closed container at 500 °C, predict the effect if . . .

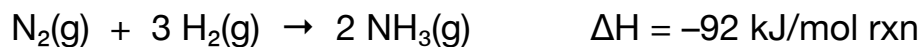


- Ⓐ Force more $\uparrow \text{H}_2$ into sys
- Ⓑ Remove $\downarrow \text{NH}_3$
- Ⓒ Remove $\downarrow \text{N}_2$
- Ⓓ \uparrow Pressure by \downarrow Vol
- Ⓔ \uparrow Temp
- Ⓕ add catalyst

SHIFT RT \rightarrow (HARSHER)
SHIFT RT \rightarrow
SHIFT LFT \leftarrow
SHIFT RT \rightarrow (to \downarrow crowding)
SHIFT LFT \leftarrow (rxn is EXO)
NO EFFECT

The Haber Process Dilemma

(a case study of when equilibrium and kinetics work against each other)



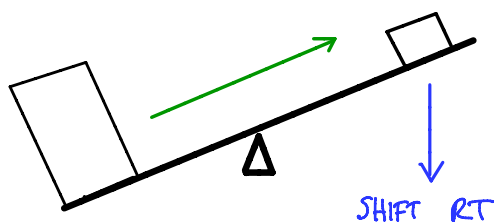
↳ Add heat shifts EQ LEFT, but ...

↳ Remove heat makes RXN uneconomically slow (slow @ 450°C)

⇓

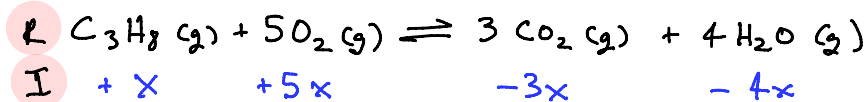
Remedy

- Remove product to drive RXN RT
- High Temp replaces product rapidly



Determining Relative Changes — The “I” in “RICE”

- Ratio per COEFF in BCE
- Sign per whether or not material is lost (-) or gained (+)

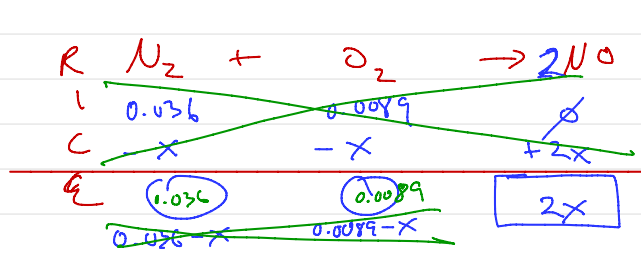


Three Basic Types of Equilibrium Problems

- Calc K_c from $[\text{R}_{\text{ACT}}, \text{P}_{\text{ROD}}]^{eq}$
- Calc $[\text{R}_{\text{ACT}}, \text{P}_{\text{ROD}}]^{eq}$ from K_c ; all $[\text{CONC}]$ known but one. leg/lunk (p732)
- Calc $[\text{R}_{\text{ACT}}, \text{P}_{\text{ROD}}]^{eq}$ from K_c ; RICE (≠ RICEICE)

(EX) Calc [conc] for 1 Unknown from K_c [ex 13.7]

NO is produced by reaction of N_2 and O_2 at high temperature. At 2000 K, $K_c = 4.1\text{E-}4$. Find the $[\text{NO}]$ in the equilibrium mixture with air at 1 atm, at this temperature, knowing that in air, $[\text{N}_2] = 0.036 \text{ M}$ and $[\text{O}_2] = 0.0089 \text{ M}$?



$$K_c = 4.1\text{E-}4 = \frac{[\text{NO}]^2}{[\text{N}_2][\text{O}_2]}$$

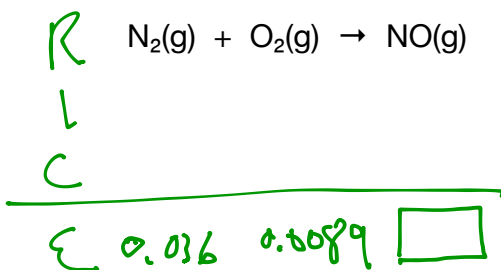


LECTURE STOP



(EX) Calc [conc] for 1 Unknown from K_c [ex 13.7]

NO_x is produced by reaction of N_2 and O_2 at high temperature. At 2000 K, $K_c = 4.1\text{E}-4$. Find the $[\text{NO}]$ in the equilibrium mixture with air at 1 atm, at this temperature, knowing that in air, $[\text{N}_2] = 0.036 \text{ M}$ and $[\text{O}_2] = 0.0089 \text{ M}$?



$$K_c = 4.1\text{E}-4$$

$$K_c = Q_c = \frac{[\text{NO}]^2}{[\text{N}_2][\text{O}_2]}$$

$$[\text{NO}]^2 = K_c [\text{N}_2][\text{O}_2]$$

$$[\text{NO}] = \sqrt{K_c [\text{N}_2][\text{O}_2]} \\ = \sqrt{(4.1 \times 10^{-4})(0.036)(0.0089)}$$

$$[\text{NO}] = \boxed{3.6 \times 10^{-4} \text{ M}}$$

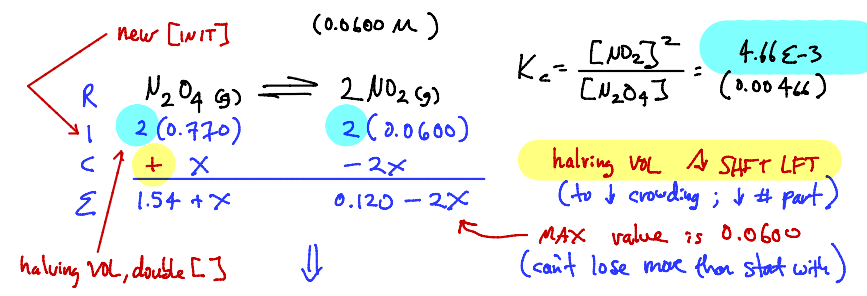
Mon, Oct 7

(EX) EQ Shift Calculation: Quantitative

¿ If a system at equilibrium has the following concentrations, what is the affect of halving the volume?

at EQ: $[NO_2] = 0.00 \text{ E-}2 \text{ M}$; $[N_2O_4] = 0.770 \text{ M}$

problem which illustrates a number of the equilibrium concepts



$K = 4.66 \text{ E-}3 = \frac{(0.120 - 2x)^2}{1.54 + x}$ Quadratic

$x^2 - 0.120x + 1.80 \text{ E-}3 = 0$

MAX = 0.0600

$x = 0.104$ $x = 0.017$

$[NO_2] = (0.120 - 2x)$
 $= 0.120 - 2(0.017)$
 $= 0.120 - 0.034$
 $= 0.086 \text{ M}$

$[N_2O_4] = (1.54 + x)$
 $= 1.54 + 0.017$
 $= 0.156 \text{ M}$

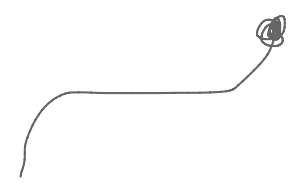
Recall: new [WIT] = 0.120 M \uparrow dec

incr [] orig [WIT] = 0.770 \uparrow incr

incr [] new [EQ] = 0.086 \leftarrow

incr more than DBL

incr less than DBL

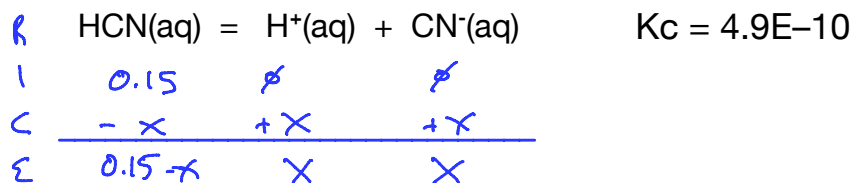


Approximate Solutions: when K is very small
(makes problem much easier)

- If K is very small, the Quadratic Eq can oft be avoided
- 5% rule is invoked

(EX) The 5% Rule Illustrated

¿What are the equilibrium concentrations in a 0.15 M HCN solution?



$K_c = 4.9 \times 10^{-10} = \frac{(x)(x)}{(0.15-x)}$
 $\Rightarrow 4.9 \times 10^{-10} = \frac{x^2}{0.15}$

very small and ... neglect →

Will discuss next section, how you know when you can and can't ignore a value

$x = \sqrt{(0.15)(4.9 \times 10^{-10})}$

Check 5% rule



$x = 8.6 \times 10^{-6} \text{ M}$

(see next page)

The 5% Rule — How does it work?

- The basic idea is that the calculated concentration is acceptable IF that calculated value varies less than 5% of the starting amount.
- Depending on the situation, your employer might accept a 10% variance, or maybe want no more than a 1% variance... but for this class, we'll go with 5%

How to calculate %Variance

QUESTION: Is the variance less than 5%?

ANSWER: Calculate variance, then compare it to 5%.

$$\% \text{ variance} = \frac{\text{calculated amount}}{\text{initial amount}} \times 100$$

(example next page)

(EX) ...continuing from the previous example problem...

¿ Having calculated equilibrium concentrations in a 0.15 M HCN solution using the 5% rule, is the final values acceptable?

$$\% \text{ variance} = \frac{\text{calculated amount}}{\text{initial amount (or } C_a)} \times 100 = \frac{x}{0.15} \times 100 = \frac{8.6 \times 10^{-6}}{0.15} \times 100 = 0.006\%$$

OK: $0.006\% < 5\%$

Alternate mathematical version (easier math)

Is C_a greater than $20x$?

$$C_a > 20x$$

$$0.15 > 20(8.6 \times 10^{-6})$$

$$0.15 > 0.0002$$

∴ good assumption

$$\frac{1}{20} > \frac{x}{C_a}$$

"BEFORE-the-calculation" best guess as to whether or not the 5% rule will work
(from source other than the textbook)

Is C_a greater than $100 K_a$?

$$C_a > 100 K_a$$

$$0.15 > 100(4.9 \times 10^{-10})$$

$$0.15 > 4.9 \times 10^{-8}$$

*∴ anticipated
good assumption*

Before-the-fact: compare C_a to K_a .

After-the-fact: compare C_a to x

$$C_a > 100 K_a$$

$$C_a > 20 x$$

Select Review Questions

(EX) Calc % Decomposition of Product <hard>

¿For the following reaction and associated data, what % of HBr is decomposed at equilibrium, at 1297 K, starting with pure HBr?

For the rxn: $\text{H}_2(\text{g}) + \text{Br}_2(\text{g}) \rightleftharpoons 2 \text{HBr}(\text{g})$

K_c values are: $K_c = 35,000$ @ 1495 K

$K_c = 160,000$ @ 1297 K

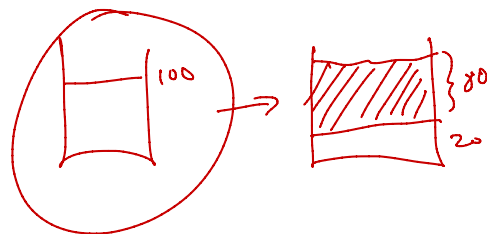
↑ K_c
↓ K_c
2 to 1

$$\% \text{ Decomposed} = \frac{\text{disappeared}}{C_a} \times 100$$

part
whole

$\frac{1}{2} \text{H}_2(\text{g}) + \frac{1}{2} \text{Br}_2(\text{g}) \rightleftharpoons \text{HBr}(\text{g})$ $K_c(\text{new}) =$

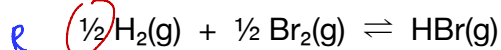
EAST



(EX) Calc % Decomposition of Product <hard>

For the following reaction and associated data, what % of HBr is decomposed at equilibrium, at 1297 K, starting with pure HBr?

For the rxn: $\text{H}_2(\text{g}) + \text{Br}_2(\text{g}) \rightleftharpoons 2 \text{HBr}(\text{g})$ } all gas rxn.
K_c values are: $K_c = 35,000$ @ 1495 K } $\uparrow \Delta H = \text{unfavorable (low } K_c)$
 $K_c = 160,000$ @ 1297 K } \therefore must be EXOTHERMIC



R			
I	0	0	1
C	-x	-x	+x
E	x	x	1-x

$$K_c = (K_{c, \text{orig}})^{1/2} = \sqrt{160,000} = 400$$

$$K_c = \frac{1-x}{(x)(x)^{1/2}} = \frac{1-x}{x} = 400$$

$$1-x = 400x$$
$$1 = 401x$$
$$x = 0.00249$$

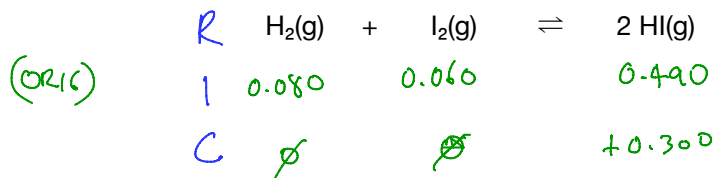
= amt dissociated

$$\% = \frac{C_{\text{diss}}}{C_{\text{init}}} \times 100$$
$$= \frac{0.00249}{1} \times 100$$
$$= 25\%$$

$$\% \text{ decomp} = \frac{C_{\text{diss}}}{C_{\text{init}}} \times 100$$

(EX) Addn of material to system at Equilibrium

H_2 and I_2 are mixed at 229°C in a sealed 1.00 L container. Equilibrium is established at $[\text{H}_2] = 0.080\text{ M}$, $[\text{I}_2] = 0.060\text{ M}$, and $[\text{HI}] = 0.490\text{ M}$. If 0.300 mol of HI is then added, what concentrations are present when equilibrium is re-established?



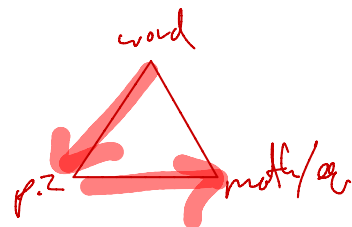
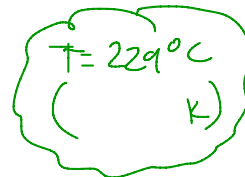
C			
Σ			

$K_c =$



problem which illustrates a number of the equilibrium concepts

(source: W9, Ex17-11)



(EX) Addn of material to system at Equilibrium

H_2 and I_2 are mixed at 229°C in a sealed 1.00 L container. Equilibrium is established at $[\text{H}_2] = 0.080\text{ M}$, $[\text{I}_2] = 0.060\text{ M}$, and $[\text{HI}] = 0.490\text{ M}$. If 0.300 mol of HI is then added, what concentrations are present when equilibrium is re-established?

NOTE: The following is a single question that illustrates many of the equilibrium concepts.
(source: W9, Ex 17-11, p602)

	$\text{H}_2(\text{g})$	+	$\text{I}_2(\text{g})$	\rightleftharpoons	$2\text{HI}(\text{g})$	R
mol >	0.080		0.060		0.490	Σ
	\emptyset		\emptyset		+ 0.300	
	0.080		0.060		0.790	I
	+X		+X		-2X	C
	$(0.080+X)$		$(0.060+X)$		$(0.790-2X)$	Σ

$$K = \frac{(0.490)^2}{(0.080)(0.060)} = 50$$

$$46X^2 + 10.2X - 0.38 = 0$$

↓ QUAD

$$X = 0.032 \text{ or } -0.25$$

X cannot be less than \emptyset

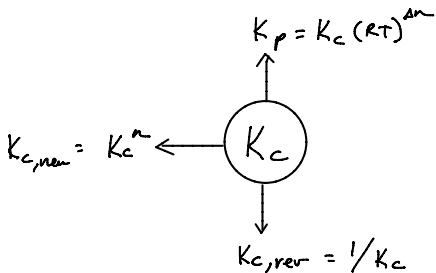
$$K = \frac{(0.790-2X)}{(0.080+X)(0.060+X)} = 50$$

!!! 1 eq / 2 unks

thus, must calc K from other data

- $[\text{H}_2] = 0.112\text{ M}$ (more than orig amt 0.080)
- $[\text{I}_2] = 0.092\text{ M}$ (more than orig amt 0.060)
- $[\text{HI}] = 0.726\text{ M}$ (less than "orig+stress" amt 0.790)

Cheat Sheet Notes



Why "K" must change w/ changing input...

K	[PROD, REACT]	INPUT
10	3	7
14	3	11
5	3	2

... must chg K so true if INPUT is changed...
 [PROD, REACT] is maintained

van Hoff

$$\ln \frac{K'}{K} = \frac{\Delta H^\circ}{R} \left(\frac{1}{T} - \frac{1}{T'} \right)$$

CC

$$\ln \frac{k'}{k} = \frac{E_a}{R} \left(\frac{1}{T} - \frac{1}{T'} \right)$$

$$\ln \frac{P'}{P} = \frac{\Delta H_v}{R} \left(\frac{1}{T} - \frac{1}{T'} \right)$$

$$\begin{aligned}
 P_T &= \sum P_i \\
 P_i &= X_i P_T \\
 PV &= nRT
 \end{aligned}$$

gas only

$$\begin{aligned}
 \Delta P &= X_{\text{solvent}} P^\circ_{\text{solvent}} \\
 P_i &= X_{(\text{in liq})} P_i^\circ \\
 C_i &= kP_i
 \end{aligned}$$

gas/liq barrier