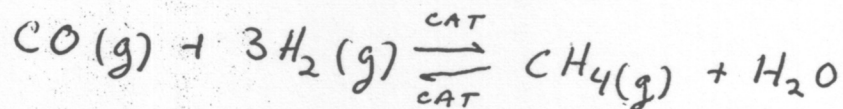


CHAPTER 14 CHEMICAL EQUILIBRIUM

MANY REACTIONS DO NOT COMPLETELY GO TO PRODUCTS
INSTEAD, PRODUCTS RE-REACT TO FORM REACTANTS
THESE REACTIONS ARE REVERSIBLE

FOR EXAMPLE



THESE ARE IMPORTANT REACTIONS IN COAL GASIFICATION

CHEMICAL EQUILIBRIUM (DYNAMIC EQUILIBRIUM) IS A STATE
REACHED BY A REACTION MIXTURE WHEN THE RATES OF FORWARD
AND REVERSE REACTIONS ARE EQUAL

INITIALLY, THE FORWARD REACTION WILL BE FAST AND THE
REVERSE REACTION SLOW.

AFTER SOME TIME, EQUILIBRIUM WILL BE REACHED

STOICHIOMETRY CAN BE APPLIED TO THE EQUILIBRIUM MIXTURE

EX. INITIALLY, 1 MOLE OF CO AND 3 MOLES H₂ ARE
PLACED IN A REACTION VESSEL. AT EQUILIBRIUM, 0.387
MOLES H₂O ARE PRESENT. WHAT IS THE MOLAR
COMPOSITION OF THE EQUILIBRIUM MIXTURE?

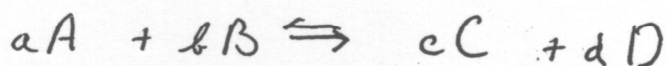
AMOUNT (MOLES)	CO	+ 3H ₂	\rightleftharpoons	CH ₄	+ H ₂ O
START	1.000	3.000		0	0
CHANGE	-0.387			0	0
EQUILIBRIUM	0.613	1.861		+ 0.387	+ 0.387
				0.387	+ 0.387

THE EQUILIBRIUM CONSTANT

THE AMOUNT OF EACH SUBSTANCE PRESENT IN THE EQUILIBRIUM DEPENDS ON THE INITIAL AMOUNT OF REACTANTS.

THE RELATIVE AMOUNTS OF EACH SUBSTANCE PRESENT ARE RELATED BY THE EQUILIBRIUM CONSTANT.

IN GENERAL:



where: A, B, C and D are reactants and products

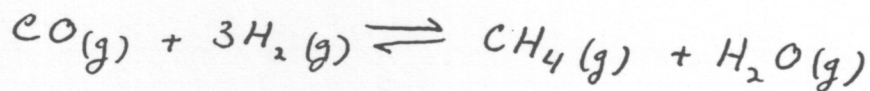
and: a, b, c, d are coefficients in the balanced reaction

THE EQUILIBRIUM CONSTANT K_c IS AN EXPRESSION OBTAINED BY MULTIPLYING THE CONCENTRATIONS OF PRODUCTS, DIVIDING BY THE CONCENTRATIONS OF REACTANTS, AND RAISING EACH TERM TO A POWER EQUAL TO THE COEFFICIENT IN THE CHEMICAL EQUATION

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

THE LAW OF MASS ACTION STATES THAT THE VALUES OF THE EQUILIBRIUM-CONSTANT EXPRESSION K_c ARE CONSTANT FOR A PARTICULAR REACTION AT A GIVEN TEMPERATURE, WHATEVER EQUILIBRIUM CONCENTRATIONS ARE SUBSTITUTED

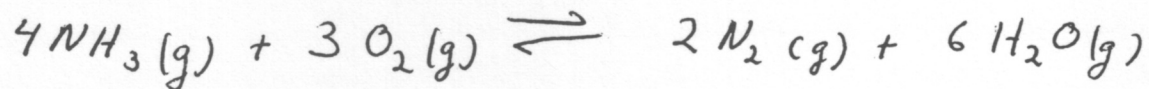
FOR THE COAL GASIFICATION REACTION



$$K_c = \frac{[CH_4][H_2O]}{[CO][H_2]^3}$$

EXAMPLES

WRITE EQUILIBRIUM CONSTANT EXPRESSION

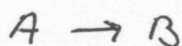


$$K_c =$$

WRITE BALANCED EQUATION

$$K_c = \frac{[\text{NH}_3]^4 [\text{O}_2]^5}{[\text{NO}]^4 [\text{H}_2\text{O}]^6}$$

THE KINETICS ARGUMENT FOR EQUILIBRIUM CONSTANTS



$$\text{rate} = k_F [A]$$

$$K_F = K_{\text{FORWARD}}$$



$$\text{rate} = k_R [B]$$

$$K_R = K_{\text{REVERSE}}$$

$$\text{AT EQUILIBRIUM } K_F = K_R$$

$$K_F [A] = K_R [B]$$

DIVIDE BY K_R AND $[A]$

$$\frac{K_F}{K_R} = \frac{[B]}{[A]} = K_c$$

$$K_c = \frac{K_F}{K_R}$$

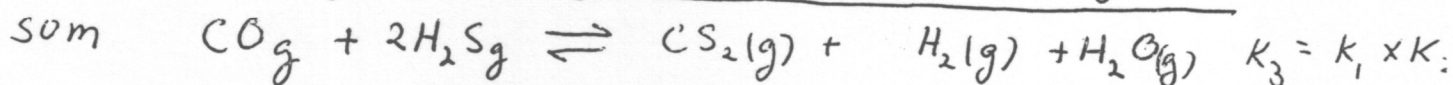
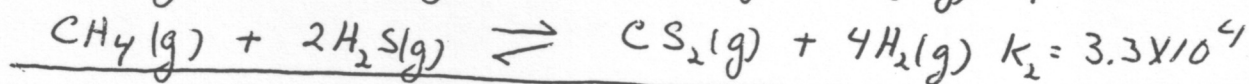
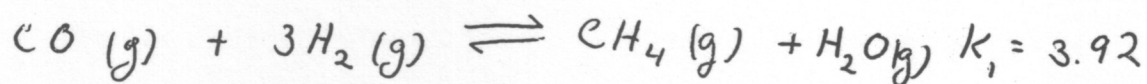
THE EQUILIBRIUM CONSTANT IS THE RATIO OF RATE CONSTANTS

EQUILIBRIUM CONSTANTS FOR THE SUM OF REACTIONS

DEFINITION:

IF A GIVEN CHEMICAL EQUATION CAN BE OBTAINED BY TAKING THE SUM OF OTHER EQUATIONS, THE EQUILIBRIUM CONSTANT FOR THE GIVEN EQUATION EQUALS THE PRODUCT OF THE EQUILIBRIUM CONSTANTS OF THE OTHER EQUATIONS

EXAMPLE:



$$K_1 = \frac{[\text{CH}_4][\text{H}_2\text{O}]}{[\text{CO}][\text{H}_2]^3}$$

$$K_2 = \frac{[\text{CS}_2][\text{H}_2]^4}{[\text{CH}_4][\text{H}_2\text{S}]^2}$$

$$K_1 \times K_2 = \frac{[\text{CH}_4][\text{H}_2\text{O}]}{[\text{CO}][\text{H}_2]^3} \times \frac{[\text{CS}_2][\text{H}_2]^4}{[\text{CH}_4][\text{H}_2\text{S}]^2}$$

$$K_1 \times K_2 = \frac{[\text{H}_2\text{O}][\text{CS}_2][\text{H}_2]}{[\text{CO}][\text{H}_2\text{S}]^2}$$

THIS IS THE EQUILIBRIUM EXPRESSION FOR THE OVERALL REACTION

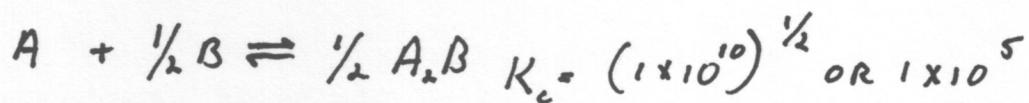
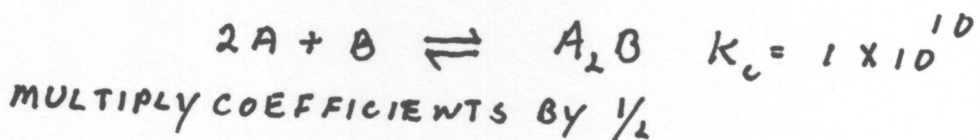
MODIFYING K_c

- 1) IF A REACTION IS REVERSED, K_c FOR THE REVERSE REACTION IS THE INVERSE OF K_c FOR THE FORWARD REACTION

$$K_F = \frac{1}{K_R} \quad \text{OR} \quad K_R = \frac{1}{K_F}$$

- 2) IF THE COEFFICIENTS OF A CHEMICAL EQUATION ARE MULTIPLIED BY A FACTOR N , OBTAIN THE NEW K_c BY RAISING THE ORIGINAL K_c TO THE POWER N

EXAMPLE



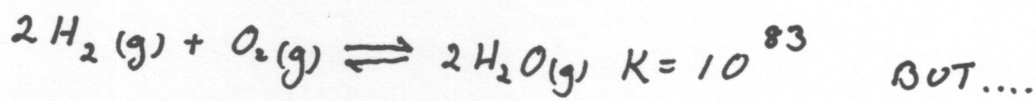
- 3) K_p IS RELATED TO K_c BY:

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

WHERE ΔN = THE CHANGE IN THE NUMBER OF MOLES OF GAS

- 4) K_c FOR THE SUM OF REACTIONS IS EQUAL TO THE PRODUCT OF EACH REACTIONS K_c

- 5) REMEMBER THAT THE RATE OF A REACTION IS NOT ALWAYS RELATED TO K_c



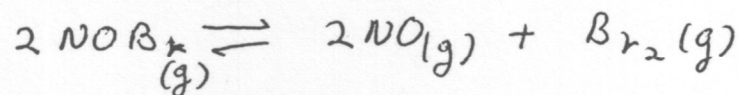
THE MIXTURE OF GASSES REACTS QUITE SLOWLY (KINETIC CONTROL)

UNLESS A SPARK IS APPLIED AND AN EXPLOSION RESULTS

(THERMODYNAMIC CONTROL)

EXAMPLE OF CALCULATING K_c FROM EQUILIBRIUM CONCENTRATIONS

FOR THE REACTION:



IF 2.00 moles NOBr_2 IN A 1L FLASK 9.4% OF NOBr_2 DISSOCIATES INTO PRODUCTS, CALCULATE K_c

	NOBr_2	NO	Br_2	
INITIAL	2.00	0	0	$.094 \times 2.00 = 0.188$
CHANGE	-0.188	+0.188	+0.094	
FINAL	1.812	0.188	0.094	

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

$$K_c = \frac{0.188^2 \times 0.094}{1.812^2}$$

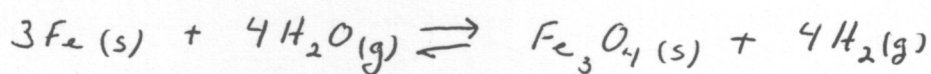
$$K_c = \frac{.00332}{3.283} = 0.00101$$

$$K_c = 1.01 \times 10^{-3}$$

IF REACTANTS AND PRODUCTS EXIST IN MORE THAN 1 PHASE, (IF THERE IS A PURE SOLID OR LIQUID PRESENT) IN A GAS PHASE REACTION, THE REACTION IS CALLED HETEROGENEOUS.

THE "CONCENTRATION" OF A PURE SOLID OR LIQUID IS DEFINED AS EQUAL TO ONE. THEREFORE, THESE TERMS ARE OMITTED FROM THE EQUILIBRIUM CONSTANT EXPRESSION

EXAMPLE:



$$K_c = \frac{[\text{H}_2]^4}{[\text{H}_2\text{O}]^4}$$

THIS IS BECAUSE THE "CONCENTRATION" OF THE SOLIDS REMAINS CONSTANT



$$K_c =$$

USING THE EQUILIBRIUM CONSTANT

SOME EASY AND USEFUL APPLICATIONS OF K_c

1) QUALITATIVE USE

SIMPLY LOOKING AT THE MAGNITUDE OF K_c TELLS IF PRODUCTS OR REACTANTS ARE FAVORED

2) PREDICTING THE DIRECTION NON-EQUILIBRIUM MIXTURES WILL TAKE

3) CALCULATING EQUILIBRIUM CONCENTRATIONS

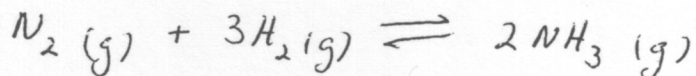
QUALITATIVE USE OF K_c

IF K_c IS LARGE, PRODUCTS ARE FAVORED

IF K_c IS SMALL, REACTANTS ARE FAVORED

IF K_c IS NEAR 1, NEITHER ARE FAVORED

EXAMPLE: K_c IS LARGE



AT 25°C $K_c = 4.1 \times 10^8$

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

← NUMERATOR IS 4.1×10^8 LARGER THAN
← DENOMINATOR

IF $[\text{N}_2] = 0.01 \text{ M}$

$[\text{H}_2] = 0.01 \text{ M}$

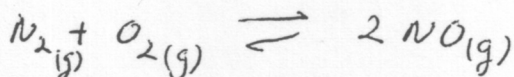
SUBSTITUTE INTO EQUILIBRIUM EXPRESSION

$$4.1 \times 10^8 = \frac{x^2}{0.01 \times 0.01^3} = \frac{x^2}{1 \times 10^{-8}}$$

$$[\text{NH}_3]^2 = 4.1$$

$[\text{NH}_3] = 2 \text{ M}$, 200 TIMES GREATER THAN 0.01 M

EXAMPLE: K_c IS SMALL



AT 25°C $K_c = 4.6 \times 10^{-31}$

IF $[\text{N}_2] = 1 \text{ M}$

$[\text{O}_2] = 1 \text{ M}$

SUBSTITUTE INTO EQUILIBRIUM EXPRESSION

DO PROBLEM

14.44

$$4.6 \times 10^{-31} = \frac{[\text{NO}]^2}{1 \times 1}$$

$$[\text{NO}]^2 = 4.6 \times 10^{-31} \quad [\text{NO}] = 6.8 \times 10^{-16}$$