PREDICTING THE DIRECTION OF A REACTION

GIVEN A SET OF NON-EQUILIBRIUM CONCENTRATIONS

CALCULATE A NUMBER CALLED THE <u>REACTION QUOTIENT</u> <u>$Q_c$</u>

FOR A GENERAL REACTION

$$aA + bB \rightleftharpoons cC + dD$$

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

SO $Q_c$ IS DEFINED EXACTLY AS $K_c$, EXCEPT NOT AT EQUILIBRIUM

THEN COMPARE $Q_c$ TO $K_c$ USING THE FOLLOWING LOGIC

IF $Q_c$ IS LARGER THAN $K_c$, REACTION GOES TOWARDS REACTANTS
REACTION GOES LEFT

IF $Q_c$ IS SMALLER THAN $K_c$, REACTION GOES TOWARDS PRODUCTS
REACTION GOES RIGHT

IF $Q_c$ IS $= K_c$, REACTION IS AT EQUILIBRIUM

EXAMPLE:

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g) \qquad K_c = 0.5 \text{ AT } 400^\circ C$$

GIVEN CONDITIONS $[N_2] = 0.020\,m$ $[H_2] = 0.06\,m$ $[NH_3] = 0.01\,m$

$$Q_c = \frac{[NH_3]^2}{[N_2][H_2]^3} = \frac{0.01^2}{0.02 \times 0.06^3} = \frac{0.0001}{0.02 \times 0.00022}$$

$$Q_c = \frac{0.0001}{0.0000043} = \frac{1}{.043} = 23.1$$

OR

$$Q_c = \frac{1 \times 10^{-4}}{4.3 \times 10^{-6}} = .231 \times 10^{2} = 23.1$$

23.1 IS GREATER THAN 0.5 SO REACTANTS ARE FAVORED

USING $Q_c$

$$2\,NOBr(g) \rightleftharpoons 2\,NO(g) + Br_2(g)$$

AT 24°C $K_c = 3.07 \times 10^{-4}$

GIVEN THE CONDITIONS
$[NOBr] = 0.0610\,M$
$[NO] = 0.0151\,M$
$[Br_2] = 0.0108\,M$

CALCULATE $Q_c$ AND PREDICT THE DIRECTION OF THE REACTION

$$Q_c = \frac{[NO]^2[Br_2]}{[NOBr]^2}$$

$$Q_c = \frac{0.0151^2 \times 0.0108}{0.06^2}$$

$$Q_c = \frac{.000228 \times .0108}{.0036}$$

$$Q_c = \frac{.0000024}{.0036} \quad \text{OR} \quad \frac{2.4 \times 10^{-6}}{3.6 \times 10^{-3}}$$

$$Q_c = .006667 \quad \text{OR} \quad 6.67 \times 10^{-4}$$

$Q_c > K_c$ SO REACTION GOES TO LEFT

CALCULATING EQUILIBRIUM CONCENTRATIONS

GIVEN $K_c$ AND ALL BUT ONE OF THE CONCENTRATIONS, CALCULATE THE UNKNOWN CONCENTRATION

$$CO(g) + 3H_2(g) \rightleftharpoons CH_4(g) + H_2O(g)$$

AT 1200°K $K_c = 3.92$ IF $[CO] = 0.30\,M$
$[H_2] = 0.10\,M$
$[H_2O] = 0.02\,M$

WHAT IS $[CH_4]$?

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

SUBSTITUTE $3.92 = \frac{[CH_4][0.02]}{0.03 \times 0.1^3}$

SOLVE FOR $[CH_4]$

$$[CH_4] = \frac{3.92 \times 0.03 \times 0.1^3}{0.02}$$

$$[CH_4] = 0.059\ M$$

MORE CALCULATING EQUILIBRIUM CONCENTRATIONS

REMEMBER
1) SET UP A TABLE OF INITIAL, CHANGE AND FINAL CONCENTRATIONS
2) SUBSTITUTE KNOWN VALUES
3) SOLVE EQUILIBRIUM CONSTANT EQUATION

EXAMPLE:

$$CO(g) + H_2O_g \rightleftharpoons CO_2(g) + H_2(g)$$

AT 1000°C, $K_c = 0.58$, $[CO] = 0.020\,m$ $[H_2O] = 0.02\,m$

| CONCENTRATIONS | $CO$ | $H_2O$ | $CO_2$ | $H_2$ |
|---|---|---|---|---|
| INITIAL | 0.020m | 0.020m | 0 | 0 |
| CHANGE | $-x$ | $-x$ | $+x$ | $+x$ |
| EQUILIBRIUM | $0.020-x$ | $0.020-x$ | $x$ | $x$ |

$$K_c = \frac{[CO_2][H_2]}{[CO][H_2O]} = 0.58 = \frac{x \times x}{(0.020-x)(0.020-x)}$$

$$K_c = 0.58 = \frac{x^2}{(0.020-x)^2}$$

$$K_c = 0.58 = \frac{x^2}{(0.020 - x)^2}$$ TAKE THE SQUARE ROOT OF BOTH SIDES

$$0.76 = \frac{x}{0.020 - x}$$ SOLVE FOR X

$$x = (0.76)(0.020 - x)$$ DISTRIBUTE

$$x = 0.0152 - 0.76x$$ ADD 0.76x TO BOTH

$$1.76x = 0.0152$$

$$x = \frac{0.0152}{1.76} = 0.0086$$

SUBSTITUTE X INTO THE LAST ROW OF THE TABLE

| $CO$ | $H_2O$ | $CO_2$ | $H_2$ |
|---|---|---|---|
| 0.0114 m | 0.0114 m | 0.0086 m | 0.0086 m |

REVIEWING:

1) SET UP A TABLE OF CONCENTRATIONS INITIAL CHANGE AND EQUILIBRIUM
2) SUBSTITUTE KNOWN VALUES AND EXPRESSIONS IN $x$ INTO THE EQUILIBRIUM CONSTANT EXPRESSION
3) SOLVE THE EQUILIBRIUM CONSTANT EQUATION

CHANGING THE REACTION CONDITIONS

LE CHATELIER'S PRINCIPLE

WHEN A SYSTEM IN CHEMICAL EQUILIBRIUM IS DISTURBED BY A CHANGE OF TEMPERATURE, PRESSURE OR CONCENTRATION, THE SYSTEM SHIFTS IN EQUILIBRIUM COMPOSITION IN A WAY THAT TENDS TO COUNTERACT THIS CHANGE

REMOVING PRODUCTS OR ADDING REACTANTS

IT IS OFTEN POSSIBLE TO DRIVE A REACTION IN THE DESIRED DIRECTION BY EITHER REMOVING PRODUCT OR ADDING REACTANT. THE SYSTEM RESPONDS TO PRODUCT REMOVAL BY RE-ESTABLISHING EQUILIBRIUM BY MAKING MORE PRODUCT.

IN THIS REACTION

$$CO(g) + 3H_2(g) \rightleftharpoons CH_4(g) + H_2O(g)$$

WATER VAPOR IS EASILY REMOVED FROM THE REACTION MIXTURE BY COOLING. ONCE THE $H_2O$ IS REMOVED, LE CHATELIER'S PRINCIPLE PREDICTS THAT THE REACTION WILL GO IN A FORWARD DIRECTION UNTIL EQUILIBRIUM IS RE-ESTABLISHED.

THIS TABLE (14-1) SHOWS THIS EFFECT

| | $CO$ | $H_2$ | $CH_4$ | $H_2O$ |
|---|---|---|---|---|
| ORIGINAL MIXTURE | 0.613 | 1.839 | 0.387 | 0.387 |
| AFTER $H_2O$ REMOVAL (BEFORE EQUILIB) | 0.613 | 1.839 | 0.387 | 0 |
| NEW EQUILIBRIUM | 0.491 | 1.473 | 0.509 | 0.122 |

INSTEAD OF REMOVING PRODUCT, REACTANT CAN BE ADDED IN THIS REACTION:

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$

IT IS POSSIBLE TO ADD SOME (CHEAP) $N_2$ TO AN EQUILIBRIUM MIXTURE. LeCHATELIER'S PRINCIPLE PREDICTS THAT THE REACTION WILL GO IN THE FORWARD DIRECTION AND MAKE MORE $NH_3$

TO SUM UP, LeCHATELIER'S PRINCIPLE SAYS THAT:

WHEN MORE REACTANT IS ADDED, OR SOME PRODUCT IS REMOVED, (AND THE CONCENTRATIONS OF PRODUCT OR REACTANT ARE CHANGED) NET REACTION OCCURS FROM LEFT TO RIGHT (FORWARD) TO GIVE A NEW EQUILIBRIUM AND MORE PRODUCTS ARE PRODUCED

CONVERSELY

WHEN MORE PRODUCT IS ADDED, OR SOME REACTANT IS REMOVED FROM AN EQUILIBRIUM MIXTURE, (AND THE CONCENTRATIONS OF PRODUCT OR REACTANT ARE CHANGED) NET REACTION OCCURS FROM RIGHT TO LEFT (REVERSE) TO GIVE A NEW EQUILIBRIUM, AND MORE REACTANTS ARE PRODUCED

KEEP IN MIND THAT A REACTION WHOSE EQUILIBRIUM CONSTANT IS EXTREMELY SMALL REMAINS ALMOST COMPLETELY AS REACTANTS AND CANNOT BE MUCH AFFECTED BY ADDING REACTANTS OR REMOVING PRODUCTS

EXAMPLE $CO_2(g) + 2H_2O(g) \rightleftharpoons CH_4(g) + 2O_2(g) \quad K_c = 10^{-140}$

# LE CHATELIER'S EXAMPLES

PREDICT THE DIRECTION IF:

$$H_2\,(g) + I_2\,(g) \rightleftharpoons 2HI\,(g)$$

IF $H_2$ IS REMOVED

$$CaCO_3\,(s) \rightleftharpoons CaO_{(s)} + CO_{2\,(g)}$$

IF THE PRESSURE [CONCENTRATION] OF $CO_2$ IS INCREASED

$$CH_4\,(g) + 2S_2\,(g) \rightleftharpoons CS_2\,(g) + 2H_2S\,(g)$$

IF $CS_2$ IS REMOVED BY CONDENSATION

FOR GASSES, PARTIAL PRESSURE IS EQUIVALENT TO CONCENTRATION

A SIMPLE SUMMARY OF LE CHATELIER'S PRINCIPLE FOR GASSES IS:

IF THE PRESSURE IS INCREASED BY DECREASING THE VOLUME (COMPRESSING) A REACTION MIXTURE, THE REACTION SHIFTS IN THE DIRECTION OF OF <u>FEWER MOLES</u> OF <u>GAS</u>

EXAMPLES

$$H_2\,(g) + Br_2\,(g) \rightleftharpoons 2HBr$$

IF PRESSURE IS INCREASED, GOES TO

$$CO_2\,(g) + C_{(s)} \rightleftharpoons 2CO_{(g)}$$

IF PRESSUREIS INCREASED, GOES TO

# EFFECT OF TEMPERATURE CHANGE

LE CHATELIER'S PRINCIPLE FOR TEMPERATORE CHANGES IS EASILY UNDERSTOOD IF YOU CONSIDER HEAT AS A PRODUCT OF A REACTION (OR A REACTANT)

EXOTHERMIC REACTIONS PRODUCE HEAT.

INCREASING THE TEMPERATURE DECREASES PRODUCTS $K_c$ SMALL

DECREASING THE TEMPERATURE INCREASES PRODUCTS $K_c$ LARGE

THE OPPOSITE IS TRUE OF ENDOTHERMIC REACTIONS

ENDOTHERMIC REACTIONS CONSUME HEAT

INCREASING THE TEMPERATORE INCREASES PRODUCTS $K_c$ LARGER

DECREASING THE TEMPERATURE DECREASES PRODUCTS $K_c$ SMALLER

EXAMPLE $CO_2(g) + C_{(s)} \rightleftharpoons 2CO$ $\Delta H = 172.5$ KJ

IS A HIGH OR LOW TEMPERATURE MORE FAVORABLE TO THE FORMATION OF CARBON MONOXIDE?

IS THE REACTION ENDO OR EXOTHERMIC?