3. $C_2H_{6(g)}$ + energy $\Rightarrow$ $C_2H_{2(g)}$ + $2H_{2(g)}$ $\Delta H = +311kJ$

← exothermic

→ more (g) molec.

system will tend to favor equilibrium.

Assignment 5: Reaction Predictions

State whether each reaction will go to completion (C), equilibrium (E), or not react (NR)

1. $4NH_{3(g)} + 5O_{2(g)} \Rightarrow 4NO_{(g)} + 6H_2O_{(g)}$ $\Delta H = +115kJ$
2. $N_2O_{4(g)} + 58.9kJ \Rightarrow 2NO_{2(g)}$
3. $2Bi^{3+}_{(aq)} + 3H_2S_{(g)} \Rightarrow BiS_{3(s)} + 6H^{+}_{(aq)}$ + energy
4. $2H_2O_{2(aq)} \Rightarrow O_{2(g)} + 2H_2O_{(l)}$ $\Delta H = -189kJ$
5. $H_2O_{(g)} + C_{(s)} \Rightarrow CO_{2(g)} + H_{2(g)}$ $\Delta H = +31.3kJ$
6. $3C_2H_{2(g)} \Rightarrow C_6H_{6(g)} + 143kJ$
7. $NaOH_{(aq)} + 2.4kJ \Rightarrow NaOH_{(s)}$
8. $CS_{2(g)} + 3O_{2(g)} \Rightarrow CO_{2(g)} + 2SO_{2(g)} + 66kJ$

9. A student predicts that the following reaction will go to completion. Do you agree or disagree? Support with an explanation.

$$CO_{(g)} + H_2O_{(l)} \Rightarrow CO_{2(g)} + H_{2(g)} \quad \Delta H = 42kJ$$

10. For the following reaction, in which direction is enthalpy increasing? In which direction is entropy maximized? Will the reaction reach equilibrium?

$$2C_4H_{10(g)} + 13O_{2(g)} \Rightarrow 8CO_{2(g)} + 10H_2O_{(g)} + 128kJ$$

V) The Equilibrium Constant

molar ratio of products over reactants at Equilibrium

The equilibrium constant is called "K_{eq}" and is found by multiplying product concentrations and dividing that by the result of multiplying reactant concentrations.

Do **not** include solids and liquids in K_{eq} expressions as the concentrations of these remain constant.

Example: Write the K_{eq} expression:

$$2HI_{(g)} \Leftrightarrow I_{2(g)} + H_{2(g)} \qquad K_{eq} = \frac{[H_2][I_2]}{[HI][HI]} = \frac{[H_2][I_2]}{[HI]^2}$$

EQUILIBRIUM LAW: $pA + qB \rightleftharpoons rC + sD$

$K_{eq} = \frac{[A]^p[B]^q}{[C]^r[D]^s}$ where p,q,r,s are the coefficients in the balanced equation.

Examples: Write a K_{eq} for each of the following:

a) $2H_{2(g)} + O_{2(g)} \Leftrightarrow 2H_2O_{(g)}$ $K_{eq} = \frac{[H_2O]^2}{[H_2]^2[O_2]}$

b) $3Sn^{2+}_{(aq)} + 2PO_4^{3-}{}_{(aq)} \Leftrightarrow Sn_3(PO_4)_{2(s)}$ $K_{eq} = \frac{1}{[Sn^{2+}]^3[PO_4^{3-}]^2}$ ← product is a (s)

c) $2Na_{(s)} + 2H_2O_{(g)} \Leftrightarrow 2NaOH_{(s)} + H_{2(g)}$ $K_{eq} = \frac{[H_2]}{[H_2O]^2}$

d) $N_{2(g)} + 3H_{2(g)} \Leftrightarrow 2NH_{3(g)}$ $K_{eq} = \frac{[NH_3]^2}{[N_2][H_2]^3}$

Go to page 40 & 41 in Hebden and look at the tables in #6 & 7 *(you did these questions in Assignment 1).* Calculate the K_{eq} constant for the equilibrium that was attained after 10 minutes (bottom of p.40):

$K_{eq} = \frac{1.00}{0.200} = 5.00$

Then, the equilibrium was disturbed by increasing [B] (see top of p.41). Calculate the K_{eq} after a new equilibrium was reached at 18 minutes:

$K_{eq} = \frac{1.500}{0.300} = 5.00$ This is why Keq is a CONSTANT.

If equilibrium is disturbed due to a *concentration* or *pressure* change, it will shift and eventually return to a new equilibrium, and though the concentrations of each gas and aqueous substance may be different than they were originally, the equilibrium constant (K_{eq}) - the ratio of products to reactants - will remain the same, hence why it is called a CONSTANT.

ΔTemp = ΔKeq.

However, if equilibrium is disturbed due to a *temperature* change, the K_{eq} constant will change.

It is mathematically impossible for the K_{eq} to remain the same after a temperature change. Because there are no immediate changes in concentration due to a temperature change, when a shift occurs, one side ↑ increases and the other side decreases. When you apply this to a fraction (the K_{eq} expression), it cannot possibly stay constant.

Lets say originally... $K_{eq} = \frac{[P]}{[R]} = \frac{2}{5} = 0.40$

after an temp. shift left (products ↓ and reactants ↑)

$K_{eq} = \frac{1}{6} = 0.17$ Mathematically, the Keq MUST change.

(same is true for a shift right.)

So how is it possible that K_{eq} mathematically can, and actually will, stay the same after a concentration or pressure change?

Because there are immediate concentration changes before shift changes. (spikes in graph)

For example, if you increase [HI} in this system: $2HI_{(g)} \Leftrightarrow H_{2(g)} + I_{2(g)}$, then all concentrations end up with a net increase, so the fraction can, and will, remain the same:

For example, originally, $K_{eq} = \frac{(3.0)(3.0)}{(2.0)^2} = 2.25$

After [HI] increase, $K_{eq} = \frac{(4.0)(4.0)}{(2.667)^2} = 2.25$ the ratio of $\frac{[products]}{[reactant]}$ remains same

all [conc.] ↑

The Size of the K_{eq} Constant:

Remember, $K_{eq} = \frac{[products]}{[reactants]}$

If the K_{eq} is small (less than 1), does the equilibrium system contain a higher concentration of reactants or products (look at the fraction above)?

$K_{eq} < 1$ means [reactants] > [products] (denominator is larger # ∴ $K_{eq} < 1$)

What if the K_{eq} is large (greater than 1)?

$K_{eq} > 1$ means [reactants] < [products] (numerator is larger # ∴ $K_{eq} > 1$)

Examples:

Do the following equilibria favour reactants or products?

a) $2HBr_{(g)} \Leftrightarrow H_{2(g)} + Br_{2(g)}$ $K_{eq} = 7.0 \times 10^{-20}$ $K_{eq} < 1$ ∴ reactants fav.

b) $C_2H_{4(g)} + H_{2(g)} \Leftrightarrow C_2H_{6(g)}$ $K_{eq} = 1.2 \times 10^{19}$ $K_{eq} > 1$ ∴ products fav.

c) $Si_{(s)} + O_{2(g)} \Leftrightarrow SiO_{2(g)}$ $K_{eq} = 2.0 \times 10^{-1}$ $K_{eq} < 1$ ∴ reactants fav.

Writing the Equation the other way around

For the following reaction:

$$H_{2(g)} + F_{2(g)} \Leftrightarrow 2HF_{(g)}$$

a) Write the K_{eq} equation. The $K_{eq} = 0.25$

$K_{eq} = \frac{[HF]^2}{[H_2][F_2]} = 0.25$ ← given

b) Now, write the K_{eq} expression for this reaction, and find the K_{eq} constant value: $2HF_{(g)} \Leftrightarrow H_{2(g)} + F_{2(g)}$

$K_{eq} = \frac{[H_2][F_2]}{[HF]^2}$

This is the reciprocal of the equation above. ∴ the Keq constant is the reciprocal of 0.25

$\frac{1}{0.25} = K_{eq}$

∴ $K_{eq} = 4.0$

VI) Temperature and the K_{eq} Constant

↑ If temperature is increased for an equilibrium system, in what direction does the system shift? endothermic direction is favored.

(recall, endo is affected more) ↓ What if temperature is decreased? exothermic is favored.

If a shift right results due to temperature change, will the K_{eq} increase or decrease? → right shift = ↑[products] ∴ Keq will increase

If a shift left results due to a temperature change, will K_{eq} increase or decrease? ← left shift = ↑[reactants] ∴ Keq will decrease

Example:

If the temperature is decreased in the following system, will K_{eq} increase or decrease? Explain.

energy + $2HI_{(g)} \Leftrightarrow H_{2(g)} + I_{2(g)}$ $\Delta H = +500$ kJ (endothermic)

Temp ↓ endo slows more.

∴ ↑[reactants] ⇐ shift to exothermic | Keq will decrease

Example: Given the following equation and data:

FWD → (endo) ← RVS (exo)

$$XY + ZM \Leftrightarrow YM + XZ$$

$K_{eq} = 60.0$ at 300°C

$K_{eq} = 45.0$ at 500°C

Keq ↓ with a temp ↑

Is the forward reaction endothermic or exothermic? Explain.

- ↑temp increase favors a shift in the endothermic direction.
- For Keq to decrease [reactants] > [products]
- Therefore a shift left is occuring.
- therefore the rvs rxn is endothermic
  ie: FWD rxn is exothermic.