Outline

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Equilibrium Condition

All reactions proceed in both directions...

$$H_2 + CI_2 \rightleftharpoons 2HCI$$

The rate of the forward and reverse rxns depend on <u>temperature</u> and the <u>concentrations</u>

 $R_{f} = k_{f} [H_{2}] [CI_{2}]$

 $R_r = k_r [HCI]^2$

The net direction of the reaction is determined by the rates of the reactions, relative to one another

In a container with H_2 , Cl_2 and HCl...

1. If $R_f > R_r$, then forward spontaneous: $H_2 + Cl_2 \rightarrow 2HCl$

2. If $R_f < R_r$, then reverse spontaneous: $H_2 + CI_2 \leftarrow 2HCI$

3. If $R_f = R_r$, then equilibrium: $H_2 + CI_2 \rightleftharpoons 2HCI$

<u>Chemical equilibrium</u> is the condition when the forward and reverse rates of reaction are equal

Reactions proceed until chemical equilibrium is established!

For a certain temperature,

 $k_f = 1.00 \text{ sec}^{-1} \text{ M}^{-1}$ and $k_r = 1.36 \text{ sec}^{-1} \text{ M}^{-1}$

where $R_f = k_f[H_2][CI_2]$ and $R_r = k_r[HCI]^2$

In which direction is the rxn spontaneous?

[H ₂], M	[Cl ₂], M	[HCI], M	R _f , M/s	R _r , M/s	Direction
10	10	0	100	0	forward
9	9	2	81	5.4	forward
8	8	4	64	22	forward
7	7	6	49	49	equilibrium

Equilibrium Constant

At equilibrium...

$$R_f = R_r$$

 $k_{f} [H_{2}] [CI_{2}] = k_{r} [HCI]^{2}$

 $\frac{k_{f}}{k_{r}} = \frac{[HCI]^{2}}{[H_{2}][CI_{2}]}$

equilibrium constant expression

 $k_f / k_r = K_{eq}$, the <u>equilibrium constant</u>

Equilibrium constants (K) are...

written without units!

constant only for constant temperature!

Equilibrium constants (K) give measure of how far a reaction goes...

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

We write... $K = \frac{[C]^{c} [D]^{d}}{[A]^{a} [B]^{b}}$ (equilibrium constant expression)

K expression contains substances whose concentrations can change

gases (g) and dissolved substances (aq) are included solids (s) and liquids (l) are not included

Find K_{eq} for

$$CO_2(g) + C(s) \rightleftharpoons 2CO(g)$$

in a 2.0-L flask that contains 6.0 mol $% 10^{-1}$ of CO $_{2}$ and 8.0 mol CO at equilibrium

$$K_{eq} = \frac{[CO]^2}{[CO_2]} = \frac{[4.0 \text{ M}]^2}{[3.0 \text{ M}]} = 5.33 \text{ M} = 5.3$$

What's [CO] if $[CO_2] = 2.0 \text{ M}$

$$\mathsf{K}_{\mathsf{eq}} = \frac{[\mathsf{CO}]^2}{[\mathsf{CO}_2]} \Longrightarrow [\mathsf{CO}] = \sqrt{[\mathsf{CO}_2]} \mathsf{K}_{\mathsf{eq}} = \sqrt{(2.0)(5.3)} = 3.\underline{2}5 \,\mathsf{M} = \underline{3.3 \,\mathsf{M}}$$

For same temperature, what is K_{eq} for,

$$2CO_{2}(g) + 2C(s) \rightleftharpoons 4CO(g)$$
$$K_{eq}^{'} = \frac{[CO]^{4}}{[CO_{2}]^{2}} = \left(\frac{[CO]^{2}}{[CO_{2}]}\right)^{2} = (K_{eq})^{2} = (5.3)^{2} = \underline{28}$$
$$2CO(g) \rightleftharpoons CO_{2}(g) + C(s)$$

$$K_{eq}^{"} = \frac{[CO_2]}{[CO]^2} = \left(\frac{1}{K_{eq}}\right) = \left(\frac{1}{5.3}\right) = 0.19$$

There are two types of K_{eq} 's:

1. K_c concentration units (M) are used in the expression

2. K_P pressure units (atm) are used in the expression

$$K_{C} = \frac{[HCI]^{2}}{[H_{2}][CI_{2}]}$$
 $K_{P} = \frac{p_{HCI}^{2}}{p_{H_{2}}p_{CI_{2}}}$

Numerical values for K_P and K_C are usually different...

 $\mathbf{K}_{\mathsf{P}}=\mathbf{K}_{\mathsf{C}}\;(\mathsf{RT})^{\!\!\!\Delta \mathsf{n}}$

R = 0.08206 L atm/mol K $\Delta n = moles of products minus moles of reactants (for gases)$ The K_C for the following rxn is 100.0 at 27 °C. Find K_P .

 $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$ $K_P = K_C (RT)^{\Delta n}$ $\Delta n = 2 - 3 = -1$

 $K_{P} = (100.0)[(0.0821 L atm / mol K) (300. K)]^{-1}$

= 4.06 mol / L atm

= <u>4.06</u>

 K_C = 25 at 20. °C for the reaction $2HCl(g)\rightleftarrows H_2(g)+Cl_2(g)$ Find $K_P.$

 $K_{P} = K_{C} (RT)^{\Delta n}$ $\Delta n = 2 - 2 = 0$ $K_{P} = (25)[(0.0821 L atm / mol K) (293 K)]^{0}$

= <u>25</u>

Reaction Quotient

<u>Reaction quotient</u> (Q) is used to predict direction to reach equilibrium...

insert concentrations into equilibrium constant expression and compare value to K

if $Q < K_{eq}$, forward reaction is spontaneous

if $Q > K_{eq}$, reverse reaction is spontaneous

if $Q = K_{eq}$, reaction is at equilibrium

For some temperature, the following equilibrium has $K_{eq} = 16$:

$$2H_2(g) + O_2(g) \rightleftharpoons 2H_2O(g)$$

In which direction is the rxn spontaneous,

if
$$[H_2] = [O_2] = [H_2O] = 1.0 M$$
?

$$Q = \frac{[H_2O]^2}{[H_2]^2[O_2]} = \frac{(1.0)^2}{(1.0)^2(1.0)} = 1.0 < 16 = K_{eq} \implies \text{forward}$$
if $[H_2] = 1.0 M$, $[O_2] = 2.0 M$, $[H_2O] = 6.0 M$?

$$Q = \frac{[H_2O]^2}{[H_2]^2[O_2]} = \frac{(6.0)^2}{(1.0)^2(2.0)} = 18 > 16 = K_{eq} \implies \text{reverse}$$

Equilibrium Problems

General types:

- 1. equilibrium conc's $\rightarrow K_{eq}$
- 2. $K_{eq} \rightarrow equilibrium \ conc's$
- 3. initial conc's, change $\rightarrow K_{eq}$

General steps:

initial conc's
 changes (from coefficients)
 ICE Table!
 equilibrium conc's
 write K_{eq} expression
 solve for "x"

A tank is filled with 0.20 atm of H_2 and 0.20 atm of I_2 . Find the equilibrium pressure of HI given

$$H_{2}(g) + I_{2}(g) \rightleftharpoons 2HI(g) \qquad K_{p} = 36.0$$

$$I \quad 0.20 \quad 0.20 \quad 0$$

$$C \quad -x \quad -x \quad 2x$$

$$E \quad 0.20 - x \quad 0.20 - x \quad 2x$$

$$K_{p} = \frac{p_{HI}^{2}}{p_{H_{2}}p_{I_{2}}} = \frac{[2x]^{2}}{[0.20 - x]^{2}} = 36.0 \quad \Rightarrow \frac{2x}{0.20 - x} = 6.00 \quad \Rightarrow \underline{x = 0.15}$$

$$p_{HI(eq)} = 2(0.15 \text{ atm}) = \underline{0.30 \text{ atm}}$$

0.10 mol of HCl gas is placed in a 2.0 L flask. What is the concentration of HCl at equilibrium?

 $H_2(g) + Cl_2(g) \rightleftharpoons 2HCl(g)$ $K_C = 75$ $I \quad 0 \quad 0 \quad 0.050$ $C \quad x \quad x \quad -2x$ $E \quad x \quad x \quad 0.050 - 2x$

 $K_{eq} = \frac{[HCI]^2}{[H_2][CI_2]} = \frac{[0.050 - 2x]^2}{[x]^2} = 75 \Rightarrow \frac{0.050 - 2x}{x} = 8.7 \Rightarrow x = 0.0047 \text{ M}$

 $[HCI]_{eq} = 0.050 \text{ M} - 2(0.0047 \text{ M}) = 0.041 \text{ M}$

Percent dissociation measures extent of reaction

% diss. =
$$\frac{\text{amount dissociated}}{\text{original amount}}$$
 (100 %)

What is the percent dissociation of HCl?

% diss. =
$$\frac{2x}{0.050}$$
 (100 %) = $\frac{2(0.0047)}{0.050}$ (100 %) = 19 %

2.0 mol NH₃ gas are placed in a 1.0 L container and at equilibrium 1.0 mol remains. Find K_c .

$$K_{C} = \frac{[N_{2}][H_{2}]^{3}}{[NH_{3}]^{2}} = \frac{(0.50)(1.5)^{3}}{(1.0)^{2}} = \underline{1.7}$$

0.84 mol PCl₅ and 0.18 mol PCl₃ are placed in a 1.0 L flask. At equilibrium 0.72 mol PCl₅ remains. Find K_C for

	PCl ₅ (g)	$\stackrel{\longrightarrow}{\leftarrow}$	PCl ₃ (g) -	+ Cl ₂ (g)
Ι	0.84		0.18	0
С	- x		X	Х
Е	0.84 – x		0.18 + x	Х

$$[PCI_{5}]_{eq} = 0.72 \text{ M} = 0.84 - x \implies x = 0.12 \text{ M}$$
$$[PCI_{3}]_{eq} = 0.18 + x = 0.30 \text{ M}$$
$$[CI_{2}]_{eq} = x = 0.12 \text{ M}$$

$$K_{C} = \frac{[PCl_{3}][Cl_{2}]}{[PCl_{5}]} = \frac{(0.30)(0.12)}{(0.72)} = \underline{0.050}$$

Le Chatelier's Principle

Le Chatelier's Principle

If an external stress is applied to a system at equilibrium, the equilibrium position will change to counteract the stress

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

If H_2 is added...

equilibrium shifts right (more products are formed)

 K_{eq} stays the same

Change in Enthalpy (Δ H): The energy change during a chemical reaction

∆H positive	E absorbed	endothermic
Δ H negative	E released	exothermic

When this reaction occurs, energy is released...

 $H_2(g) + I_2(g) \rightleftharpoons 2HI(g) + energy$ ΔH_{298} for reaction = -10.2 kJ (exothermic!)

If T increases...

equilibrium shifts left (more reactants are formed) K_{eq} decreases

If T decreases... equilibrium shifts right K_{eq} increases $4\text{HCl}(g) + \text{O}_2(g) \rightleftharpoons 2\text{Cl}_2(g) + 2\text{H}_2\text{O}(I) \qquad \Delta \text{H} = + 3.1 \text{ kJ} / \text{ mol } \text{O}_2$

If T increases... equilibrium shifts right K_{ea} increases If Cl₂ removed... equilibrium shifts right K_{eq} stays the same If H₂O added... no change; not in K_{eq} expression! If P increases... equilibrium shifts right K_{ea} stays the same (pressure affects gases, less gas on right)

 $CO(g) + H_2O(I) \rightleftharpoons CO_2(g) + H_2(g)$

 $\Delta H = + 4.1 \text{ kJ}$

Stress	Shift	$\Delta[CO_2]$
add CO	right	incr
add H ₂ O	none	no
add H ₂	left	decr
add CO ₂	left	incr
incr T	right	incr
decr T	left	decr
incr P	left	decr
decr P	right	incr

The equilibrium concentrations of 0.30 M HCl, 0.20 M H₂, and 0.10 M Cl₂ are all in a 1.0 L flask. Then 0.10 mol Cl₂ is added. Find the new equilibrium concentration of HCl.

	2HCl(g)	\rightleftharpoons	H ₂ (g) ·	+ Cl ₂ (g)
Е	0.30		0.20	0.10
Ι	0.30		0.20	0.20
С	+ 2x		- x	- x
Е	0.30 + 2	x 0).20 – x	0.20 – x

Find K_c from initial eq. conc.'s:

$$K_{C} = \frac{[H_{2}][CI_{2}]}{[HCI]^{2}} = \frac{[0.20 \text{ M}][0.10 \text{ M}]}{[0.30 \text{ M}]^{2}} = 0.22$$

The equilibrium concentrations of 0.30 M HCl, 0.20 M H₂, and 0.10 M Cl₂ are all in a 1.0 L flask. Then 0.10 mol Cl₂ is added. Find the new equilibrium concentration of HCl.

Find new eq. conc.'s:

$$0.22 = \frac{[0.20 - x]^2}{[0.30 + 2x]^2} \implies 0.47 = \frac{0.20 - x}{0.30 + 2x} \implies x = 0.030 \text{ M}$$
$$[\text{HCI}] = 0.30 + 2x = 0.36 \text{ M}$$

A flask is filled with the equilibrium pressures 0.25 atm N_2 , 0.25 atm O_2 , and 0.40 atm NO. Then 0.10 atm of NO is added. What are the new equilibrium pressures.

	N ₂ (g) +	• O ₂ (g)	\rightleftharpoons 2NO(g)
Е	0.25	0.25	0.40
Ι	0.25	0.25	0.50
С	x	Х	– 2x
Е	0.25 + x	0.25 + 3	x 0.50 – 2x

Find K_P from initial eq. prs.'s:

$$K_{P} = \frac{p_{NO}^{2}}{p_{N_{2}}p_{O_{2}}} = \frac{[0.40 \text{ atm}]^{2}}{[0.25 \text{ atm}]^{2}} = 2.56$$

A flask is filled with the equilibrium pressures 0.25 atm N₂, 0.25 atm O₂, and 0.40 atm NO. Then 0.10 atm of NO is added. What are the new equilibrium pressures.

Find new eq. prs.'s:

$$2.\underline{5}6 = \frac{[0.50 - 2x]^2}{[0.25 + x]^2} \implies 1.6 = \frac{0.50 - 2x}{0.25 + x} \implies x = 0.028 \text{ atm}$$

 $[N_2] = 0.25 + x = 0.28 \text{ atm}$ $[O_2] = 0.25 + x = 0.28 \text{ atm}$ [NO] = 0.50 - 2x = 0.44 atm