Worksheet 17 - Le Chatelier's Principle

Le Chatelier's Principle states that if a **stress** is applied to a system at equilibrium, the system will adjust, to partially offset the stress and will reach a new state of equilibrium.

The "stresses" that can be applied to the system include changes in **concentration**, **pressure**, **volume** and **temperature**.

- Changes in concentration of either reactants or products will change the value of **Q**, the reaction quotient.

> Adding more reactant will drive the forward reaction.
> Adding more product will drive the reverse reaction.
>
> Removal of reactants or products will shift the equilibrium in the direction needed to produce more of the substance that was removed.

Solids and pure **liquids** can **not** change concentration. Changing the amount of these present in the system will have no effect on equilibrium, unless they are removed entirely.

Catalysts are species that speed up the rate of a reaction. However, they speed up both the forward and reverse reactions, leaving ***K*** unchanged.

- Changes in pressure and **volume** will affect the equilibrium of reactions involving gases.

> **Increasing** the **volume** of the system (**lowering** the **pressure**) drives the equilibrium toward the state with the **larger** number of **moles** of **gas**.
>
> **Increasing** the **pressure** of the system by adding an **inert gas** has **no effect** on the equilibrium of the system.

- Changes in temperature change the **value** of the equilibrium constant, ***K***. This is a fairly complex process, but can be thought of in simple terms, using Le Chatelier's Principle.

> **Heat** can be treated as a **product** in **exothermic** reactions ($\Delta H < 0$) and as a **reactant** in **endothermic** reactions ($\Delta H > 0$).
>
> Raising the temperature of a reaction can be thought of as adding heat. In endothermic reactions (heat = reactant) this will drive the forward reaction. In exothermic reactions (heat = product) and raising the temperature will drive the reverse reaction.

1. Predict what will happen when the reaction **volume** is **decreased** in each of the following, after balancing the reactions.

a) _**6**_ CO_2 (g) + _**6**_ H_2O (l) ⇆ _**1**_ $C_6H_{12}O_6$ (s) + _**6**_ O_2 (g)

6 moles of gas → 6 moles of gas; no effect

b) _**1**_ PCl_5 (g) ⇆ _**1**_ PCl_3 (g) + _**1**_ Cl_2(g)

1 mole of gas → 2 moles of gas; when volume is decreased, the reaction shifts to the side with fewer moles of gas, in this case the reactant side

c) _**1**_ H_2 (g) + _**1**_ CO_2 (g) ⇆ _**1**_ H_2O (g) + _**1**_ CO (g)

2 moles of gas → 2 moles of gas; no effect

2. Balance the exothermic reaction below:

_**2**_ NO_2 (g) ⇆ _**1**_ N_2O_4 (g) $\Delta H = -58.0$ kJ

Predict the effect of each of the following changes on this system at equilibrium (drive forward reaction, drive reverse reaction, no effect).

a) add N_2O_4

reverse (add product)

b) remove NO_2

reverse (remove reactant)

c) increase the volume

reverse (shift to side with *more* gas moles)

d) decrease the temperature

forward (heat is a product)

e) Add N_2 **No change; N_2 is an inert gas**

3. The equilibrium constant, K_P, for the reaction

$$H_2\,(g) + I_2\,(s) \leftrightharpoons 2\,HI\,(g)$$

is 0.35 at 25° C. Decide if each of the following mixtures is at equilibrium, at 25° C. If it is not at equilibrium, decide which way the reaction will proceed to reach equilibrium.

a) $P_{H2} = 0.10$ atm, $P_{HI} = 0.90$ atm and solid I_2 is present

$Q = (P_{HI})^2 / P_{H2} = 8.1$ $Q > K_p$ reverse reaction proceeds

b) $P_{H2} = 0.55$ atm, $P_{HI} = 0.44$ atm and solid I_2 is present

$Q = (P_{HI})^2 / P_{H2} = 0.35$ $Q = K_p$ at equilibrium

c) $P_{H2} = 0.25$ atm, $P_{HI} = 0.15$ atm and solid I_2 is present

$Q = (P_{HI})^2 / P_{H2} = 0.09$ $Q < K_p$ forward reaction proceeds

4. **10.0 g** of the weakly soluble solid Ag_2CO_3 is added to **1.00 L** of water and the following equilibrium is established:

$$Ag_2CO_3\,(s) \leftrightarrows 2Ag^+\,(aq) + CO_3^{2-}\,(aq)$$

For this reaction, at 25° C, $K = 8.2 \times 10^{-12}$. This is usually called $\boldsymbol{K_{sp}}$ or the solubility constant, which is a measure of how much of an "insoluble" solid will dissolve.

Write the expression for the solubility constant in terms of [reactants] and [products].

K_{sp} = **$[Ag^+]^2\,[CO_3^{2-}] = 8.2\times10^{-12}$** **(Don't include solid)**

Make an ICE table for this reaction and calculate the equilibrium concentrations of Ag+ and CO_3^{2-}.

	$[Ag^+]$ (M)	$[CO_3^{2-}]$ (M)
Initial	**0**	**0**
Change	**+2x**	**+x**
Equilibrium	**0+2x**	**0+x**

Substitute these values into the expression for K_{sp} (above) and solve for:

$(2x)^2\,(x) = 4x^3 = 8.2\times10^{-12}$, $x = 1.27\times10^{-4}$

$[Ag^+]_{eq}$ = **$2x = 2.54\times10^{-4}$** $[CO_3^{2-}]_{eq}$ = **$x = 1.27\times10^{-4}$**

In which direction will each of the following changes force the equilibrium?

a) adding 1.00 L of water (Hint: calculate a value for Q)

Adding 1.00 L of water doubles the total volume, so it cuts each concentration in half. $Q = (1.27\times10^{-4})^2\,(0.635\times10^{-4}) = 1.03\times10^{-12}$
Q < K, so the reaction will proceed forward

b) adding 1.00 moles of NaCl (Hint: remember the solubility rules. Which reactants or products are affected by the addition of NaCl?)

$Ag^+ + Cl^- \rightarrow AgCl(s)$; Adding the NaCl effectively reduces the amount of Ag^+ present in the solution (decreases product), so the reaction proceeds forward

c) adding 10.0 g of Ag_2CO_3 (s)

Adding solid reactant has no effect on the equilibrium

d) adding 0.5 moles of $AgNO_3$ (s) (Hint: more solubility rules)

$AgNO_3 \rightarrow Ag^+ + NO_3^-$; Adding $AgNO_3$ increases the amount of Ag^+ present (increases product), so the reaction proceeds in the reverse direction

5. 0.100 moles of HCN, hydrocyanic acid are added to 1.00 L of water. The following reaction takes place:

$HCN\ (aq) + H_2O \leftrightarrows H^+\ (aq) + CN^-\ (aq)$

For this reaction at 25° C, $K = 6.2 \times 10^{-10}$.

Write the expression for K in terms of [reactants] and [products].

$K =$ **$[H^+]\ [CN^-]\ /\ [HCN] = 6.2x10^{-10}$**

Make an ICE table for this reaction.

	[HCN] (M)	$[H^+]$ (M)	$[CN^-]$ (M)
Initial	**0.100**	**0**	**0**
Change	**-x**	**+x**	**+x**
Equilibrium	**0.100-x**	**0+x**	**0+x**

Since K is so small, the [HCN] will not change appreciably (0.100 M – x is approximately equal to 0.100 M if x is very small).

Put the equilibrium concentration values into the expression for K (above) and solve for:

$(x)(x)\ /\ (0.100-x) \cong x^2\ /\ 0.100 = 6.2x10^{-10}$, $x = 7.87x10^{-6}$

$[H^+]_{eq}$ = **$x = 7.87x10^{-6}$** $[CN^-]_{eq}$ = **$x = 7.87x10^{-6}$** $[HCN]_{eq} \cong 0.100$ M

In which direction will each of the following changes force the equilibrium?

a) adding 1.00 L of water (Hint: calculate a value for Q)

Adding 1.00 L of water doubles the total volume, so it cuts each concentration in half. $Q = (3.94x10^{-6})^2\ /\ (0.050) = 3.1x10^{-10}$
Q < K, so the reaction will proceed forward

b) adding 1.00 moles of HCl (aq)

$HCl \rightarrow H^+ + Cl^-$; Adding the HCl effectively increases the amount of H^+ present in the solution (increases product), so the reaction proceeds in the reverse direction

c) adding 0.1 moles of NaCN (s), a soluble salt

$NaCN \rightarrow Na^+ + CN^-$; Adding the NaCN effectively increases the amount of CN^- present in the solution (increases product), so the reaction proceeds in the reverse direction