

## 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**.

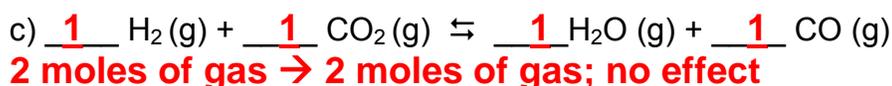
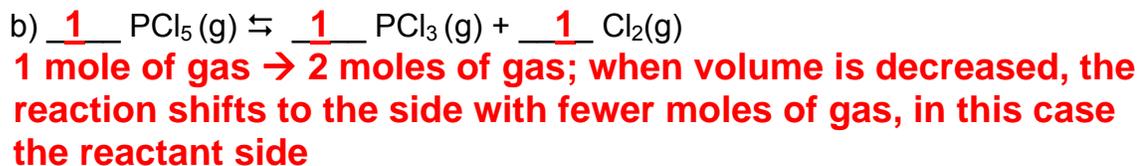
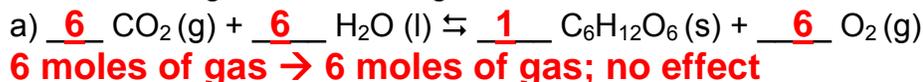
**Increasing** the **pressure** of the system by adding an **inert gas** has **no effect** on the equilibrium of the system.

- **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.

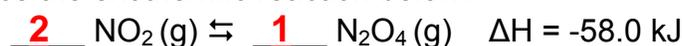
**Heat** can be treated as a **product** in **exothermic** reactions ( $\Delta H < 0$ ) and as a **reactant** in **endothermic** reactions ( $\Delta H > 0$ ).

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.



2. Balance the exothermic reaction below:



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<sub>2</sub>O<sub>4</sub>

**reverse (add product)**

b) remove NO<sub>2</sub>

**reverse (remove reactant)**

c) increase the volume

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

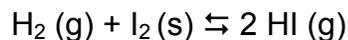
d) decrease the temperature

**forward (heat is a product)**

e) Add N<sub>2</sub>

**No change; N<sub>2</sub> is an inert gas**

3. The equilibrium constant,  $K_p$ , for the reaction



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)  $P_{\text{H}_2} = 0.10$  atm,  $P_{\text{HI}} = 0.90$  atm and solid I<sub>2</sub> is present

**$Q = (P_{\text{HI}})^2 / P_{\text{H}_2} = 8.1$        $Q > K_p$       reverse reaction proceeds**

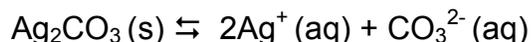
b)  $P_{\text{H}_2} = 0.55$  atm,  $P_{\text{HI}} = 0.44$  atm and solid I<sub>2</sub> is present

**$Q = (P_{\text{HI}})^2 / P_{\text{H}_2} = 0.35$        $Q = K_p$       at equilibrium**

c)  $P_{\text{H}_2} = 0.25$  atm,  $P_{\text{HI}} = 0.15$  atm and solid I<sub>2</sub> is present

**$Q = (P_{\text{HI}})^2 / P_{\text{H}_2} = 0.09$        $Q < K_p$       forward reaction proceeds**

4. **10.0 g** of the weakly soluble solid  $\text{Ag}_2\text{CO}_3$  is added to **1.00 L** of water and the following equilibrium is established:



For this reaction, at  $25^\circ\text{C}$ ,  $K = 8.2 \times 10^{-12}$ . This is usually called  $K_{\text{sp}}$  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].

$$K_{\text{sp}} = [\text{Ag}^+]^2 [\text{CO}_3^{2-}] = 8.2 \times 10^{-12} \quad \text{(Don't include solid)}$$

Make an ICE table for this reaction and calculate the equilibrium concentrations of  $\text{Ag}^+$  and  $\text{CO}_3^{2-}$ .

	$[\text{Ag}^+]$ (M)	$[\text{CO}_3^{2-}]$ (M)
Initial	<u>0</u>	<u>0</u>
Change	<u>+2x</u>	<u>+x</u>
Equilibrium	<u>0+2x</u>	<u>0+x</u>

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

$$(2x)^2 (x) = 4x^3 = 8.2 \times 10^{-12}, \quad x = 1.27 \times 10^{-4}$$

$$[\text{Ag}^+]_{\text{eq}} = \underline{2x = 2.54 \times 10^{-4}} \quad [\text{CO}_3^{2-}]_{\text{eq}} = \underline{x = 1.27 \times 10^{-4}}$$

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.  $Q = (1.27 \times 10^{-4})^2 (0.635 \times 10^{-4}) = 1.03 \times 10^{-12}$**

**$Q < K$ , 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?)

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

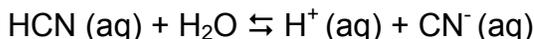
c) adding 10.0 g of  $\text{Ag}_2\text{CO}_3(\text{s})$

**Adding solid reactant has no effect on the equilibrium**

d) adding 0.5 moles of  $\text{AgNO}_3(\text{s})$  (Hint: more solubility rules)

**$\text{AgNO}_3 \rightarrow \text{Ag}^+ + \text{NO}_3^-$ ; Adding  $\text{AgNO}_3$  increases the amount of  $\text{Ag}^+$  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:



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

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

$$K = \frac{[\text{H}^+][\text{CN}^-]}{[\text{HCN}]} = 6.2 \times 10^{-10}$$

Make an ICE table for this reaction.

	[HCN] (M)	[H <sup>+</sup> ] (M)	[CN <sup>-</sup> ] (M)
Initial	<u>0.100</u>	<u>0</u>	<u>0</u>
Change	<u>-x</u>	<u>+x</u>	<u>+x</u>
Equilibrium	<u>0.100-x</u>	<u>0+x</u>	<u>0+x</u>

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:

$$(x)(x) / (0.100-x) \approx x^2 / 0.100 = 6.2 \times 10^{-10}, \quad x = 7.87 \times 10^{-6}$$

$$[\text{H}^+]_{\text{eq}} = \underline{x = 7.87 \times 10^{-6}} \quad [\text{CN}^-]_{\text{eq}} = \underline{x = 7.87 \times 10^{-6}} \quad [\text{HCN}]_{\text{eq}} \approx 0.100 \text{ M}$$

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.  $Q = (3.94 \times 10^{-6})^2 / (0.050) = 3.1 \times 10^{-10}$   
 $Q < K$ , so the reaction will proceed forward**

- b) adding 1.00 moles of HCl (aq)

**$\text{HCl} \rightarrow \text{H}^+ + \text{Cl}^-$ ; Adding the HCl effectively increases the amount of  $\text{H}^+$  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

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