**Unit 10 Thermodynamics, Kinetics and Equilibrium Notes**

**What is Thermodynamics?**

Almost all chemical reactions involve a _____ between the _____ and its _____.

Thermo = _____

Dynamics = _____

What is energy?

What is heat?

Thermochemistry - _____

Heat is absorbed: _____

Heat is evolved/released: _____

**Measuring Heat Transfer**

**Heat** (**q)** flows from _____ to _____

Heat is measured in _____.

_____J = _____ kJ, _____ calorie = _____ J, 1 kcal = _____ cal = _____ food calorie (Cal)

**Examples:**

1. A fruit and oatmeal bar contains 142 Calories. Convert this energy to calories.

2. Convert 256 J to kcal.

3. The breakfast I at this morning contains 230 nutritional Calories. How much energy in joules will this breakfast supply?

**Temperature vs. Heat**

| | **Temperature** | **Heat** | **Thermal (Heat) Energy** |
|---|---|---|---|
| **Definition** | | | |

Temperature measures _____

The _____ the molecules are moving, the _____the temperature

The _____ the molecules are moving, the _____ the temperature

**Example:** Compare and contrast the temperature and thermal energy of the Pacific Ocean to a boiling pot of water

**Enthalpy and Reactions**

**Enthalpy (ΔH ) -** _____

Formula:

Each reaction will have an enthalpy value ($\Delta H$), which indicates _____

**If $\Delta H$ is negative then _____**

Reactions that release heat are called **_____** (exo = out, exiting).

$H_2(g) + Cl_2(g) \rightarrow 2HCl(g)$ $\Delta H = -185{,}000$ J

**If $\Delta H$ is positive then _____**

Reactions that require an input of energy (heat) are called **_____** (endo = in, entering).

$CO_2(g) + 2H_2O(g) \rightarrow 2O_2(g) + CH_4(g)$ $\Delta H = 890{,}000$ J

To determine if a reaction is exothermic or endothermic you must know the value of $\Delta H$.

**Example:** Rewrite the following equations including the $\Delta H$ value as a reactant or product and if it is exothermic or endothermic

$H_2 + ½\ O_2 \rightarrow H_2O$ $\Delta H = -241.8$ kJ _____

$H_2O \rightarrow H_2 + ½\ O_2$ $\Delta H = 241.8$ kJ _____

Enthalpy is an extrinsic physical property because it depends on the amount present!

**Example:** Determine the $\Delta H$ for the following reactions:

$N_2 + 3H_2 \rightarrow 2NH_3$ $\Delta H = -91.8$ kJ

$½\ N_2 + 3/2\ H_2 \rightarrow NH_3$ $\Delta H =$ _____ kJ

$2NH_3 \rightarrow N_2 + 3H_2$ $\Delta H =$ _____ kJ

**Phase Changes**

**Phase Change**: _____

**To change phases, _____**

| | States of matter | Energy | Endo or Exo? | $\Delta H$ Sign |
|---|---|---|---|---|
| **Melting** | | | | |
| **Freezing/Solidification** | | | | |
| **Evaporation** | | | | |
| **Condensation** | | | | |

**Let's Review!**

**Kinetic Energy:**

**Potential Energy:**

**During a phase change, temperature _____**

**Because kinetic energy _____**

**As potential energy _____ depending on the _____ _____**

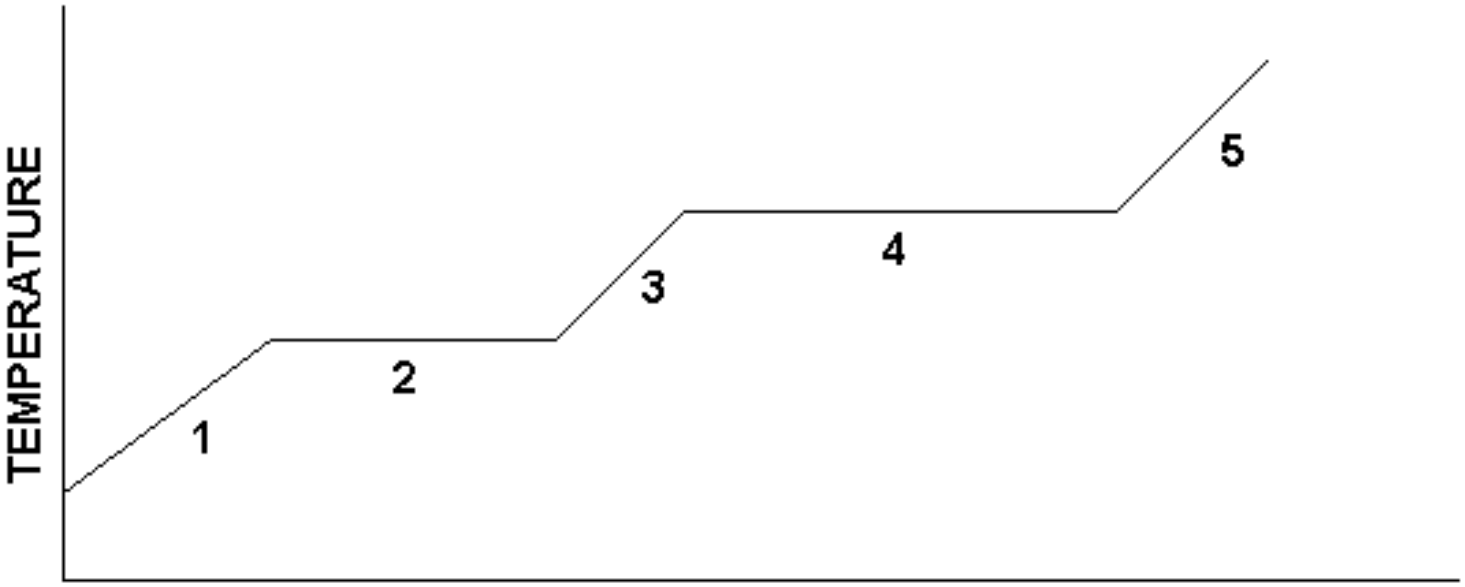
**What does heat do?**

If a substance is heated, the heat can do **ONE** of these two things:

1. _____ **OR**
2. _____

**KEY IDEA:** _____

**Label the following heating curve!**




| | Definition | Sign and Energy Movement |
|---|---|---|
| $\Delta H_{fusion}$ | | |
| $-\Delta H_{fusion}$ | | |
| $\Delta H_{vaporization}$ | | |
| $-\Delta H_{vaporization}$ | | |

**Summary**

$$\text{Solid} \xrightarrow{\Delta H \text{ fusion}} \text{Liquid} \xrightarrow{\Delta H \text{ vaporization}} \text{Gas}$$

$$\text{Solid} \xleftarrow{-\Delta H \text{ fusion}} \text{Liquid} \xleftarrow{-\Delta H \text{ vaporization}} \text{Gas}$$

**Phase Change Problems**

The equation used to calculate the amount of energy absorbed or released during a phase change is

**$q = m\Delta H$**

Depending on the phase change, you will use either $\Delta H_{fus}$ or $\Delta H_{vap}$.

**Example 1:** Calculate the heat required to melt 25.7 g of solid water at its melting point.

**Example 2:** How much heat is evolved when 275 go of water vapor condenses to a liquid at its boiling point?

**Specific Heat ($C_p$)**

**Specific Heat**: _____

Units for Specific Heat = J/g·°C

Which has a higher specific heat:
Water or sand?

Metal pan or oven mitts?

Equation to use for thermal processes:

**$q = mC_p\Delta T$**

| Heat: | Mass: | Specific heat: | Change is temperature: |
|---|---|---|---|
| | | | |

**Example 1:** How much heat is lost when 4110 g of aluminum metal cools from 660.°C to 25.0°C?

**Example 2**: Calculate the heat required to heat up 124 g of water from 17.5˚C to 25.0˚C.

**Example 3:** How much heat is required to heat 15.8 g of liquid water at 30.˚C to water vapor at 122˚C?

**Example 4:** How much heat is released when 21.2 g of water cools from 113.7˚C to -24.8˚C?

**Calorimetry:**

This process uses a calorimeter, which is used _____

_____

One kind of calorimeter works like this:

A known amount of or reactants are sealed in a reaction chamber.
The reaction chamber is immersed in a known quantity of water
The water and reaction chamber are in an insulated vessel
The energy given off (or absorbed) during the reaction is transferred to the water
If the reaction released energy the water temperature increases
If the reaction needs energy the water temperature decreases.
Heat is not measured directly.
Temperature is measured.
Temperature is affected by the transfer of heat (energy).

**Calorimetry Problems:**

Since heat is transferred, the following equation is used: $q_{lost} = -q_{gained}$

**Example:** A 20.0 g piece of metal at a temperature of 90.0°C is dropped into an insulated container holding 125 g of water at 20.0°C. If the final temperature is 23.0°C, what is the specific heat capacity of the metal?

***Hess's Law***

***Definition:*** _____

_____

Key Ideas:

- The major utility of Hess's Law is in calculating the enthalpy changes of reactions that would be difficult to measure.
- Note: according to the law of conservation of energy, energy cane neither be created nor destroyed in an ordinary chemical reaction. Hess's law tells us that we will never get more energy (or less energy for that matter) from a chemical reaction.

**Example:** Calculate the $\Delta H$ for the following reaction using the information given.

$C(s) + 2\ H_2(g) \rightarrow CH_4(g)$

$C(s) + O_2(g) \rightarrow CO_2(g)$ $\Delta H = -393.5$ kJ/mol

$H_2(g) + ½\ O_2(g) \rightarrow H_2O(l)$ $\Delta H = -285.8$ kJ/mol

$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(l)$ $\Delta H = -890.8$ kJ/mol

**Entropy**

Entropy ($\Delta S$) –

The Law of Disorder –

**Example:** Which of the following represents more disorder?

a) Increasing temperature or decreasing temperature of a substance
b) Reactants or products in the following reaction: $2NH_3(g) \rightarrow N_2(g) + 3H_2(g)$
c) Ice or water or steam

**Example:** Predict the sign of $\Delta S_{system}$ for each of the following changes.

a) $ClF(g) + F_2(g) \rightarrow ClF_3(g)$ $\Delta S =$
b) $NH_3(g) \rightarrow NH_3(aq)$ $\Delta S =$
c) $CH_3OH(l) \rightarrow CH_3OH(aq)$ $\Delta S =$
d) $C_{10}H_8(l) \rightarrow C_{10}H_8(s)$ $\Delta S =$

**Entropy and the phases of matter:**
Place the phases of matter in order of increasing entropy:

**<u>The Driving Forces of Reaction</u>**

There are **<u>two factors</u>** that determine whether a reaction will occur **<u>spontaneously</u>**.

1. **_____** ($\Delta H$) – measure of amount of heat absorbed/released in a chemical reaction

   The tendency in nature →

2. **_____** ($\Delta S$) – the measure of randomness of the particles in a system

   The tendency in nature →

3. **<u>Gibb's Free Energy</u>** –

   Negative $\Delta G$ means the reaction is _____
   Positive $\Delta G$ means the reaction is _____

   The tendency in nature →

   $\Delta G = \Delta H - T\Delta S$ T = Kelvin Temperature

**Example:** Predict the value of $\Delta G$ and spontaneity of a reaction using the following data:

| **ΔH** | **ΔS** | **ΔG** | **Spontaneous?** |
|---|---|---|---|
| + | + | | |
| - | - | | |
| + | - | | |
| - | + | | |

**Example:** Is the following spontaneous?

$NH_4NO_3(s) + heat \rightarrow NO_3^-(aq) + NH_4^+(aq)$

**Kinetics - The Reaction Process**

According to **collision theory**, in order to react, particles must collide with

a)

b)

Many reactions actually take place through a series of steps involving two particle collisions. This step by step sequence is called a _____.

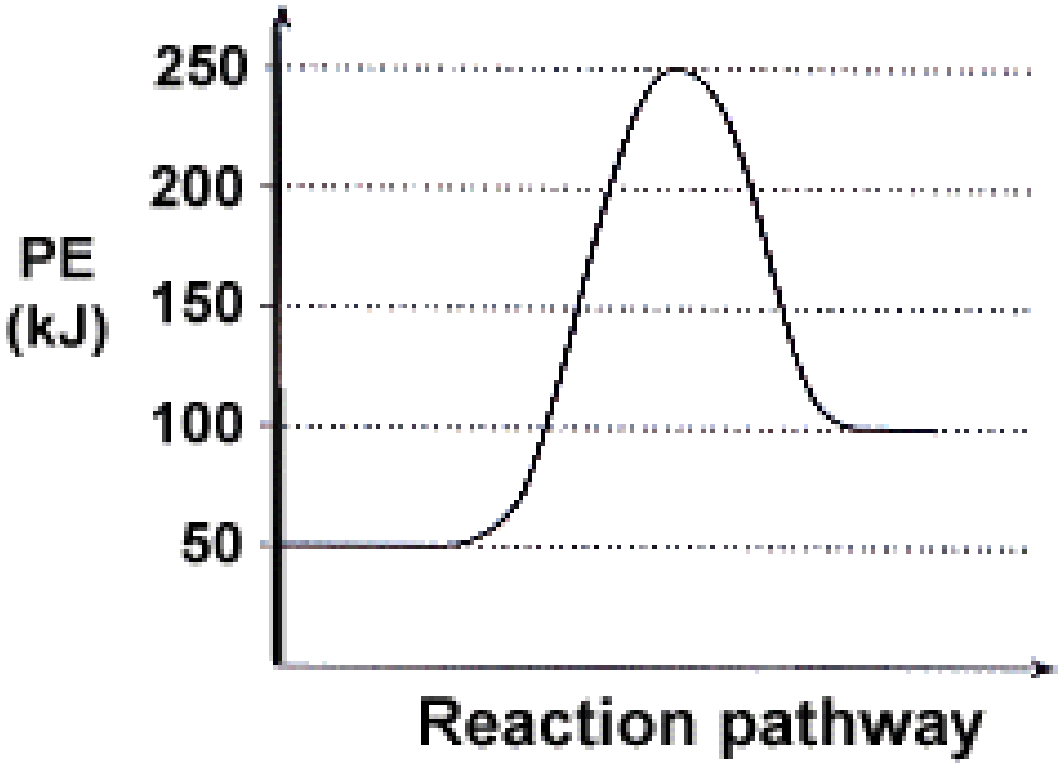
**Example:** For $H_2(g) + I_2(g) \leftrightarrow 2\ HI(g)$

Step 1: $I_2 \leftrightarrow 2I^-$

Step 2: $2I^- + H_2 \leftrightarrow 2HI$

**Potential Energy Diagram**

Label the following potential energy diagram:




The forward reaction is _____
The reverse reaction is _____

**What is Chemical Kinetics?** - _____
_____

Reaction rate = _____
_____

**Factors that affect the rate of reaction**:

a) Nature of the reactants

b) Surface area

c) Temperature

d) Concentration

e) Catalysts

What is a catalyst?

Draw a potential energy diagram with a catalyst included:

**What is Chemical Equilibrium?** - _____
_____

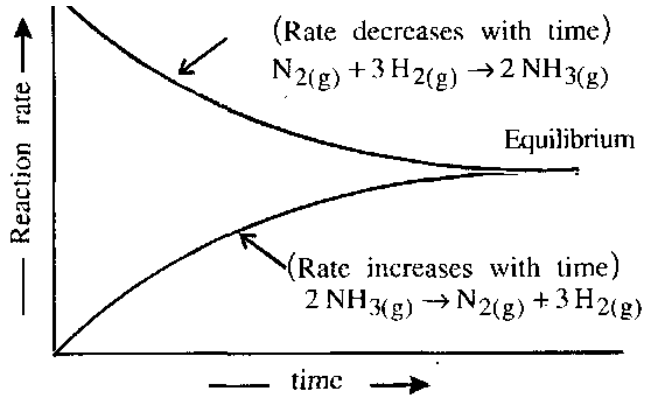
Reversible Reaction – ( ↔ ) _____
Equilibrium can only be established if the reaction is reversible.
Is equilibrium DYNAMIC or STATIC? Explain:

**Equilibrium Expression:**

aA + bB ⇆ cC + dD

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

**The Equilibrium Constant - $K_{eq}$**
Definition: _____
_____
_____
_____



This is the formula for the equilibrium expression:

1) Ignore all pure solids and pure liquids in the reaction. (*Why?*) Only the concentrations of substances that can actually change are included in K. This means that pure solids and liquids are omitted because their concentrations cannot change.
2) Make a ratio of [products] / [reactants]
   The concentrations are all expressed as Molarity (mol/L)
3) Make all coefficients in the balanced chemical equation into exponents in the ratio.

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

Try it!
Find the Equilibrium Expression for the following:

1. $N_2O_4(g) \leftrightarrow 2NO_2(g)$

2. $CO(g) + 3H_2(g) \leftrightarrow CH_4(g) + H_2O(g)$

3. $Ca(OH)_2(s) + H_2O(l) \leftrightarrow Ca^{2+}(aq) + 2OH^-(aq)$

4. $CaCO_3(s) \leftrightarrow CaO(s) + CO_2(g)$

5. $2H_2(g) + O_2(g) \leftrightarrow 2H_2O(l)$

**Setting Up and Calculating the Equilibrium Constant**

*Example 1:* The following equilibrium concentrations were observed for the Haber process at 127°C. The Haber process is: $N_2(g) + 3H_2(g) \leftrightarrow 2NH_3(g)$. Calculate 'K'.

$[NH_3] = 2.0$ mol/L
$[N_2] = 1.0$ mol/L
$[H_2] = 2.0$ mol/L

*Example 2*: A different experiment was performed using the same process (Haber) as above and at the same temperature, but different concentrations. Calculate 'K'. $[NH_3] = 0.86$ mol/L, $[N_2] = 0.75$ mol/L, $[H_2] = 1.25$ mol/L

Why are the values for 'K' the same between the two problems?
Because the value for 'K' is a constant for a given reaction at a given temperature. The only way to change 'K' for a given reaction is to change the temperature.

**Interpretation of Keq**

If Keq = 1, then _____
If Keq < 1, then _____
If Keq > 1, then _____

**Other Equilibrium Expressions**

**Ionization of an Acid** $K_a$

a) How does Ka relate to the strength of an acid?

b) Set up the equilibrium expression for the following reaction:

$CH_3COOH(aq) + H_2O(l) \leftrightarrow H_3O^+(aq) + CH_3COO^-(aq)$

Ka =

**Ionization of a Base** $K_b$

Set up the equilibrium expression for the following reaction:

$NH_3(aq) + H_2O(l) \leftrightarrow NH_4^+(aq) + OH^-(aq)$

Kb =

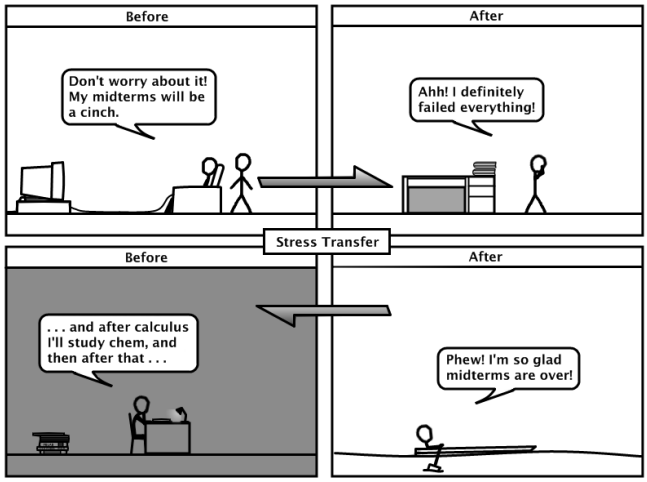
**Solubility of a Slightly Soluble Salt** $K_{sp}$

a) How does Ksp relate to the solubility of a salt?

b) Set up the equilibrium expression for the following reaction:

$AgCl(s) \leftrightarrow Ag^+(aq) + Cl^-(aq)$

Ksp =




**Le Chatelier's Principle** -

**3 Stresses for an Equilibrium System**

1.
2.
3.

KEY – Remember to predict the direction of equilibrium shift, use **AITD** (**A**way from **I**ncrease, **T**owards a **D**ecrease)

Changing Concentration:

**Try it!**

$N_{2(g)} + 3H_2(g) \leftrightarrow 2NH_3(g) + heat$

What happens to the reaction if you increase the concentration of $N_2$?

$2SO_3(g) \leftrightarrow 2SO_2(g) + O_2(g)$

Describe what happens when:

You decrease $SO_2$

You increase $O_2$

Changing Temperature:
Where is heat added for an **endothermic** reaction?

Where is heat added for an **exothermic** reaction?

Keq is only affected by a_____ change

Treat heat the same way you do concentration changes. If temperature increases, heat increases!

Temperature Examples:
$N_{2(g)} + 3H_2(g) \leftrightarrows 2NH_3(g)$ + heat
What happens to the reaction if you increase the temperature?

$2SO_3(g)$ + heat $\leftrightarrow 2SO_2(g) + O_2(g)$

a) Increase the temperature

b) Decrease the temperature

Changing Pressure
*Only affects equilibrium reactions with _____.
*When you increase pressure ( ) you want _____ _____ in your system
*When you decrease pressure ( ) you want to _____ _____ in your system.
When you **increase pressure** it always shifts toward _____ _____ of gas.
When you **decrease pressure** it always shifts toward _____ _____ of gas.

Pressure Examples:
$N_{2(g)} + 3H_2(g) \leftrightarrows 2NH_3(g)$ + heat

a) Increase the pressure

b) Decrease the pressure

$2SO_3(g) \leftrightarrow 2SO_2(g) + O_2(g)$

a) Increase the pressure

b) Decrease the pressure

More Practice
$CH_4(g) + 2H_2S(g) \leftrightarrow CS_2(g) + 4H_2(g)$ $\Delta H = 215.5$ kJ/mol

| **Stress** | **Shift** | **$[CH_4]$** | **$[H_2S]$** | **$[CS_2]$** | **$[H_2]$** | **$K_{eq}$** |
|---|---|---|---|---|---|---|
| Increase $CS_2$ | | | | | | |
| Decrease $H_2$ | | | | | | |
| Increase Temp | | | | | | |
| Increase Pressure | | | | | | |