CHEM 123 Lecture Notes – 1

# Energy and Thermochemistry

## Energy

* **Energy** : the capacity to do work
  + **Work** is done when motion occurs against a force
  + A reaction that gives out E and heats its surroundings is **exothermic**
  + A reaction that takes E and cools its surroundings is **endothermic**
* **Internal energy** : total kinetic + potential energy in the system
  + **Kinetic energy** : energy of a system from its motion
  + **Potential energy** : energy of a system from its position/configuration

## Systems

* **Open system**: matter and energy can be exchanged with surroundings
* **Closed system**: fixed matter, energy can be exchanged
* **Isolated system**: no matter or energy can be exchanged
* **Diathermic**: boundary permits heat to be transferred between system and surroundings
* **Adiabatic**: boundary does not permit heat to be transferred between system and surroundings

## Heat

* **Heat**: energy transferred between system and its surroundings as a result of a temperature change
  + **Heat capacity** : quantity of heat required to change temperature of system by one degree (Celsius or Kelvin)
  + **Molar heat capacity** : quantity of heat required to change temperature of one mole of a substance by one degree
  + **Specific heat capacity** : quantity of heat required to change temperature of one gram of a substance by one degree
* For pure substances, the **quantity of heat** :

### Law of Conservation of Energy

## Heats of Reaction (Calorimetry)

* – reaction is **exothermic**
* – reaction is **endothermic**
* An **enthalpy change** is the energy E transferred at constant pressure P
* Energy may also be transferred as a result of work – pressure in atm, volume in L
* A system loses energy (w < 0) when:
  + It does work
  + It transfers heat to surroundings (exothermic)
* A system gains energy (w > 0) when:
  + Work is done on it
  + It gains heat from surroundings (endothermic)

### First Law of Thermodynamics

* The **internal energy** of an isolated system is constant:
* For a closed system, (where )
  + For a reaction at constant volume, hence
  + For a reaction at constant pressure,
  + For systems containing no gases,
  + When ideal gases are involved ( ),
* The value of depends on temperature, pressure, and physical state of components

E.g. = heat of reaction under standard conditions (, pure components at concentration of 1 mol/L) at 298 K

* + follows stoichiometric coefficients (e.g. of coefficients halved, halved)
  + changes sign when a reaction is reversed

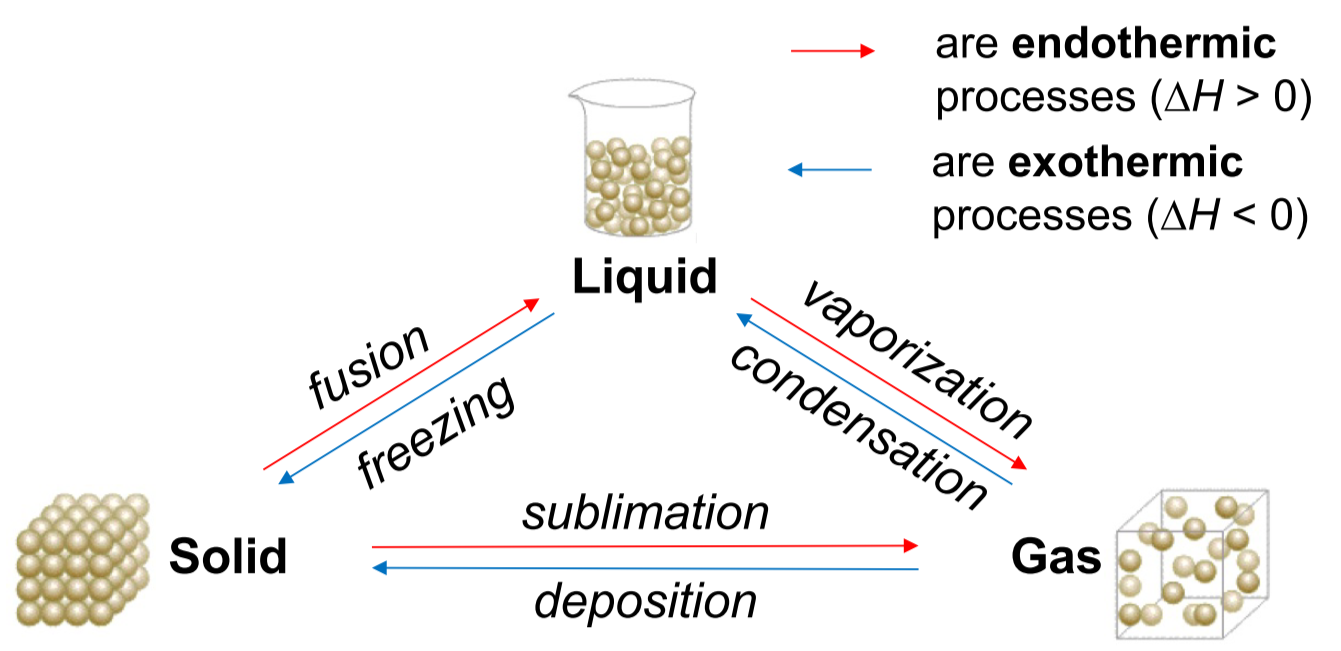
### Hess’s Law of Constant Heat Summation

For a process that occurs in steps,

Heat of reaction is equal to the heat of formation of its products minus that of its reactants:

* is the stoichiometric coefficient

# States of Matter and Phase Changes





### Clausius-Clapeyron Equation

Relates the heat of vaporization of a substance at two different pressures and temperatures

* To find the **boiling point**, set
* If , is the **normal boiling point**

# Intermolecular Forces

The types of intermolecular forces are:

* **London dispersion forces** (instantaneous dipole-induced dipole forces)
* **Dipole-dipole** **interactions**
* **Hydrogen bonds**
* Polar compounds: molecular dipole moment
* Non-polar compounds: molecular dipole moment

Important factors:

* Polar bonds (covalent bonds between atoms with unequal electronegativity)
* Molecular shape (linear, bent, pyramidal, tetrahedral)
* Unshared valence electrons

### London Dispersion Forces

* Exists in all molecules; compounds with greater molecular mass have greater LDF
* Temporary dipoles due to uneven distribution of electrons, as they are constantly moving
* Polarizability (ability of electron cloud to be distorted) is very important
  + Depends on number of electrons and molecular shape
* As electron cloud charge , LDF
* For molecules with same molecular mass, elongation , LDF

### Dipole-Dipole Interactions

* Only exists in polar molecules (
* Dipoles tend to line up head-to-tail, with positive end of one molecule directed to negative end of neighbouring molecule
* Stronger intermolecular attraction = stronger dipole-dipole

### Hydrogen Bonds

* Very strong dipole-dipole interaction between molecules containing H and N, O, or F

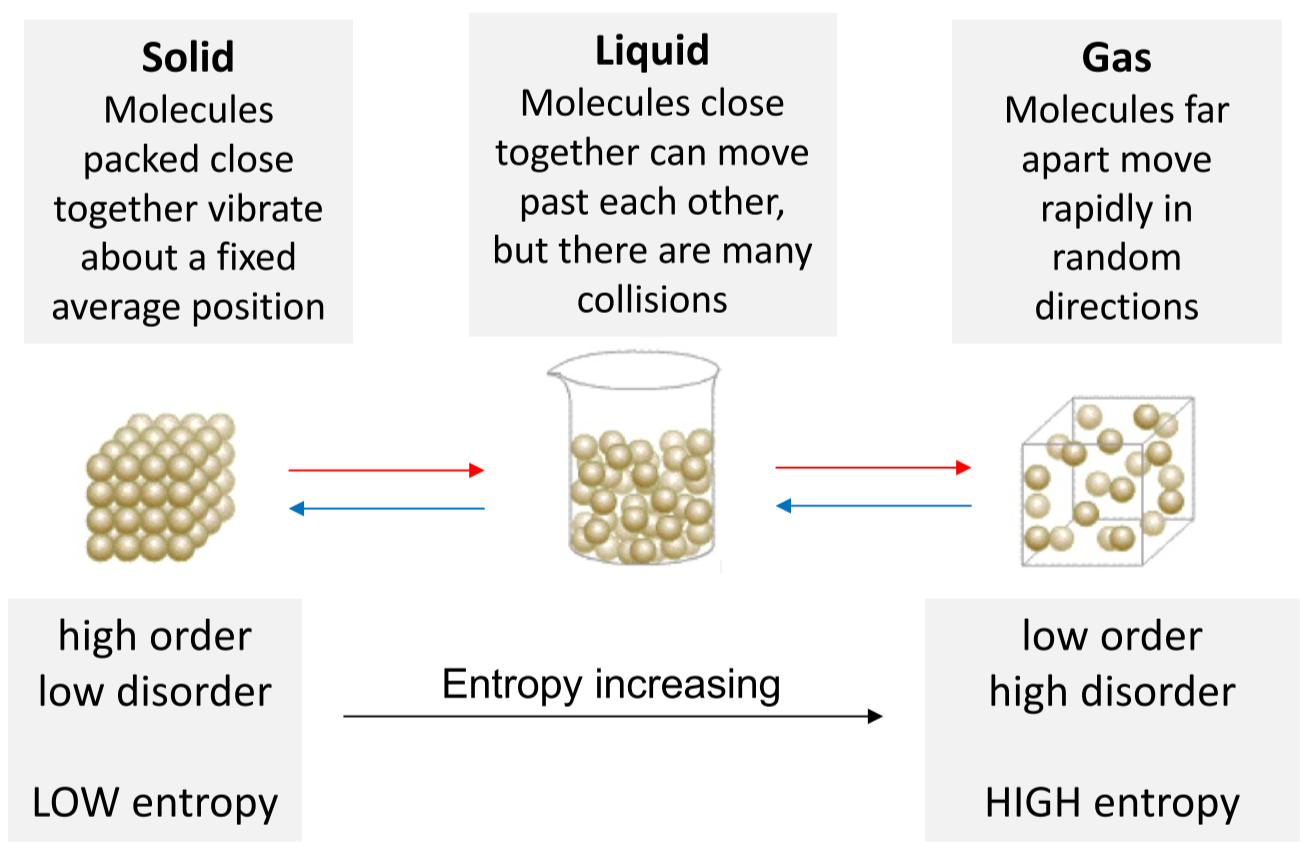
As intermolecular interactions :

* Surface tension, viscosity, boiling point, melting point
* Vapor pressure

The **solubility** of ionic solids as ionic bond strength , aka as **charge** and **molecular mass**

# Entropy and Gibbs Energy

* **Entropy** : the amount of dispersal of matter and energy in a system
  + measures the randomness/disorder in a system
  + As the energy of a system increases, the entropy of the system will increase because there are more microstates
* The more **degrees of freedom** (DOF, translational/rotational/vibrational motions) there are, the greater is
  + DOF increases as **molecular complexity increases**



For a chemical process:

**Phase transition**:

= the heat of transition, is in Kelvin

**Heating/cooling at constant P**:

= heat capacity at pressure P

**Change in ideal gas state from () to ():**

### Second Law of Thermodynamics

**Spontaneous** processes increase the total entropy of the universe

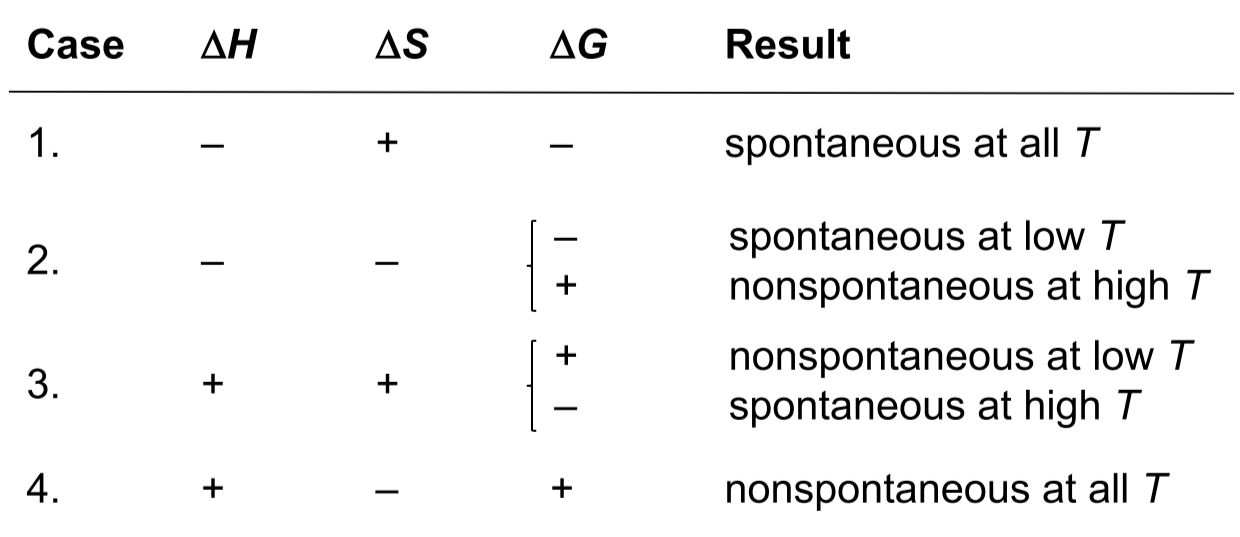
* – **spontaneous** reaction
* – process is at **equilibrium**
* – **non-spontaneous** reaction

## Gibbs Energy

The change in Gibbs energy of a system is denoted by:

Where

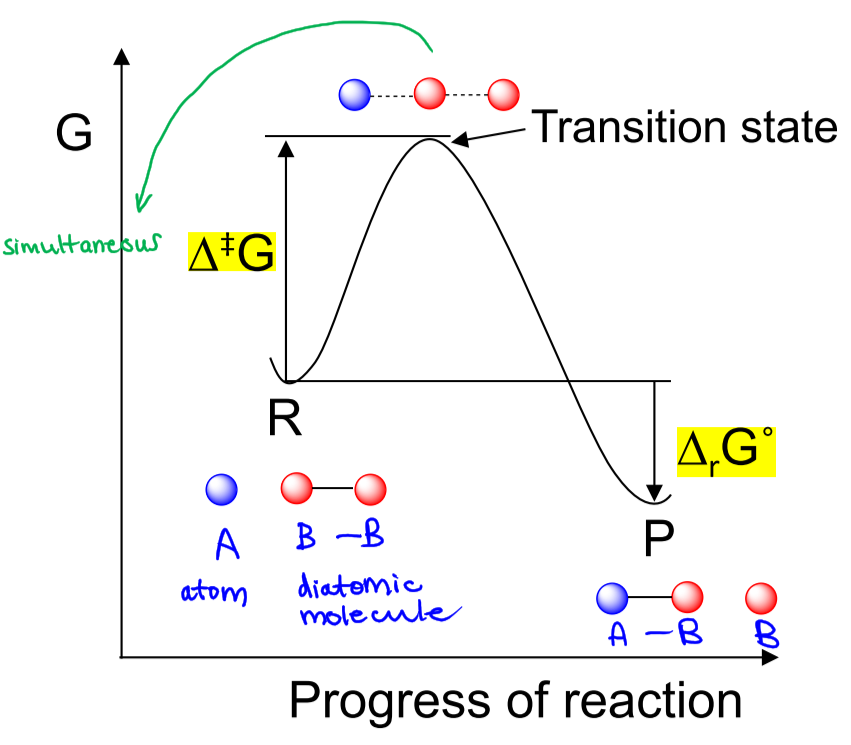
* – **spontaneous** reaction
* – process at **equilibrium**
* – **non-spontaneous** reaction



The change in Gibbs energy for a reaction is given by:

Where = change in Gibbs energy when 1 mol of a compound is formed

* A **negative**  is a necessary but not sufficient condition for a reaction to occur
* For a reaction to occur, must factor in **Gibbs Energy of Activation**



# Chemical Kinetics

* The quantitative study of reaction rates, to determine how reactants are converted into products
* **Rate of reaction** – how fast the concentration of R or P changes with time (always positive)
  + Expressed as change of concentration per unit time (mol/L/s):  
    For , is the **average rate** and is the **instantaneous rate**
  + For gaseous reactions, rates are often measured in terms of change in pressure (atm/s):  
    For ,

The rate of reaction varies with:

* **Concentration**: as concentration , collision frequency , so rate
* **Temperature**: as temperature, number of molecules with enough kinetic energy for reaction to occur , so rate
* **Catalyst**: increases rate of reaction

For a general reaction :

## The Rate Law

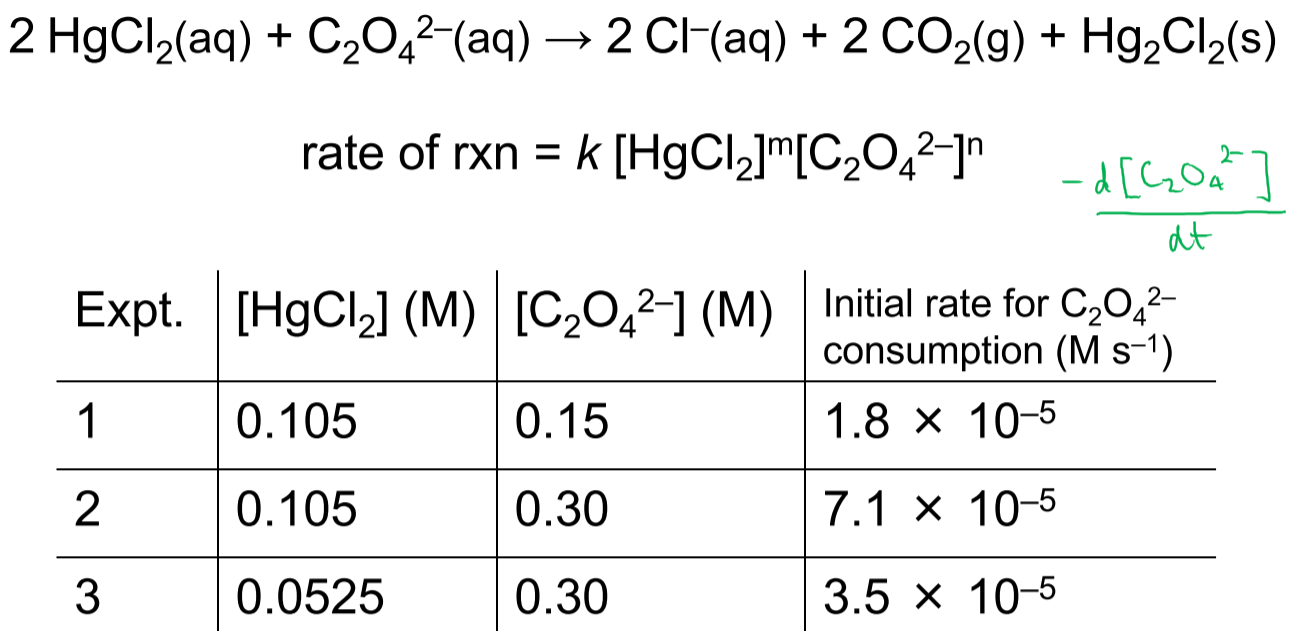
Mathematical expression showing the relationship between rate of reaction and concentration of reactants

For a reaction :

* = the **rate constant** of the reaction
* = the **order of the reaction** with respect to , respectively
  + The **overall order of the reaction**
  + These values are determined experimentally, not related to stoichiometric coefficients

### Method of Initial Rates

Determines the initial rate of reaction for a set of different starting concentrations of reactants:



Hence, the reaction is order 2 with regards to

Hence, the reaction is order 1 with regards to

Then, and the overall order of reaction is 3

* Any experiment can be used to calculate
* The units of vary depending on the order of the reaction:

## Integrated Rate Laws

Determines how the concentration of reactant changes over time

### Zero-order reactions

Integrating,

* Units of
* In a plot of , slope is **negative ()**

### First-order reactions

Integrating,

* Units of
* In a plot of , slope is **negative ()**

### Second-order reactions

Integrating,

* Units of
* In a plot of , slope is **positive ()**

**To determine order of reaction from concentration data over time:**

Calculate to determine which one is **constant (linear)**

## Half Life

The time it takes to decrease to half of its initial value:

At

### Zero-order reactions

* **depends on how much reactant** we start with
* Each subsequent is **half** the previous one

### First-order reactions

* **does not depend on how much reactant** we start with
* Each subsequent is **same** as the previous one

### Second-order reactions

* **depends on how much reactant** we start with
* Each subsequent is **double** the previous one