

PHYSICAL CHEMISTRY FOR
ENGINEERS
ChE 156

Required Text & Student Responsibilities

- ***Required Text:***
 - Raymond Chang Chemistry, seventh edition
- ***Student Responsibility:***
 - Attendance and Participation
 - Students miss class at their own risk.

Exams

- There are two exams:
 - Mid-semester and
 - Final exams.
- Each will consist of multiple choice, true/false, short answers and /or essay questions. The questions will be drawn from both lecture and the text.

Grades

- Grades will be assigned according to the following distribution:
 - Midterm 30%
 - Final 60%
 - Question of the day(attendance) or homework problems 10%

Syllabus and Course outline

- *States of Matter:* Gas Laws; Ideal and real gases. Kinetic theory of gases.
- *Thermodynamics:* The first law; Heat engines; Heat capacity; Enthalpy; Thermochemistry.
- *Chemical Kinetics;* Elementary chemical kinetics; Basic rate laws; Effect of temperature and the Arrhenius Equation.

Syllabus and Course outline

- ***Equilibrium I:*** Description of chemical equilibria; Equilibrium constant calculation; predicting direction of equilibria; Heterogeneous equilibria
- ***Response of equilibria to conditions:*** Pressure, Temperature and added reagents.
- ***Acids, Bases and Salts:*** Definitions of strong and weak acids and bases, pH, salts as acids and bases; Titration curve; Solubility equilibrium; K_{sp} .
- ***Thermodynamics II:*** Second and Third Laws. Entropy and Free energy of chemical reactions.

1. States of Matter

- 3 States
- **Solids:** molecules are held close together in an orderly fashion with little freedom of motion.
- **Liquids:** molecules in liquids are close together but not held so rigidly in position and can move past one another.
- **Gases:** molecules are separated by distances that are large compared with the size of the molecules.
- Can be interconverted without changing the composition of the substance.

1. States of Matter

- Heating a solid(ice) melts to liquid(water) – the transition temperature is called **melting point**.
- Further heating converts the liquid(water) to gas(steam) – the transition temperature is **boiling point**.

1.1 Properties of Matter

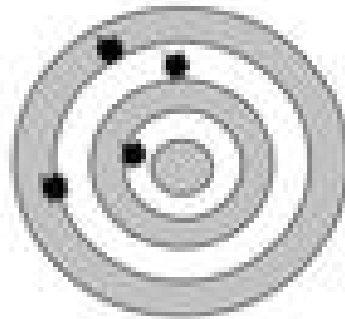
Physical and Chemical

- **Physical properties:** can be measured and observed without changing the composition or identity of the substance. Eg. Colour, melting point of a substance.
- **Chemical properties:** here a chemical change must occur. In this case burning.

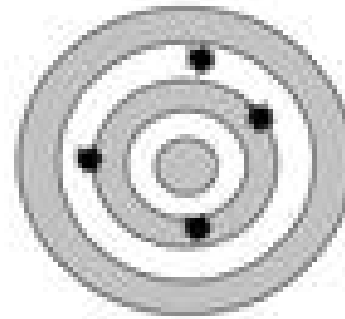
Properties of Matter

- All measurable properties of matter fall under either intensive or extensive property.
- **Extensive properties:** are additive, value depends on the size of the system. E.g. mass, volume
- **Intensive Properties:** not additive. E.g. temperature, density
- **Accuracy and Precision:**
 - Accuracy is the closeness of a measured value to the true value
 - Precision is how closely repeated measurements or observation come to duplicating measured or observed value.

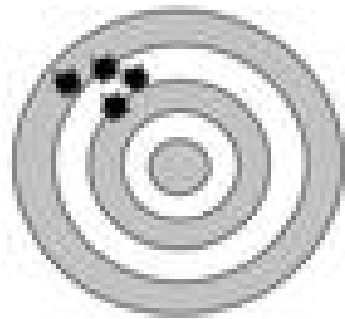
Accuracy vs. Precision



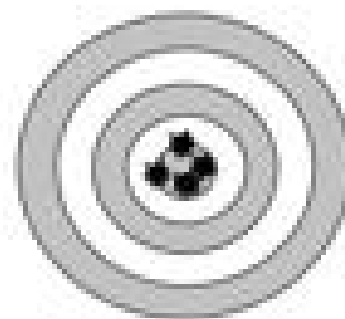
Not Accurate
Not Precise



Accurate
Not Precise



Not Accurate
Precise



Accurate
Precise

Properties of Solid, Liquids and Gases

- **Properties of Solid:** rigid, definite shape and volume
- **Properties of Liquids:** can flow through conduits but exhibit much resistant than gases; have definite volume; much more difficult to compress than gases and also more denser and viscous under normal conditions.
- **Properties of gases:** easily compressible than liquid and has no definite volume; can flow through conduits; have low densities and viscosities at normal conditions.

1.2 Measurements

- Measurements to consider in our study of chemistry
 - Time, Mass, Volume, Density, Temperature
- Density = Mass/volume
- Temperature scale: degree $^{\circ}\text{C} = (^{\circ}\text{F} - 32^{\circ}\text{F}) * 5^{\circ}\text{C} / 9^{\circ}\text{F}$

	Kelvin	Celsius	Fahrenheit	Rankin
Absolute Zero	0K	-273°C	-460°F	0R
Freezing Pt of water	273	0	32	492
Interval	100	100	180	180
Boiling pt of water	373	100	212	672

2. The Gas laws

- The Pressure-Volume Relationship: Boyles Law
 - $P \propto 1/v$ (constant n and Temperature)
- Temperature-Volume Relationship: Charle's Law
 - $V \propto T$ (constant n and P)
- The Volume –Amount Relationship: Avogadro's Law
 - $V \propto n$ (constant P and T)

2.1 The Ideal and real gases

- Combine all the three gas laws
 - $V \propto nT/P$
 - $V = RnT/P$
 - $PV = nRT$ Ideal gas equation
 - R = proportionality constant or gas constant
 - An Ideal gas is a hypothetical gas whose pressure-volume-Temperature behavior can be completely accounted for by the ideal gas equation. The **molecules of an ideal gas** do **not attract or repel** one another and their **volume** is **negligible compared** with the **volume of the container**.

Ideal and real gases(contd.)

- Before we can apply the ideal gas equation to real system, we must evaluate the gas constant, R.
- At **0°C (273.15K)** and **1 atm** pressure, many real gases behave like an ideal gas. Experiment show that under this conditions, **1 mole** of an **ideal gas** occupies **22.414 L**. The conditions 0°C and 1 atm. are called **STP**.

Ideal and Real gases(contd.)

- **$R = PV/nT$**
- **$= ((1 \text{ atm}) * (22.414\text{L})) / ((1\text{mol}) * (273.15\text{K}))$**
- **$= 0.082057\text{L.atm/K.mol}$**

Ideal and real gases: Density calculations(contd)

- Rearranging the ideal gas equation to calculate the density of a gas;

$$\frac{n}{V} = \frac{P}{RT}$$

$$n = \frac{m}{M}$$

$$\frac{m}{MV} = \frac{P}{RT}$$

$$d = \frac{m}{V} = \frac{PM}{RT}$$

Ideal and real gases: Molar Mass of a Gaseous Substance(contd)

$$M = \frac{dRT}{P}$$

Questions on Ideal Gas laws

- 1. Sulphur hexafluoride (SF_6) is colorless, odorless and a very unreactive gas. Calculate the pressure (in atm) exerted by 1.82 moles of the gas in a steel vessel of volume 5.43L at 69.5°C . (Ans = 9.42atm)
- 2. Calculate the volume (in litres) occupied by 7.40g of NH_3 at S.T.P. (Ans = 9.74L)
- Try the following questions using the ideal gas equation
 - 1. A small bubble rises from the bottom of a lake, where the temperature and pressure are 8°C and 6.4atm, to the water's surface, where the temperature is 25°C and pressure is 1atm. Calculate the final volume (in mL) of the bubble if its initial volume was 2.1mL. (Ans= 14mL)
 - 2. Argon is an inert gas used in light bulbs to retard the vapourization of the filament. A certain light bulb containing argon at 1.2atm and 18°C is heated to 85°C at constant volume. Calculate its final pressure. (Ans=1.48atm)

Dalton's Law of Partial Pressures(contd)

- Total gas pressure is related to ***partial pressures, that is, the pressures of individual gas components in the mixture.***
- Dalton's law of partial pressures states that, ***the total pressure of a mixture of gases is the sum of the pressures that each gas would exert if it were present alone.***

Ideal and real gases: Dalton's Law of Partial pressures(contd)

- Let pressure exerted by gas A is:

$$P_A = \frac{n_A RT}{V}$$

- Let pressure exerted by gas B be:

$$P_B = \frac{n_B RT}{V}$$

- In a mixture of gases A and B, the total pressure P_T is given as:

$$P_T = P_A + P_B$$

$$P_T = \frac{n_A RT}{V} + \frac{n_B RT}{V}$$

$$P_T = \frac{RT}{V} (n_A + n_B)$$

$$P_T = \frac{nRT}{V}$$

Ideal and real gases: Dalton's Law of Partial pressures(contd)

- Where **n** is the total number of gas present, and is given by:

$$n = n_A + n_B$$

- Generally, total pressure of a gas is given by:

$$P_T = P_1 + P_2 + P_3 + \dots$$

- Each partial pressure is related by the total pressure (considering a mixture of 2 gases) by:

$$\frac{P_A}{P_T} = \frac{n_A RT/V}{(n_A + n_B) RT/V}$$

$$\frac{P_A}{P_T} = \frac{n_A}{n_A + n_B}$$

$$\frac{P_A}{P_T} = X_A$$

Ideal and real gases: Dalton's Law of Partial pressures(contd)

- Where X_A is the mole fraction of gas A.
- The ***mole fraction*** is ***a dimensionless quantity that expresses the ratio of the number of moles of one component to the number of moles of all components present.***

- similarly $P_A = X_A P_T$

$$P_B = X_B P_T$$

- ***Sum of the mole fractions for a mixture of gases must be unity.***

$$X_A + X_B = \frac{n_A}{n_A + n_B} + \frac{n_B}{n_A + n_B} = 1$$

- ***For a system with more than 2 gases, the partial pressure of the i th component is:***

$$P_i = X_i P_T$$

2.2. The Kinetic Molecular Theory of Gases

- Gas laws help to **predict behavior** of gases but do not explain what happens at the molecular level to cause the changes.
- Why does gas expand on heating?
 - Physical properties of gases can be explained in terms of the **motion** of individual molecules, (according to Boltzmann, Maxwell)
 - This molecular movement is a form of energy which can be defined as the capacity to do work
 - In mechanics, work is defined as force times distance. Since energy can be measured as work;

$$\begin{aligned} \text{energy} &= \text{work done} \\ &= \text{force} \times \text{distance} \end{aligned}$$

SI units of energy is joule (J)

$$1 \text{ J} = 1 \text{ kgm}^2 / \text{s}^2 = 1 \text{ Nm}$$

The Kinetic Molecular Theory of Gases (contd)

- ***Kinetic energy (K.E)*** is the energy expended by a moving object, or *energy of motion*.
- The kinetic theory of gases assumes that;
 - A gas is composed of molecules that are separated from each other by distances far greater than their own dimensions. The molecules can be considered to be “points”, that is **they possess mass but have negligible volume**.
 - Gas molecules are in constant motion in random directions, and they frequently collide with one another. **Collision among molecules are perfectly elastic** (that is energy can be transferred from one molecule to another as a result of collision). **Nevertheless**, the **total energy** of all molecules in a **system remains the same**.
 - Gas molecules **neither exert attractive or repulsive forces** on one another.

The Kinetic Molecular Theory of Gases (contd)

- The average kinetic energy of the molecules is proportional to the temperature of the gas in Kelvin. Any two gases at the same temperature will have the same average K.E. The average K.E of a gas is given by;

$$\overline{KE} = \frac{1}{2} m \overline{u^2}$$

where

m = mass of the molecule

u = its speed

$\overline{u^2}$ = *mean square speed :*

$$\overline{u^2} = \frac{u_1^2 + u_2^2 + \dots + u_N^2}{N}$$

N is the number of molecules

The Kinetic Molecular Theory of Gases (contd)

- Based on assumption 4

$$\overline{KE} \propto T$$

$$\frac{1}{2} m \overline{u^2} \propto T$$

$$\frac{1}{2} m \overline{u^2} = CT$$

C = constant and T is absolute temperature

2.3 Application to the Gas Laws

- **Compressibility of Gases:** since molecules in the gas phase are separated by large distances, gases can be compressed easily to occupy less volume.
- **Boyle's law:** the pressure exerted by a gas results from the impact of its molecules on the walls of the container. The collision rate is proportional to the number density (number of molecules per unit volume) of the gas. **Decreasing the volume of a given amount of gas increases its number density and hence its collision rate.** For this reason, the pressure of a gas is inversely proportional to the volume it occupies.
- **Charles's law:** The fact that average kinetic energy of gas molecules is proportional to the sample's absolute temperature, raising the temperature increases the average K.E. Consequently molecules collide frequently with the walls of the container and with a greater impact if the gas is heated, and thus the pressure increases. The volume of the gas expands until the gas pressure is balanced by the constant external pressure.

Application to the gas laws(contd)

- **Avogadro's law:** as shown, pressure of a gas is proportional to both density and temperature of the gas. Since the mass of a gas is directly proportional to the number of moles (n) of the gas, we can represent density by n/V . Therefore,

$$P \propto \frac{n}{V} T$$

for two gases 1 and 2,

$$P_1 \propto \frac{n_1 T_1}{V_1} = C \frac{n_1 T_1}{V_1}$$

$$P_2 \propto \frac{n_2 T_2}{V_2} = C \frac{n_2 T_2}{V_2}$$

if $P_1 = P_2$, $T_1 = T_2$, $V_1 = V_2$, then $n_1 = n_2$,

which is a mathematical expression of Avogadro's law.

2.4 Root-mean square speed

- One way to estimate molecular speed is to calculate **root-mean-square speed** (u_{rms}).
- One of the results of the kinetic theory of gases is that the total K.E of a mole of any gas equals $\frac{3}{2}RT$. We also saw that the average K.E of one molecule is $\frac{1}{2}m\overline{u^2}$ and so we can write

$$N_A \left(\frac{1}{2} m \overline{u^2} \right) = \frac{3}{2} RT$$

where N_A is Avogadro's number.

$$\text{but } N_A m = M$$

$$\Rightarrow \overline{u^2} = \frac{3RT}{M}$$

$$\sqrt{\overline{u^2}} = u_{rms} = \sqrt{\frac{3RT}{M}}$$

2.5 Deviation from Ideal behavior

- Ideal behavior: a gas that satisfies the following two conditions is said to exhibit ***ideal behavior***.
 - *that molecules in the gaseous state do not exert any force, either attractive or repulsive on one another.*
 - *that the volume of the molecules is negligibly small compared with that of the container*

$$P_{ideal} = P_{real} + \frac{an^2}{V^2}$$

where

P_{real} = observed pressure

$\frac{an^2}{V^2}$ = correction term

Deviation from Ideal behavior(contd)

- The correction

$$\left(P + \frac{an^2}{V^2}\right)(V - nb) = nRT \quad \text{Van der Waals Equation}$$

where

$$\left(P + \frac{an^2}{V^2}\right) = \text{corrected pressure}$$

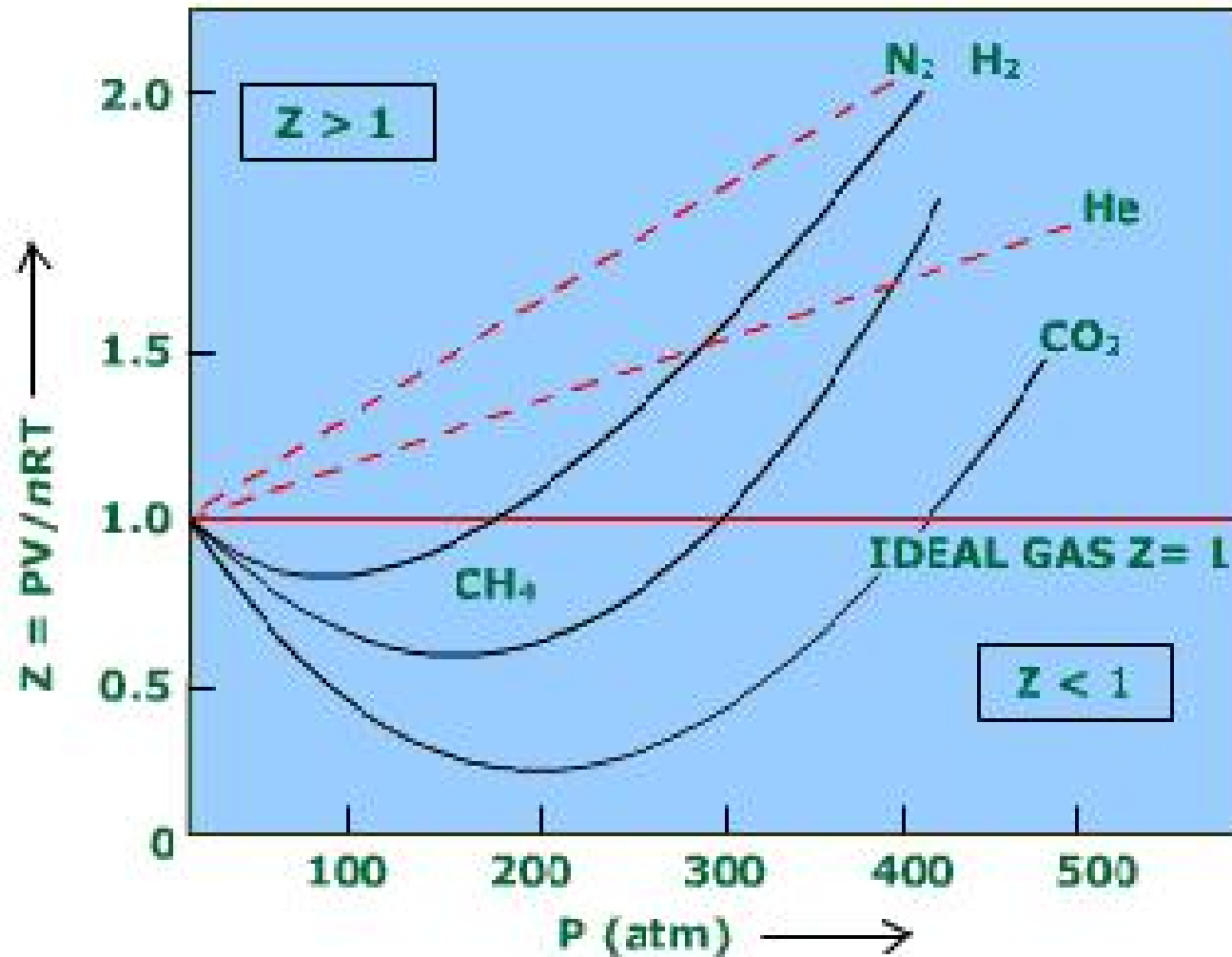
$$(V - nb) = \text{corrected volume}$$

- Given that 3.50 moles of NH_3 occupy 5.20L at 47°C , Calculate the pressure of the gas (in atm) using (a) the ideal gas equation (b) the van der Waal's equation. Let $a=4.16585\text{atmL}^2/\text{mol}^2$ and $b=0.03713\text{L/mol}$. $R=0.08205\text{atm.L/mol.K}$ (Ans= 17.7atm, 16.2atm).

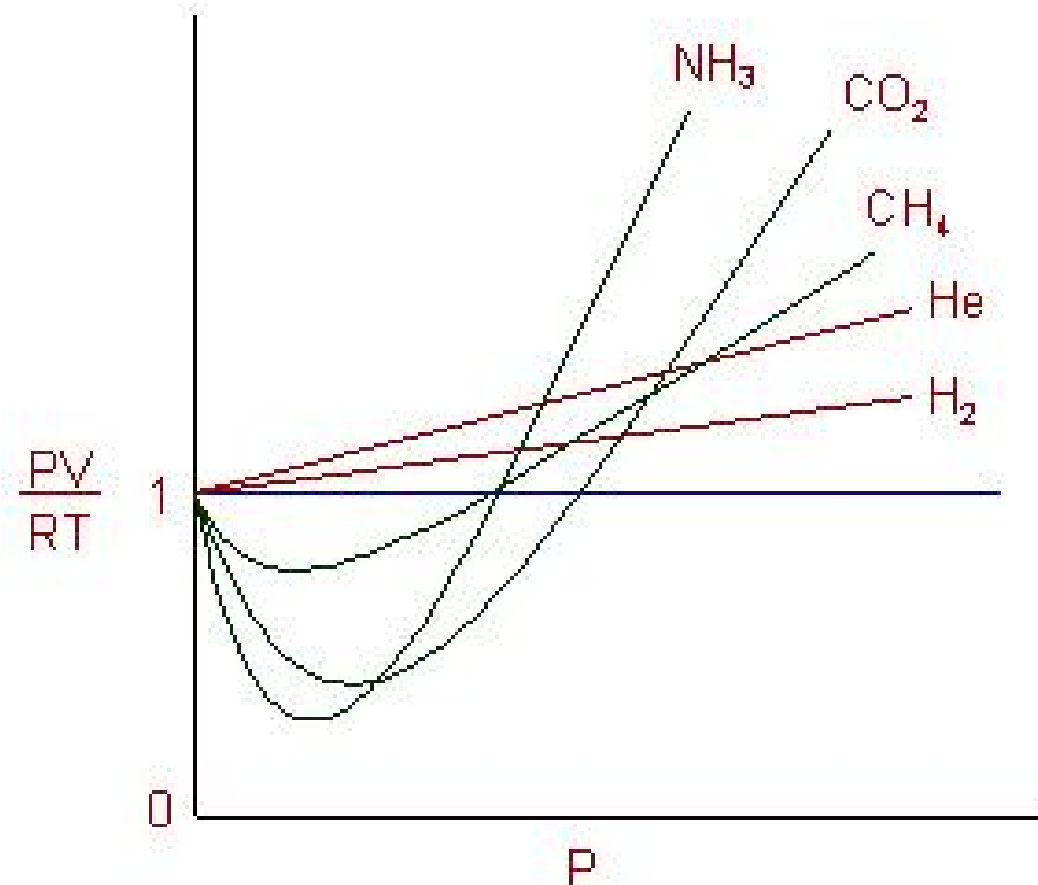
Ideal Gas vs. Real Gases

Ideal gases	Real Gases
Ideal gases obey all gas laws under all conditions of temperature and pressure.	Real gases obey gas laws only at low pressures and high temperature.
The volume occupied by the molecules is negligible as compared to the total volume occupied by the gas.	The volume occupied by the molecules is not negligible as compared to the total volume of the gas.
The force of attraction among the molecules are negligible.	The force of attraction are not negligible at all temperatures and pressures.
Obeys ideal gas equation $PV=nRT$	Obeys Van der Waals equation $\left(P + \frac{an^2}{V^2} \right) (V-nb) = nRT$

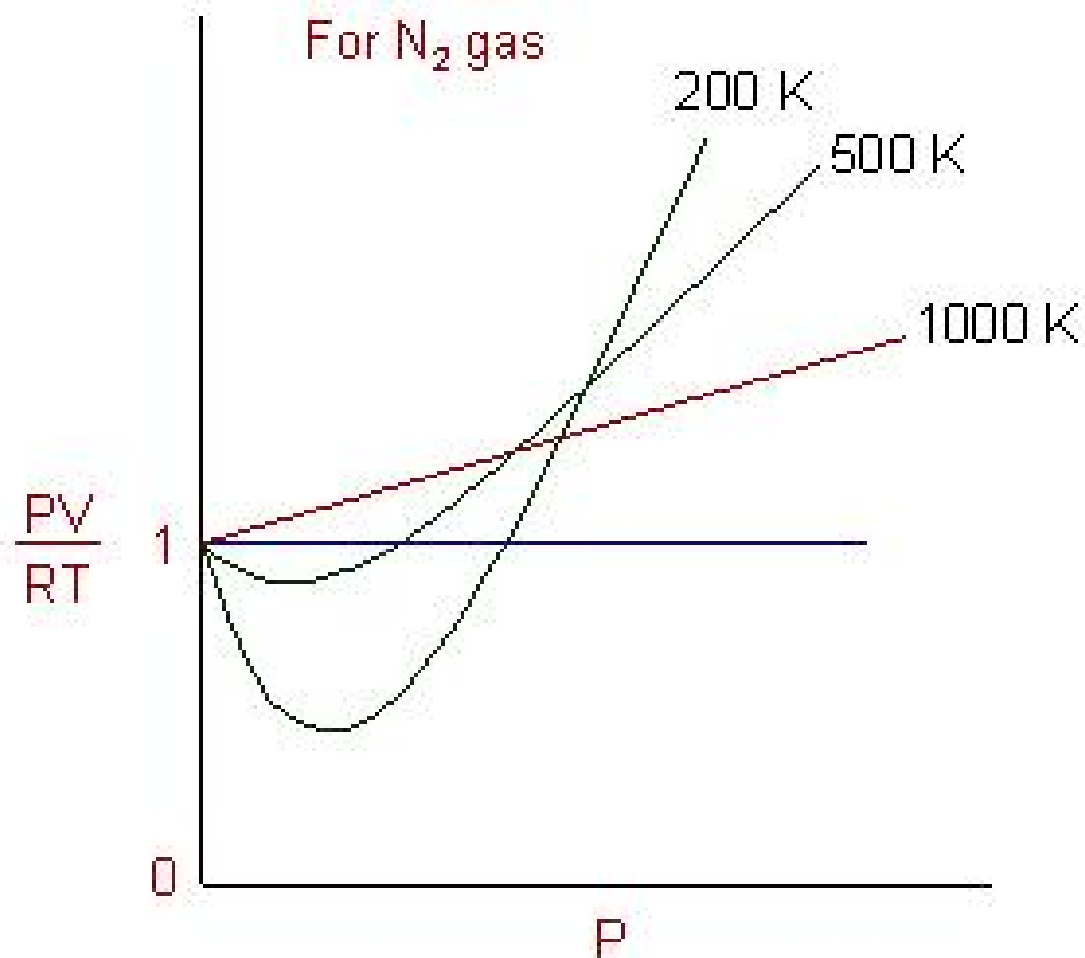
Graph of compressibility, Z vs. P



Graph of compressibility, Z vs. P



Graph of compressibility, Z vs. P for Nitrogen



The compressibility factor

- Z is a measure of deviation from ideality
- $Z=1$, ideal situation
- $Z>1$, pressure increases, repulsive forces are dominant and more difficult to compress
- $Z<1$, pressure decreases, attractive forces dominant and favors compression.
- Z increases with pressure but decreases with temperature.

Equation of State

- Proposed equations of state describe the behavior of real gases.
- They are based on theoretical models of fitting experimental P,V,T data.

$$PV/nRT = 1 + nB(T)/V + n^2C(T)/V^2 + n^3D(T)/V^3 + \dots$$

Condensation of Gases – critical point

- T_c : temp. above which it is not possible to liquify a given gas.
- P_c : minimum pressure required to liquify a given gas at its critical temperature.

$$T_r = \frac{T}{T_c} \quad ; \quad P_r = \frac{P}{P_c}$$

- For compressibility of gases, the principle of corresponding states indicates that any pure gas at the same reduced temperature, T_r , and reduced pressure, P_r , should have the same compressibility factor.

Kirchoff's law

- Kirchoff's law

$$\int_{\Delta H_1}^{\Delta H_2} d(\Delta H) = \int_{T_1}^{T_2} \Delta C_p dT$$

- Applicable if there is no change in phase in moving from T1 to T2.

Joule Thomson Effect

- Throttling of gases: the Joule Thomson effect
- The change in temperature of the gas in throttling is known as J.T effect.
- If $\mu = +ve$, gas shows cooling effect on expansion
- If $\mu = -ve$, gas shows heating effect on expansion
- If $\mu = 0$, gas shows no J.T effect. This is the case with ideal gas /inversion of temperature
- Gas showing no cooling or heating on adiabatic expansion is called inversion temperature of a gas.

3. CHEMICAL KINETICS :

3.1 Elementary Chemical Kinetics

- Chemical kinetics is the area of chemistry that deals with the speeds, or rates at which a chemical reaction occurs.
 - Kinetics refers to reaction rate which is the change in concentration of a reactant or a product with time.
 - General reaction equation is represented by:



For the above reaction, we can express the rate as:

$$\text{rate} = - \frac{\Delta [A]}{\Delta t} \qquad \text{Or} \qquad \text{rate} = \frac{\Delta [B]}{\Delta t}$$

3.1 Chemical kinetics

- Where $\Delta[A]$ and $\Delta[B]$ are changes in concentration over a time period $\Delta[t]$
- These rates are *average rates* because they averaged over a certain period of time.

3.2 Reaction of Molecular bromine and Formic Acid



- Measuring the change (decrease) in bromine concentration at some initial time and final time enables us to calculate the average rate of the reaction during that interval.

- Average rate
$$= - \frac{\Delta [Br_2]}{\Delta t}$$
$$= - \frac{[Br_2]_{final} - [Br_2]_{initial}}{t_{final} - t_{initial}}$$

using table 13.1.

- Figure 13.6 is a plot of the rate vs. Br₂ concentration. The fact that the graph is a straight line shows that the rate is directly proportional to the concentration. The higher the concentration the higher the rate.

Reaction of Molecular bromine and Formic Acid (contd)

- The higher the rate:

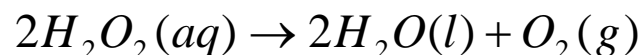
$$\begin{aligned} \text{rate} &\propto [\text{Br}_2] \\ &= k [\text{Br}_2] \end{aligned}$$

- The term k is known as the **rate constant**, a constant of proportionality between the reaction rate and the concentrations of the reactants.
- Rearranging

$$k = \frac{\text{rate}}{[\text{Br}_2]}$$

3.3 Decomposition of Hydrogen Peroxide

- If one of the products of the **reactants is a gas**, we can use a **manometer** to find the reaction rate. Consider the decomposition of hydrogen peroxide at 20°C.



- In this case the rate of decomposition can be determined by monitoring the rate of the oxygen evolution with a monitor. The **oxygen pressure** can be readily **converted to concentration** by using the ideal gas equation:

$$PV = nRT$$

$$P = \frac{n}{V}RT = [O_2]RT$$

$$[O_2] = \frac{1}{RT}P$$

$$rate = \frac{\Delta[O_2]}{\Delta t} = \frac{1}{RT} \frac{\Delta P}{\Delta t}$$

3.4 Reaction rates and Stoichiometry

- Consider the reaction:



$$rate = -\frac{1}{2} \frac{\Delta[A]}{\Delta t} \qquad rate = \frac{\Delta[B]}{\Delta t}$$

- In general, for the reaction:



the rate is given by:

$$rate = -\frac{1}{a} \frac{\Delta[A]}{\Delta t} = -\frac{1}{b} \frac{\Delta[B]}{\Delta t} = \frac{1}{c} \frac{\Delta[C]}{\Delta t} = \frac{1}{d} \frac{\Delta[D]}{\Delta t}$$

3.5 The Rate Law

- The rate Law expresses the relationship of the rate of a reaction to the rate constant and the concentrations of the reactants raised to some power.

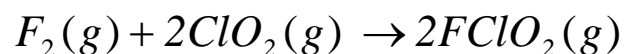


$$rate = k [A]^x [B]^y$$

Where **x** and **y** are numbers and need to be determined experimentally. They are not equal to the stoichiometric coefficients **a** and **b**. When **x** and **y** are added together, they give the overall reaction order, *defined as the sum of the powers to which all reactant concentrations appearing in the rate law are raised*. In the above equation the overall order of reaction is **x+y**.

The Rate Law(contd)

- To determine the rate law of a reaction, consider the following reaction.



- Table 13.2
- Rate is hence: $rate = k[F_2][ClO_2]$
- The reaction is a first order reaction because both $[F_2]$ and $[ClO_2]$ are raised to the first power. But second order overall.
- Calculate the rate constant , assuming

$$[F_2] = 0.10 M, [ClO_2] = 0.010 M \text{ and } rate = 1.2 \times 10^{-3} M/s$$

$$\Rightarrow k = \frac{rate}{[F_2][ClO_2]} = \frac{1.2 \times 10^{-3} M/s}{(0.10 M)(0.010 M)}$$
$$k = 1.2 / M.s$$

The Rate Law(contd)

- Suppose that for the general reaction $aA + bB \longrightarrow cC + dD$

$$x = 1 \text{ and } y = 2$$

then

$$\text{rate} = k[A][B]^2$$

- The reaction is first order in A and second order in B but third order overall.
- If for a certain reaction, $x = 0$ and $y = 1$, then the rate law is

$$\text{rate} = k[A]^0[B]$$

$$\text{rate} = k[B]$$

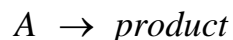
- The exponent zero tells us that the reaction is **independent** of the concentration of A. Note that the reaction order can also be a fraction.

Summary of rate law discussion(contd)

- **Rate laws are always determined experimentally. From the concentration of the reactants and the initial reaction rate, we can determine the reaction order and then the rate constant of the reaction.**
- **Reaction order is always defined in terms of reactants (not products) concentrations**
- **The order of a reactant is not related to the stoichiometric coefficient of the reactant of the overall balanced equation.**

3.6 Relationship between Reactant Concentration and Time

- **First-Order Reactions:** first order reaction is a reaction whose rate depends on the reactant concentration raised to the first power. In a first order reaction of the type



the rate is

$$\text{rate} = - \frac{\Delta[A]}{\Delta t}$$

from the rate law, we also know that

$$\text{rate} = k[A]$$

Unit of k for this rate law

$$k = \frac{\text{rate}}{[A]} = \frac{M / s}{M} = 1/s \text{ or } s^{-1}$$

combining the first two equations for the rate we get

$$- \frac{\Delta[A]}{\Delta t} = k[A]$$

using calculus, the above equation can be written as

$$\ln \frac{[A]}{[A]_0} = -kt$$

3.7 First Order Reaction

$[A]_0$ and $[A]$: – concentrations of A at $t = 0$ and $t = t$, respectively

Rearranging above equation,

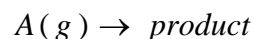
$$\ln[A] = -kt + \ln[A]_0$$

above equation has the form of $y = mx + b$, where m is the slope.

- Practice problems!

3.8 First Order Reaction

- For a **gas-phase reactions**, we can replace the concentration terms in the above equation with the pressures of the gaseous reactants. For the first order reaction



using the ideal gas equation

$$PV = n_A RT$$

$$\frac{n_A}{V} = [A] = \frac{P}{RT}$$

$$\text{s substitute } [A] = \frac{P}{RT} \text{ into } \ln \frac{[A]}{[A]_0} = -kt$$

$$\Rightarrow \ln \frac{P/RT}{P_0/RT} = -kt$$

$$\ln P = -kt + \ln P_0$$

- Practice Problem!

3.9 Half-Life

- Another measure of the rate of a reaction, relating concentration to time, is the **half-life**, $t_{1/2}$ which is the time required for the concentration of a reactant to decrease to half of its initial concentration.

For a first order reaction,

$$\ln \frac{[A]}{[A]_0} = -kt$$

$$\ln \frac{[A]_0}{[A]} = kt$$

$$t = \frac{1}{k} \ln \frac{[A]_0}{[A]}$$

by definition of half - life, when $t = t_{1/2}$, $[A] = [A]_0 / 2$

$$t_{1/2} = \frac{1}{k} \ln \frac{[A]_0}{[A]_0/2} = \frac{1}{k} \ln 2 = \frac{0.693}{k}$$

$$t_{1/2} = \frac{0.693}{k}$$

3.10 Second Order Reaction

- **A second-order reaction** is a reaction whose rate depends on the concentration of one reactant raised to the second power or the concentrations of two different reactants, each raised to the first power.

1. $A \rightarrow \text{product}$
where

$$\text{rate} = -\frac{\Delta[A]}{\Delta t}$$

from the rate law

$$\text{rate} = k[A]^2$$

Units of k is given by

$$k = \frac{\text{rate}}{[A]^2} = \frac{M/s}{M^2} = l/M.s$$

2. $A + B \rightarrow \text{Product}$

rate law is given by

$$\text{rate} = k[A][B] \quad \text{overall order is 2}$$

3.11 Second Order Reaction

- Second

*For "A → product" a second order reaction
using calculus,*

$$\frac{1}{[A]} = \frac{1}{[A]_0} + kt$$

(the corresponding equation for $A + B \rightarrow \text{product}$ is complex for our discussion)

$$\text{At } t = t_{1/2}, [A] = [A]_0/2$$

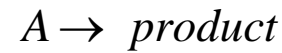
$$\frac{1}{[A]_0/2} = \frac{1}{[A]_0} + kt_{1/2}$$

$$t_{1/2} = \frac{1}{k[A]_0}$$

- Practice problem!

3.12 Zero Order Reaction

- Zero order reactions are very rare. For a zero order reaction



the rate law is given by

$$\text{rate} = k[A]^0$$

$$\text{rate} = k$$

- Thus the rate of a zero order reaction is a constant, independent of a reaction concentration.

3.13 Activation Energy and Temperature Dependence of Rate Constants

- With very few exceptions, reaction rates increase with increasing temperature.
 - Time required to hard-boil an egg is shorter at 100°C (10mins) than at 80°C (30mins).
 - Exception is storing food at subzero temperature, thereby slowing the rate of bacteria decay.

3.14 The collision theory of chemical kinetics

- Kinetic molecular theory of gases postulates that gas molecules frequently collide with one another.
- Chemical reactions occur as a result of collision between reacting molecules.
- In terms of the collision theory of chemical kinetics, we expect the rate of a reaction to be directly proportional to the number of molecular collisions per second, or to the frequency of molecular collision.

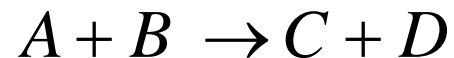
$$\text{rate} \propto \frac{\text{number of collisions}}{s}$$

The collision theory of chemical kinetics (contd)

- Product formation begins when molecules with greater K.E collide with each other and break bonds.
- For a reaction to occur, the colliding molecules must have a **total K.E equal to or greater** than the ***activation energy, E_a*** , *which is the **minimum** amount of energy required to **initiate** a chemical reaction.*
- Activation energy can be regarded as a barrier that prevents less energetic molecules from reacting.

3.15 Potential Energy Profiles

- For reaction



- For more stable products than reactants as in plot (a), the reaction is accompanied by a release of heat (exothermic).
- Potential energy profile (b) shows products less stable than reactants, hence reaction is accompanied by absorption of heat (endothermic reaction) by the reacting mixture from the surroundings.

Potential Energy Profiles(contd)

3.16 The Arrhenius Equation

- Dependence of the rate constant of a reaction on temperature can be expressed by the Arrhenius equation.

$$k = Ae^{-E_a/RT}$$

where E_a = activation energy, KJ/mol

R = gas constant, 8.314 J/K.mol

T = absolute temperature, K

e = base of the natural log

- Expressing the Arrhenius equation in a more useful way

$$\ln k = \ln (Ae^{-E_a/RT})$$

$$\ln k = \ln A - \frac{E_a}{RT}$$

rearranging

$$\ln k = \left(-\frac{E_a}{R}\right)\left(\frac{1}{T}\right) + \ln A$$

the above equation is in the form $y = mx + b$

Thus a plot of $\ln k$ versus $1/T$ gives a straight line whose slope m is equal to $-E/R$ and intercept b is on the y -axis is $\ln A$.

The Arrhenius Equation (contd)

- An equation relating the rate constant k_1 and k_2 at temperatures T_1 and T_2 can be used to calculate the activation energy or to find the rate constant at another temperature if the activation energy is known. Deriving such equation;

$$\ln k_1 = \ln A - \frac{E_a}{RT_1}$$

$$\ln k_2 = \ln A - \frac{E_a}{RT_2}$$

subtracting $\ln k_1$ from $\ln k_2$ gives

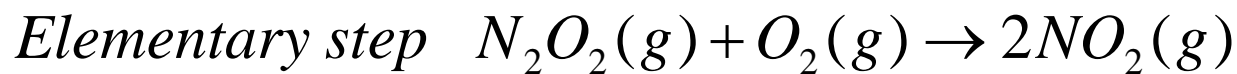
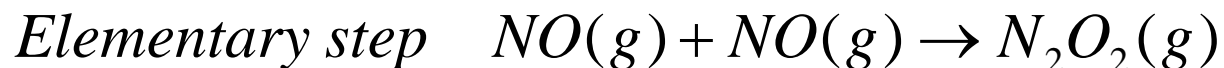
$$\ln k_1 - \ln k_2 = \frac{E_a}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$$

$$\ln \frac{k_1}{k_2} = \frac{E_a}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$$

$$\ln \frac{k_1}{k_2} = \frac{E_a}{R} \left(\frac{T_1 - T_2}{T_1 T_2} \right)$$

Reaction Mechanism

- **Reaction Mechanism:** a term used for the sequence of steps that leads to product formation.



4. Thermochemistry:

4.1 Nature and Types of Energy

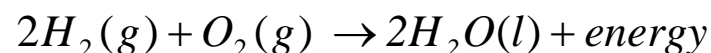
- ***Energy*** is the capacity to do work. ***Work*** is directed energy change resulting from a process.
- ***Types of energy***
 - **Radiant or solar energy**: is energy from the sun
 - **Thermal energy**: associated with the random motion of atoms and molecules
 - **Chemical energy**: stored within the structural unit of a chemical substances.
 - **Potential energy**: energy available by virtue of an object's position
- Law of conservation of energy: *the total quantity of energy in the universe is assumed constant.*

4.2 Energy changes in chemical reaction

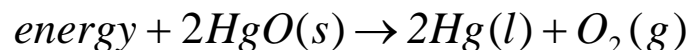
- **Definitions:**
 - **Heat:** *is the transfer of thermal energy between two bodies that are at different temperatures*
 - **Thermo chemistry:** *it is the study of heat change in chemical reactions*
 - **System:** *the specific part of the universe that is of interest .*
 - **Surroundings:** *the rest of the universe outside the system*
- **3 types of systems exists**
 - **Open system:** *can exchange mass and energy, usually in the form of heat, with its surroundings.*
 - **Closed system:** *allows the transfer of energy(heat) but not mass with its surroundings.*
 - **Isolated system:** *does not allow the transfer of either mass or energy*

Energy changes in chemical reaction(contd)

- Exothermic process : any process that gives off heat, that is, transfers thermal energy to the surroundings
 - E.g. combustion of hydrogen gas in oxygen



- Endothermic process: any process or system that absorbs heat.
 - E.g. decomposition of mercury(II) oxide at high temperatures



4.3 Enthalpy

- Enthalpy of a reaction, ΔH , is the difference between the enthalpies of the product and the enthalpies of the reactants.

$$\Delta H = H(\text{products}) - H(\text{reactants})$$

4.4 Calorimetry

Specific Heat Capacity and Heat Capacity

- **Calorimetry:** is the measurement of heat changes
- **Specific heat, s (j/g.°C),** *of a substance is the amount of heat required to raise the temperature of one gram of the substance by one degree Celsius.*
- **Heat capacity, C (j/°C),** *of a substance is the amount of heat required to raise the temperature of a given quantity of a substance by one degree Celsius.*
- Relationship between heat capacity and specific heat
$$C = ms$$

Calorimetry(contd)

- Knowing the **specific heat** and the **amount of substance**, then the **change in the sample's temperature** (Δt), will tell the **amount of heat(q)** that has been absorbed or released in the process. Equation for the **heat change** is given as:

$$q = ms\Delta t$$

$$q = C\Delta t$$

where m is the mass of the sample and Δt the temperature change

$$\Delta t = t_{final} - t_{initial}$$

- Sign convention for q , is the same as that for enthalpy; q is positive for endothermic processes and negative for exothermic.

Calorimetry(contd)

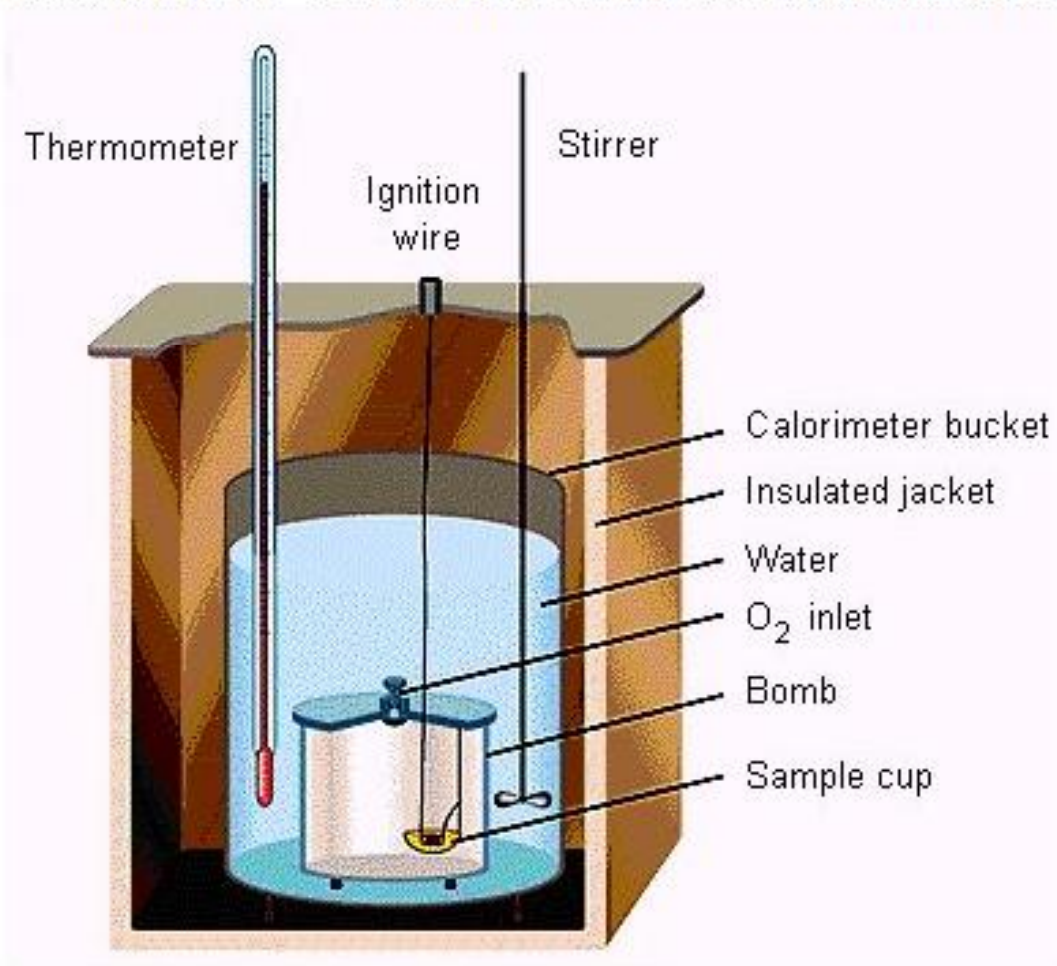
- *E.g. A 400g sample of water is heated from 8.50°C to 74.6°C. Calculate the amount of heat absorbed by the water. (specific heat of water = 4.184 j/g.°C).*
- *E.g. An iron bar of mass 869g cools from 94°C to 5°C. Calculate the heat released (kilojoules) by the metal.*

Constant-Volume Calorimetry(contd)

- If we place a known mass of a compound in a steel container, ***constant-volume calorimeter***, and fill it with oxygen at about 30 atm. of pressure, then we can measure the ***heat of combustion***.
- The closed bomb is immersed in a known amount of water as shown in Fig.
- The sample is ignited electrically, and the heat produced by the combustion reaction can be calculated accurately by recording the rise in temperature of the water.
- The heat given off by the sample is absorbed by the water and the calorimeter.
- The bomb calorimeter and the water in which it is submerged is referred to as an isolated system: No heat enters or leaves the system throughout the process.

Constant-Volume Calorimetry(contd)

CONSTANT VOLUME BOMB CALORIMETER



Constant-Volume Calorimetry(contd)

- Thus,

$$q_{system} = q_{water} + q_{bomb} + q_{rxn} = 0$$

where

q_{water} = heat change for water

q_{bomb} = heat change for the bomb

q_{rxn} = heat change for the reaction

$$q_{rxn} = -(q_{water} + q_{bomb})$$

the quantity q_{water} is obtained by

$$q = ms\Delta t$$

$$q_{water} = m_{water}(4.184J / g.^{\circ}C)\Delta t$$

heat capacity of the bomb remains constant for all experiments carried out in the bomb calorimeter

$$C_{bomb} = m_{bomb} \times s_{bomb}$$

$$q_{bomb} = C_{bomb}\Delta t$$

since the reaction in a bomb calorimeter occurs under constant – volume rather than constant – pressure conditions, the heat changes do not correspond to the enthalpy change, ΔH .

Constant-Volume Calorimetry(contd)

- E.g.

Constant-Pressure Calorimetry(contd)

- A simpler device than the constant-volume calorimeter is the constant-pressure calorimeter used to determine the heat changes for **non combustion** reactions.
- A constant-pressure calorimeter constructed from two Styrofoam coffee cups is used, shown in Fig.
- As the pressure is constant, the heat change for the process is equal to the enthalpy change (ΔH).
- Heat effects of acid -base neutralization reactions, heat of solution, heats of dilution can be studied with constant-pressure calorimeter device.

Constant-Pressure Calorimetry(contd)

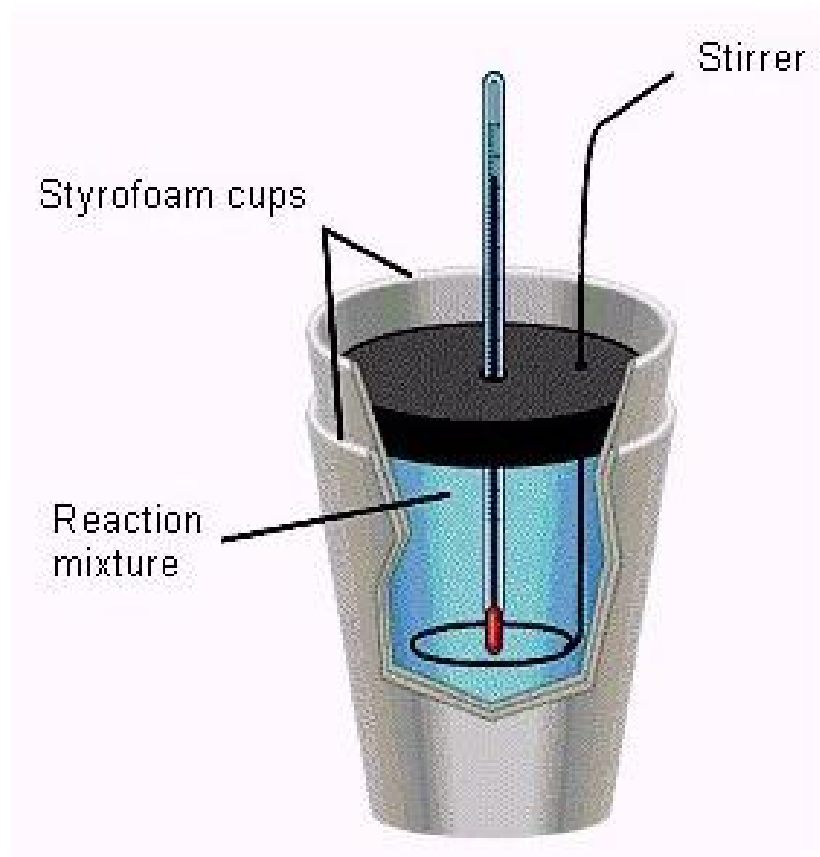


Image from CyberChem CD, Ashour-Abdalla & Chang

Constant-Pressure Calorimetry(contd)

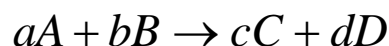
- E.g

4.5 Standard Enthalpy of Formation and Reaction

- Enthalpy change that accompanies a reaction can be determined by measuring the heat absorbed or released (at constant pressure)
- **Standard enthalpy of formation, (ΔH°_f)** : *the heat change that results when 1 mole of a compound is formed from its elements at a pressure of 1 atm.*
- ΔH°_f values measured at 25°C will always be used.
- Standard enthalpy of formation of any element in its most stable form is zero. See Table.
- **Standard enthalpy of reaction, ΔH°_{rxn}** : *enthalpy of a reaction carried out at 1 atm.*

Standard Enthalpy of Formation and Reaction(contd)

- For



$$\Delta H^{\circ}_{rxn} = [c\Delta H^{\circ}_f(C) + d\Delta H^{\circ}_f(D) - [a\Delta H^{\circ}_f(A) + b\Delta H^{\circ}_f(B)]]$$

where a, b, c, d are in moles

Generally

$$\Delta H^{\circ}_{rxn} = \sum n\Delta H^{\circ}_f(\text{products}) - \sum m\Delta H^{\circ}_f(\text{reactants})$$

where m, n = stoichiometry coefficients in moles for the reactants and products.

- Direct method: E.g.**



calculate $\Delta H^{\circ}_f(CO_2, g)$

$$\Delta H^{\circ}_{rxn} = (1\text{mol})\Delta H^{\circ}_f(CO_2, g) - [(1\text{mol})\Delta H^{\circ}_f(C, \text{graphite}) + (1\text{mol})\Delta H^{\circ}_f(O_2, g)]$$

$$\Delta H^{\circ}_{rxn} = (1\text{mol})\Delta H^{\circ}_f(CO_2, g) - [0 + 0] = -3935KJ$$

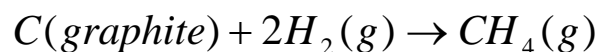
$$\Delta H^{\circ}_f(CO_2, g) = -3935KJ/mol$$

Standard Enthalpy of Formation and Reaction(contd)

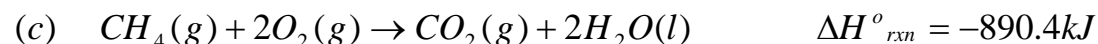
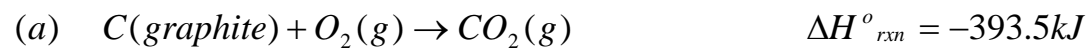
- **Indirect method:** *determination of standard heat of formation based on the law of heat summation or **Hess's Law**.*
- **Hess's Law:** *when reactants are converted to products, the change in enthalpy is the same whether the reaction takes place in one step or in a series of steps.*

Standard Enthalpy of Formation and Reaction(contd)

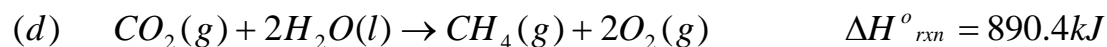
- E.g. calculate standard enthalpy of formation of methane (CH_4) from:



given that



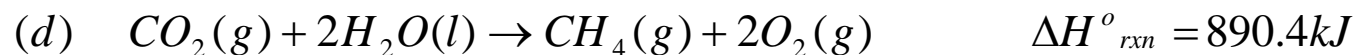
- Obtaining equation containing only C and H_2 as reactants and CH_4 as product, (c) must be reversed.



- Add equations *a*, *b* and *d*

Standard Enthalpy of Formation and Reaction(contd)

- This gives:



- Since the above equation represent the synthesis of 1 mole of CH_4 from its elements, we have $\Delta H^\circ_f(CH_4) = -74.7kJ / mol$

4.6 Heat of Solution and Dilution

- **Heat of Solution (or enthalpy of solution), ΔH_{soln} :** *is the heat generated or absorbed when a certain amount of solute dissolves in a certain amount of solvent.*
- ΔH_{soln} represents the enthalpy of the final solution and the enthalpies of its original components (i.e. solute and solvent) before they are mixed.

$$\Delta H_{\text{soln}} = H_{\text{soln}} - H_{\text{components}}$$

- Obtain enthalpy of solution of NaCl(s).



$$\Delta H_{\text{soln}} = ?$$

Heat of Solution and Dilution(contd)

- Two steps are required to obtain the enthalpy of solution of NaCl(s).

- *The energy required to completely separate 1 mole of a solid ionic compound into gaseous ions, is **lattice energy**.*

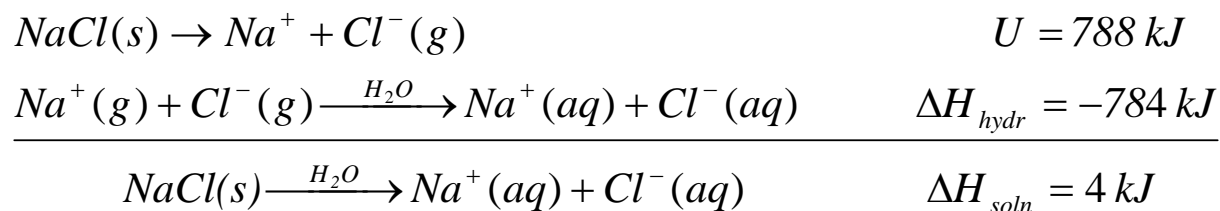


- *The gaseous ions enter the water and become hydrated. The energy change associated with the hydration process is the **heat of hydration**, ΔH_{hydr}*



Heat of Solution and Dilution(contd)

- Applying Hess's law, it is possible to consider ΔH_{soln} as the sum of two related quantities, ***lattice energy and heat of hydration***.



- Heat of Dilution:** *is the heat change associated with the dilution process.*

4.7 Introduction to Thermodynamics

- **Thermodynamics** *is the scientific study of the interconversion of heat and other kinds of energy.*
- In thermodynamics, changes in the **state of a system**, *defined by the values of all relevant macroscopic properties, example, composition, energy, temperature, pressure and volume are studied.*
- Energy, pressure volume and temperature are known as **state functions** – *properties that are determined by the state of a system regardless of how that condition was achieved.*

First law of Thermodynamics(contd)

- **The First Law of Thermodynamics:**

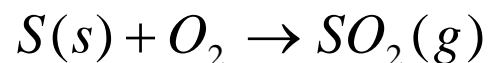
- The first law of thermodynamics is based on the law of conservation of energy.
- The first law ***states that energy can be converted from one form to another , but cannot be created or destroyed.***
- Validity of the first law can be tested by measuring the *change* in internal energy of a system between its initial state and its final state. That is;

$$\Delta E = E_f - E_i$$

- The internal energy of a system has two components:
 - Kinetic energy: *consist of various types of molecular motion and the movement of electrons within molecules.*
 - Potential energy: *determined by the attractive interaction between electrons and nuclei and by repulsive interactions between electrons and between nuclei in individual molecules, as well as by interaction between molecules.*

First law of Thermodynamics(contd)

- Changes in energy are determined experimentally. Consider the reaction



- The internal energy of the reactant molecules are not known, but can accurately measure the change in energy content, ΔE .

$$\Delta E = E(\text{product}) - E(\text{reactant})$$

$$\Delta E = \text{energy content of } 1 \text{ mol } SO_2(g) - [\text{energy content of } 1 \text{ mol } S(s) + 1 \text{ mol } O_2(g)]$$

- The reaction gives off heat. ΔE is negative, energy of product is less than that of reactant.
- Interpreting the heat released, some of the chemical energy in the reactants is converted to thermal energy. Transfer of energy from reactants to surroundings does not change the total energy of the universe. That is, the sum of the energy changes must be zero.

First law of Thermodynamics (contd)

$$\Delta E_{sys} + \Delta E_{surr} = 0$$

$$\Delta E_{sys} = -\Delta E_{surr}$$

- Thus, if system undergoes an energy change, the rest of the universe or surroundings must undergo a change in energy that is equal in magnitude but opposite in sign.
- Thus energy gained in one place must have been lost somewhere else.
- Energy changes associated with a system is of more importance to that of the surroundings. Hence a more useful form of the first law is

$$\Delta E = q + w$$

where

ΔE = change in internal energy of the system

q = heat exchange between the system and the surroundings

w = workdone on the system

First law of Thermodynamics(contd)

- Sign convention for **work and heat**:

<i>Process</i>	<i>sign</i>
<i>workdone by the system on the surroundings</i>	–
<i>workdone on the system by the surroundings</i>	+
<i>Heat absorbed by the system from the surroundings (endothermic)</i>	+
<i>Heat absorbed by the surroundings from the system(exothermic)</i>	–

4.8 Work and Heat

- Work is defined as

$$W = Fd$$

- In thermodynamics, it includes mechanical work (e.g. a crane lifting a still beam), electrical work (a battery supplying electrons to light the bulb of a flashlight), etc.
 - Mechanical work will be considered here. E.g. is the expansion of a gas.
 - The work done by the gas on the surroundings is
- $$w = -P\Delta V$$
- For gas expansion, $\Delta V > 0$, so $-P\Delta V$ is a negative quantity. For gas expansion(workdone on the system), $\Delta V < 0$ and $-P\Delta V$ is positive.

Work and Heat(contd)

- Pressure x Volume can be expressed as (force/area)x volume: that is:

$$P \times V = \frac{F}{d^2} \times d^3 = Fd = w$$

pressure volume

- The other component of internal energy is *heat, q*. Like work, heat is not a state function.
 - Suppose the change can be brought about in two different ways. In one case the work done is zero and we have:

$$\Delta E = q_1 + w_1$$

$$\Delta E = q_1$$

In the second case, work is done and heat is transferred,

$$\Delta E = q_2 + w_2$$

- *Since ΔE is the same for both cases, it follows that $q_1 \neq q_2$*

Work and Heat(contd)

- This show that heat associated with a given process, like work, depends on how the process is carried out; that is we cannot write $\Delta q = q_f - q_i$
- Though heat or work are not state functions, their sum($q+w$) is equal to ΔE , and E is a state function.
- Heat and work are not state functions, because they are not properties of a system. They manifest themselves only during a process(during a change).

4.9 Enthalpy and the First Law

- For a reaction run under constant-volume condition, $\Delta V=0$. Therefore change in energy is equal to the heat change.

$$\Delta E = q + w = q_v$$

- For a constant-pressure process,

$$\Delta E = q + w$$

$$\Delta E = q_p - P\Delta V$$

$$q_p = \Delta E + P\Delta V$$

enthalpy of a system is defined as,

$$H = E + PV$$

- E,P,V and H are all state functions.

Enthalpy and the First Law (contd)

- For any process, the change in enthalpy is given by

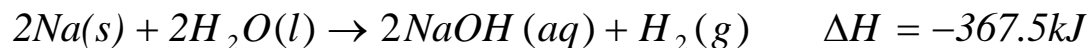
$$\Delta H = \Delta E + \Delta(PV)$$

holding pressure constant,

$$\Delta H = \Delta E + P\Delta V$$

considering the previous equation, it implies $\Delta H = q_p$

Consider the constant – pressure reaction



calculate the internal energy change assuming temperature is 25° C

and ignore the small change in volume of the solution, the volume of 1mole of H_2 gas at 1.0atm is 24.5 L.

rearranging above equation

$$\Delta E = \Delta H - P\Delta V$$

$$- P\Delta V = -24.5\text{L} \cdot \text{atm or } -2.5 \text{ kJ}$$

$$\Delta E = -367.5 \text{ kJ} - 2.5\text{kJ} = -370.0 \text{ kJ}$$

Enthalpy and the First Law(contd)

- Another way to calculate the internal energy change of a gaseous reaction is to assume ideal gas behavior and constant temperature.

$$\begin{aligned}\Delta E &= \Delta H - \Delta(PV) \\ &= \Delta H - \Delta(nRT) \\ \Delta E &= \Delta H - RT\Delta n\end{aligned}$$

where Δn is defined as

$\Delta n = \text{number of moles of product gases} - \text{number of moles of reactant gases}.$

Chemical Equilibrium and Equilibrium Constant

- **Chemical Equilibrium:**

- it is achieved when the rate of forward and reverse reactions are equal and the concentrations of the reactants and products remain constant.
- a dynamic process and it involves different substances as reactants and products.



- **Physical Equilibrium:**

- Equilibrium between two phases of the same substance
- The changes that occur are physical



Chemical Equilibrium and Equilibrium Constant(contd.)

- **Equilibrium Constant, K:**

Consider the reversible reaction



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

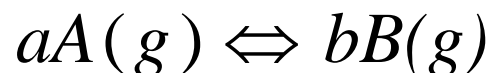
- **Law of mass action:** the above equation is the mathematical expression of the law of mass action, which holds that for a **reversible reaction at equilibrium** and **constant temperature**, a certain ratio of reactants and product concentrations has a constant value, K.

Chemical Equilibrium and Equilibrium Constant(contd.)

- If K is much greater than 1, the equilibrium will lie to the right and favor the formation of products.
- Conversely, if K is much less than 1, the equilibrium will lie to the left and favor the formation of the reactants.

Chemical Equilibrium and Equilibrium Constant(contd.)

- **Homogeneous equilibrium:** applies to reactions with all reacting species in the same phase.
 - Consider the rxn



$$K_c = \frac{[B]^b}{[A]^a} \quad \& \quad K_p = \frac{P_B^b}{P_A^a}$$

- K_p refers to equilibrium concentrations expressed in terms of pressure.
- Show that $K_p = K_c(RT)^{b-a}$

Chemical Equilibrium and Equilibrium Constant(contd.)

- **Heterogeneous Equilibrium:** reversible reaction involving reactants and products in different phases.

$$K_c = \frac{[B]^b [C]^c}{[A]^a}$$

$$K_c = [C]^c$$

$$K_p = P_c$$

Chemical Equilibrium and Equilibrium Constant(contd.)

- **Multiple Equilibrium:** a type of reaction in which the product molecules in one equilibrium system are involved in a second equilibrium process.



separate equilibrium constants can be written

$$K_c' = \frac{[C][D]}{[A][B]} \quad \& \quad K_c'' = \frac{[E][F]}{[C][D]}$$

For the overall reaction

$$K_c = K_c' K_c'' = \frac{[C][D]}{[A][B]} \times \frac{[E][F]}{[C][D]} = \frac{[E][F]}{[A][B]}$$

Chemical Equilibrium and Equilibrium Constant(contd.)

- **Factors that affect chemical Equilibrium**
 - Four factors affect chemical equilibrium
 - Concentration, volume, pressure, temperature
 - Only changes in **temperature** changes the equilibrium constant
 - Changes in Conc., V, P, can alter the equilibrium concentration of the reacting mixture but cannot change the equilibrium constant as long as T does not change.
 - A catalyst does not affect the K_c or equilibrium concentrations of the reacting species.
- **Le Chatelier's Principle:**
 - it is a rule that helps us to predict the direction in which a reaction will move when a change in Conc., T, P, V occurs.
 - It states that if an external stress (Conc., T,V,P) is applied to a system at equilibrium, the system adjusts in such a way that the stress is partially offset as the system reaches a new equilibrium position.

Chemical Equilibrium and Equilibrium Constant(contd.)

- **Chemical Reactors**

ACIDS, BASES and SALTS

- **Acids:**

- sour taste,
- changes blue litmus to red,
- reacts with certain metals to produce hydrogen gas,
- reacts with carbonates and bicarbonates to release carbon dioxide
- Aqueous acid solution conducts electricity

- **Bases:**

- Have bitter taste
- Feels slippery
- Change red litmus to blue
- Aqueous base solution conducts electricity

- **Salts:**

- Ionic compounds made of cations and anions other than H^+ and OH^- resp.

pH of a solution

- pH is the –ve logarithm of the hydrogen ion concentration in mol/L, mol/dm³

$$pH = -\log[H^+]$$

Acid Solutions; $[H^+] > 1.0 \times 10^{-7} M$, $pH < 7.00$

Basic Solutions; $[H^+] < 1.0 \times 10^{-7} M$, $pH > 7.00$

Neutral Solutions; $[H^+] = 1.0 \times 10^{-7} M$, $pH = 7.00$

Strength of Acids and Bases

- **Strong acid:** are strong electrolyte; at equilibrium, solutions of strong acids will not contain any nonionized acid molecules.
- **Weak acids:** weak electrolyte; at equilibrium, aqueous solutions of weak acids contain a mixture of nonionized acid molecules, H_3O^+ and the conjugate base. E.g. HF
- **Strong Bases:** strong electrolyte; e.g. $\text{Ba}(\text{OH})_2$
- **Weak bases:** weak electrolytes; e.g. aqueous ammonia

Acid-Base Titration

- It is a quantitative study of acid-base neutralization reactions.
- **Standard Solution:** a solution whose concentration is known
- **Equivalent Point:** the point at which the acid has completely reacted or being neutralized by the base.
- Strong acid-strong base titration: $\text{pH}=7$
- Weak acid-strong base titration: $\text{pH}>7$
- Strong acid-Weak base titration: $\text{pH}<7$

Acid-Base Titration(contd.)

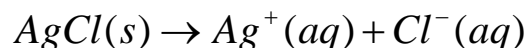
- E.g. A solution of sodium hydroxide contained 0.25 mol dm^{-3} . Using phenolphthalein indicator, titration of 25.0 cm^3 of this solution required 22.5 cm^3 of a hydrochloric acid solution for complete neutralisation.
- (a) write the equation for the titration reaction.
- (b) what is the indicator colour change at the end-point?
- (c) calculate the moles of sodium hydroxide neutralised.
- (d) calculate the moles of hydrochloric acid neutralised.
- (e) calculate the concentration of the hydrochloric acid in mol/dm^3 (molarity)

- **Acid-base indicators:**

- An indicator is a weak organic acid or base that has distinctly different colors in its non ionized and ionized forms.
- the end point of a titration occurs when the indicator changes color.

- **Solubility Equilibria:**

- the maximum amount of solute that will dissolve in a given quantity of solvent at a specific temperature.



the equilibrium constant for the dissolution of AgCl can be written as

$$K_{sp} = [Ag^{+}][Cl^{-}]$$

- The smaller the value of K_{sp} , the less soluble the compound in water.

ENTROPY

- For a given system, two things need to be known.
 - The enthalpy
 - The entropy: it is the disorderliness of a system

$$S_{solid} < S_{Liquid} < S_{gas}$$

- At **absolute zero** all physical and chemical changes occur at constant entropy. A process where there is no change in entropy is called **Isentropic**. This is true for **Adiabatic** process.

ENTROPY(contd)

- Entropy is a state function

$$\Delta S = S_f - S_i$$

- An increase in disorder implies $\Delta S > 0$. Both melting and vaporization processes have $\Delta S > 0$.

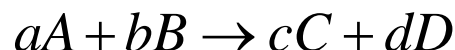
ENTROPY(contd.)

- **Second Law of Thermodynamics:** Mathematically, the 2^o law of thermodynamics can be expressed as:

For a spontaneous process : $\Delta S_{univ} = \Delta S_{sys} + \Delta S_{surr} > 0$

For an equilibrium process : $\Delta S_{univ} = \Delta S_{sys} + \Delta S_{surr} = 0$

- **Entropy changes in a system:** For a reaction



standard entropy of reaction ΔS°_{rxn} is

$$\Delta S^{\circ}_{rxn} = [cS^{\circ}(C) + dS^{\circ}(D)] - [aS^{\circ}(A) + bS^{\circ}(B)]$$

or

$$\Delta S^{\circ}_{rxn} = \sum nS^{\circ}(\text{products}) - \sum mS^{\circ}(\text{reactants})$$

where m, n = stoichiometric coefficients in the reaction

- Entropy changes in the surroundings:

$$\Delta S_{surr} = -\Delta S_{sys}$$

- Indicates an exothermic process, and hence an increase in entropy.
- Inverse relationship between ΔS_{surr} and Temperature(in Kelvin) is represented as

$$\Delta S_{surr} = \frac{-\Delta H_{sys}}{T}$$

- According to the third law of thermodynamics , the entropy of a perfect crystalline substance is zero at absolute zero.

Gibbs Free Energy

- The second law of thermodynamics states that a **spontaneous reaction** increases the entropy of the universe; i.e $\Delta S_{\text{univ}} > 0$.

For a spontaneous process

$$\Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}} > 0$$

$$\text{but } \Delta S_{\text{surr}} = \frac{-\Delta H_{\text{sys}}}{T}$$

$$\Delta S_{\text{univ}} = \Delta S_{\text{sys}} - \frac{\Delta H_{\text{sys}}}{T} > 0$$

$$T\Delta S_{\text{univ}} = T\Delta S_{\text{sys}} - \Delta H_{\text{sys}} > 0$$

multiply through by -1

$$-T\Delta S_{\text{univ}} = \Delta H_{\text{sys}} - T\Delta S_{\text{sys}} < 0$$

Gibbs Free Energy(contd)

- To express the spontaneity of a reaction more directly, another thermodynamic function G can be used:

$$G = H - TS$$

all quantities in above equation pertains to the system and T , the system's temperature.

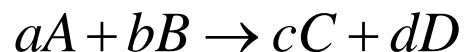
G has the unit of energy and also a state function.

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

- Generally, conditions for spontaneity and equilibrium at constant temperature and pressure in terms of ΔG is:
 - $\Delta G < 0$, the reaction is spontaneous in the forward rxn.
 - $\Delta G > 0$, the reaction is spontaneous in the reverse rxn
 - $\Delta G = 0$, system is at equilibrium. There is no net change

Standard Free-Energy Changes

- Standard free energy change for the reaction below is



$$\Delta G^{\circ}_{rxn} = [c\Delta G^{\circ}_f(C) + d\Delta G^{\circ}_f(D)] - [a\Delta G^{\circ}_f(A) + b\Delta G^{\circ}_f(B)]$$

or

$$\Delta G^{\circ}_{rxn} = \sum \Delta G^{\circ}_f(\text{products}) - \sum \Delta G^{\circ}_f(\text{reactants})$$

m, n = stoichiometric coefficients

ΔG°_{rxn} = is in kJ

ΔG°_f = is in kJ/mole

van der Waals Constants for Various Gases

<i>Compound</i>	<i>a (L²-atm/mol²)</i>	<i>b (L/mol)</i>
He	0.03412	0.02370
Ne	0.2107	0.01709
H ₂	0.2444	0.02661
Ar	1.345	0.03219
O ₂	1.360	0.03803
N ₂	1.390	0.03913
CO	1.485	0.03985
CH ₄	2.253	0.04278
CO ₂	3.592	0.04267
NH ₃	4.170	0.03707