1.Physical Chemistry:

Physical chemistry is the study of the underlying physical principles that govern the properties and behavior of chemical systems.

Chemical System:

A chemical system can be studied from either a microscopic or a macroscopic viewpoint.

The microscopic viewpoint is based on the concept of molecules.

The macroscopic viewpoint studies large-scale properties of matter without explicit use of the molecule concept.

2. Thermodynamics:

Thermodynamics: (Greek words for "thermo=heat" and "dynamics=power") is the study of heat, work, energy, and the changes they produce in the states of systems.

Thermodynamics studies the relationships between the macroscopic properties of a system

A key property in thermodynamics is temperature

Thermodynamics is sometimes defined as

the study of the relation of temperature to

the macroscopic properties of matter

Equilibrium Thermodynamics:

It deals with systems in equilibrium

It is a macroscopic science and is independent of any theories of molecular structure

Irreversible Thermodynamics:

It deals with non-equilibrium systems and rate processes.

3. Thermodynamic Systems:

The macroscopic part of the universe under study in thermodynamics is called the System

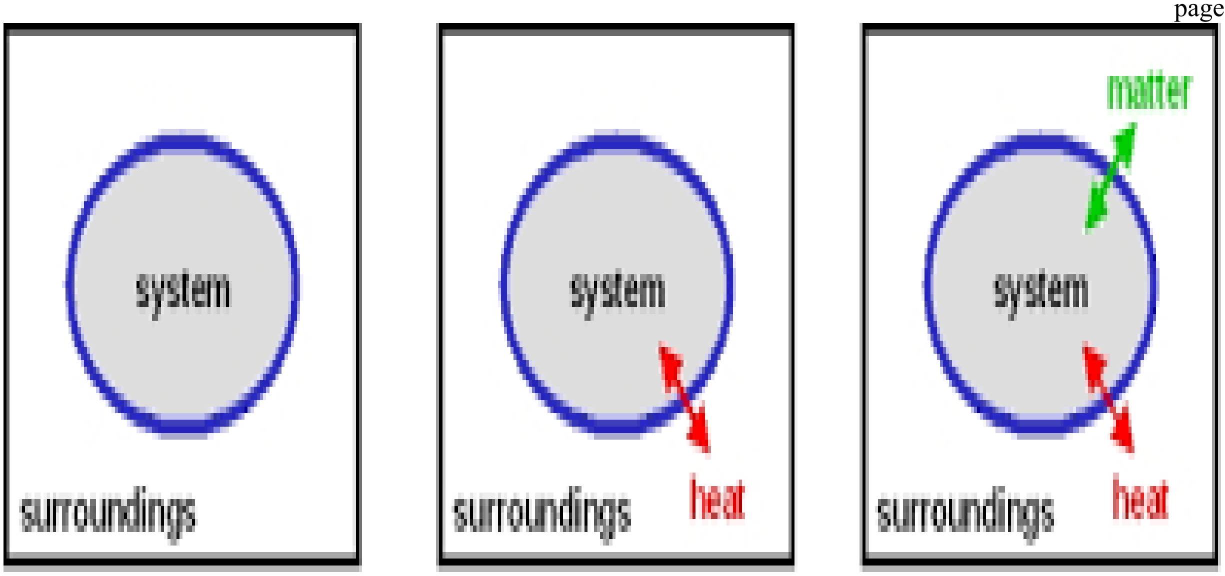
The parts of the universe that can interact with the system are called the surroundings.

Open system is one where transfer of matter between system and surroundings can occur.

Closed system is one where no transfer of matter can occur between system and surroundings.

Isolated system is one that does not interact in any way with its surroundings.

An isolated system is obviously a closed system, but not every closed system is isolated.



"Isolated" system:
- no exchange of matter
- no exchange of heat

"Closed" system:
- no exchange of matter
- can exchange heat energy

"Open" system:
- can exchange matter
- can exchange heat energy

---

4. Equilibrium

Equilibrium thermodynamics deals with systems in equilibrium

An isolated system is in equilibrium when its macroscopic properties remain constant with time

A non-isolated system is in equilibrium when the following two conditions hold

A. The system's macroscopic properties remain constant with time

B. Removal of the system from contact with its surroundings causes no change in the properties of the system

If condition (A) holds but (B) does not hold, the system is in a steady state.

Mechanical Equilibrium:

No unbalanced forces act on or within the

system; hence the system undergoes no

acceleration, and there is no turbulence

within the system.

Material Equilibrium:

No net chemical reactions are occurring in the

system, nor is there any net transfer of matter from one part of the system to another or

between the system and its surroundings

Thermal Equilibrium between a system and its surroundings, there must be no change in the properties of the system or surroundings when they are separated by a thermally conducting wall.

For thermodynamic equilibrium, all three kinds of equilibrium must be present.

---

5. Thermodynamic Properties:

An extensive thermodynamic property is one whose value is equal to the sum of its values for the parts of the system. Thus, if we divide a system into parts, the mass of the system is the sum of the masses of the parts; mass is an extensive property. So is volume.

Intensive thermodynamic property is one whose value does not depend on the size of the system, provided the system remains of macroscopic size-recall nanoscopic systems

Density and pressure are examples of intensive properties.

If each intensive macroscopic property is constant throughout a system, the system is homogeneous.

If a system is not homogeneous, it may consist of a number of homogeneous parts. A homogeneous part of a system is called a phase

A system composed of two or more phases is heterogeneous

Suppose that the value of every thermodynamic property in a certain thermodynamic system equals the value of the corresponding property in a second system. The systems are then said to be in the same thermodynamic state

---

6. Temperature:

Suppose two systems separated by a movable wall are in mechanical equilibrium with each other

Because we have mechanical equilibrium, no unbalanced forces act and each system exerts an equal and opposite force on the separating wall.

- Systems in mechanical equilibrium with each other have the same pressure.

- Just as systems in *mechanical* equilibrium have a common *pressure*, it seems plausible that there is some thermodynamic property common to systems in *thermal* equilibrium.

- This property is what we *define* as the **temperature,** symbolized by θ (theta).

By definition,

Two systems in thermal equilibrium with each other have the same temperature; two systems not in thermal equilibrium have different temperatures.

Although we have asserted the existence of temperature as a thermodynamic state function that determines whether or not thermal equilibrium exists between systems, we need experimental evidence that there really is such a state function. Suppose that we find systems A and B to be in thermal equilibrium with each other when brought in contact via a thermally conducting wall. Further suppose that we find systems B and C to be in thermal equilibrium with each other. By our definition of temperature, we would assign the same temperature to A and B (uA uB) and the same temperature to B and C (uB uC). Therefore, systems A and C would have the same temperature (uA uC), and we would expect to find A and C in thermal equilibrium when they are brought in contact via a thermally conducting wall. If A and C were not found to be in thermal equilibrium with each other, then our definition of temperature would be invalid. It is an experimental fact that:

Two systems that are each found to be in thermal equilibrium with a third system

will be found to be in thermal equilibrium with each other.

7. Pressure:

Pressure is defined as the magnitude of the perpendicular force per unit area exerted by the system on its surroundings:

P = F/A

For a system in mechanical equilibrium, the pressure throughout the system is uniform and equal to the pressure of the surroundings.

If external electric or magnetic fields act on the system, the field strengths are thermodynamic variables; we won't consider systems with such fields

We are ignoring the effect of the earth's gravitational field, which

causes a slight increase in pressure as one goes from the top to the bottom of the system.

8. Mole:

The ratio of the average mass of an atom of an element to the mass of some chosen standard is called the atomic weight or relative atomic mass   Ar

(the r stands for "relative)

The standard used since 1961 is 1/12 times the mass of the isotope 12 C

The ratio of the average mass of a molecule of a substance to 1/12 times the mass of a 12 C atom is called the molecular weight or relative molecular mass Mr of that substance.

The number of 12 C atoms in exactly 12 g of 12 C is called Avogadro's number.

The average mass of an atom or molecule is called the atomic mass or the molecular mass.

Molecular masses are commonly expressed in units of atomic mass units (amu)

where 1 amu is one-twelfth the mass of a 12 C atom

A mole of some substance is defined as an amount of that substance which contains Avogadro's number of elementary entities.

For example, a mole of hydrogen

atoms contains 6.02 1023 H atoms; a mole of water molecules contains 6.02 1023

H2O molecules. We showed earlier in this section that, if Mr,i is the molecular weight

of species i, then the mass of 1 mole of species i equals Mr,i grams. The mass per

mole of a pure substance is called its molar mass M. For example, for H2O, M

18.015 g/mole. The molar mass of substance i is

Mi = mi / ni

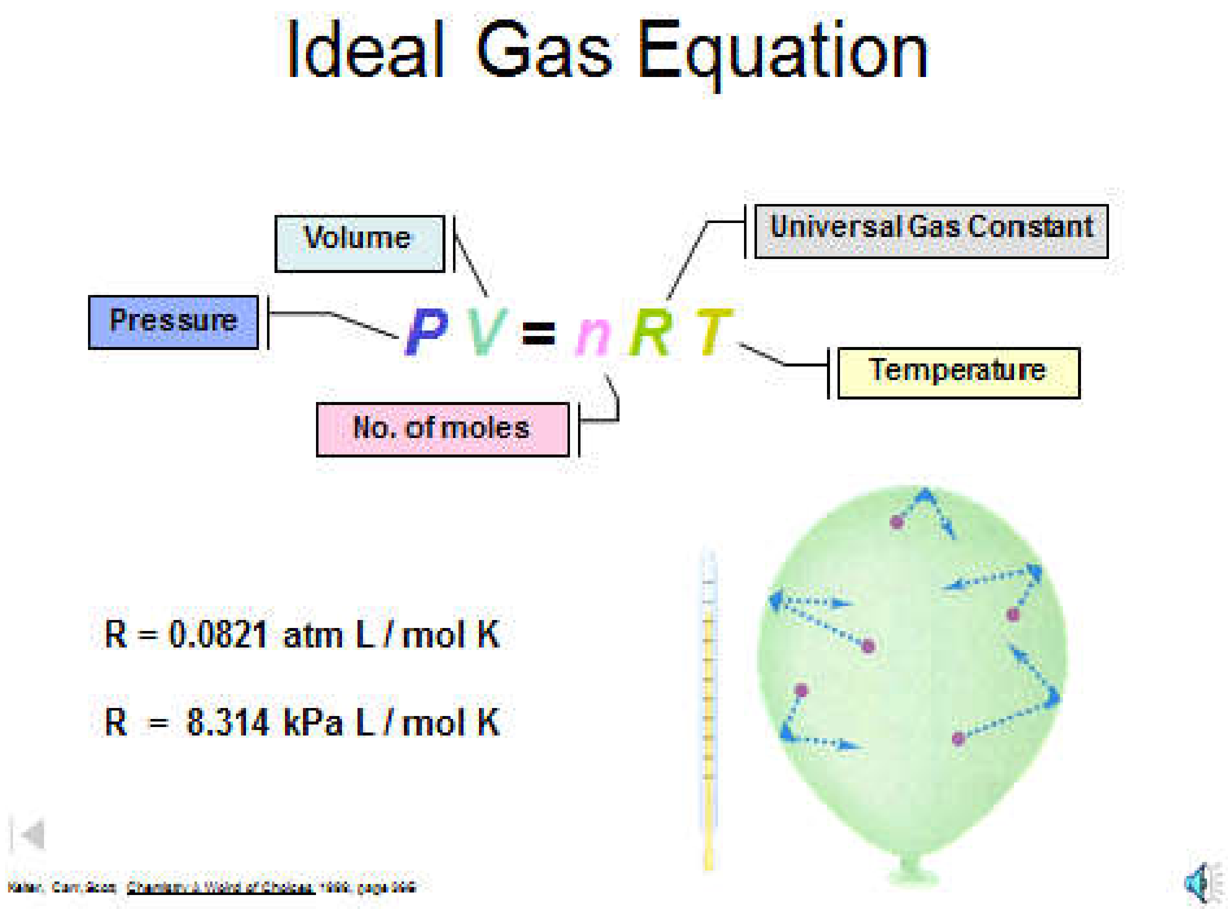
where mi is the mass of substance i in a sample and ni is the number of moles of i in the sample. The molar mass Mi and the molecular weight Mr,i of i are related by Mi Mr,i 1 g/mole, where Mr,i is a dimensionless number.

9.Ideal Gas vs. Real Gases:

No gas is ideal.

Most gases behave ideally (almost) at pressures of approximately 1 atm or lower, when the temperature is approximately 0 °C or higher.

When we do calculations, we will assume our gases are behaving as ideal gases



Ideal Gas Equation

$$PV = nRT$$

R = 0.0821 atm L / mol K

R = 8.314 kPa L / mol K

Gas Laws:

A large number of experiments have determined that 4 variables are sufficient to define the physical condition (or state) of a gas: the gas laws.

Boyle’s Law, Charles’ Law, Avogadro’s hypothesis

10.Boyle’s Law:

Robert Boyle: (1627-1691) the first modern chemist, known as the father of chemistry.

His 1661 book The Sceptical Chymist marks the introduction of the scientific method, a definition of elements and compounds and a refutation of alchemy and magic potions.

Boyle investigated the variation of the volume occupied by a gas as the pressure exerted upon it was altered and noted that the volume of a fixed quantity of gas, at constant temperature is inversely proportional to the pressure

Where ‘k’ is constant

Boyle’s law is understandable from the picture of a gas as consisting of a huge number of molecules moving essentially independently of one another

The pressure exerted by the gas is due to the impacts of the molecules on the walls

A decrease in volume causes the molecules to hit the walls more often thereby increasing the pressure.

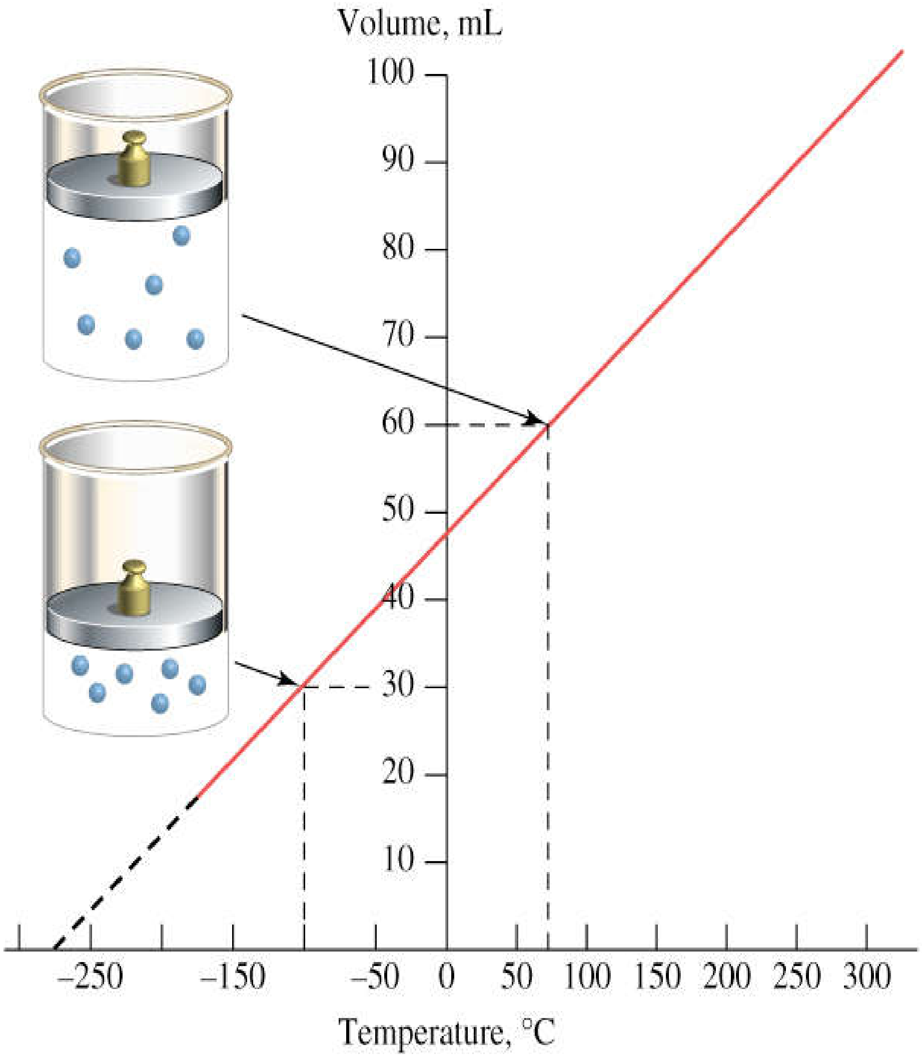
In actuality, the molecules of a gas exert forces on one another, so Boyle’s law does not hold exactly.

In the limit of zero density (reached as the pressure goes to zero or as the temperature goes to infinity), the gas molecules are infinitely far apart from one another, forces between molecules become zero, and Boyle’s law is obeyed exactly. We say the gas becomes ideal in the zero-density limit.

11. Charles’ Law

A French scientist, Jacques Charles discovered that the volume of a fixed amount of gas, as constant pressure, is proportional to the absolute temperature.

$$V = \text{constant} \times T \text{ or } \frac{V}{T} = \text{constant}$$



Charles' law is obeyed most accurately in the limit of zero pressure

But even in this limit, gases still show small deviations

These deviations are due to small differences between the thermal expansion behavior of ideal gases

pressure limit. Therefore, to get a temperature scale that is independent of the properties of any one substance, we shall define an ideal-gas temperature scale T by the requirement that the T-versus-V behavior of a gas be exactly linear (that is, obey Charles' law exactly) in the limit of zero pressure. Moreover, because it seems likely that the temperature at which an ideal gas is predicted to have zero volume might well have fundamental significance, we shall take the zero of our ideal-gas temperature scale to coincide with the zero-volume temperature. We therefore define the absolute ideal-gas temperature T by the requirement that the relation T BV shall hold exactly in the zero-pressure limit, where B is a constant for a fixed amount of gas at constant P, and where V is the gas volume. Any gas can be used.

12.Avogadro's Hypothesis:

In 1811 Avogadro stated that,

At constant temperature and pressure, the volume of a gas is directly related to the number of moles.

$V = K n$

$V1 / n1 = V2 / n2$

K is constant

N is number of moles of gas

Equal volumes of gases at the same temperature and pressure contain equal numbers of molecules

Since the number of molecules is proportional to the number of moles, Avogadro's hypothesis states that equal volumes of different gases at the same T and P have equal numbers of moles.

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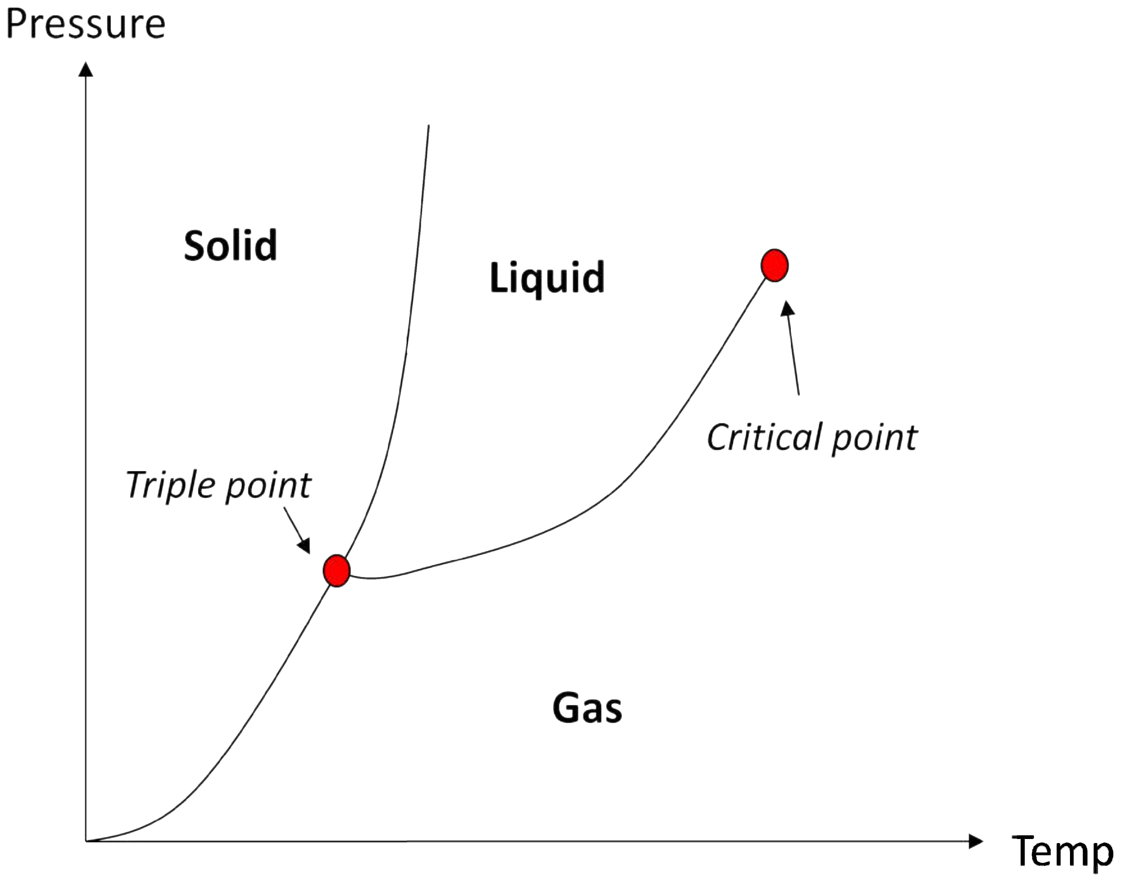
13. Equations of state:

How are states represented



How are states represented:

Mathematically

Using equations of state we relate state variables to describe property of matter

Examples of state variables

Pressure

Volume

Temperature

Equations of state are mainly used to describe fluids

Liquids

Gases

Particular emphasis on gases

ABCs of gas equations:

Avogadro's Hypothesis

Boyle's Law

Charles' Law

Combining all 3 laws…

Thus we get the ideal gas equation:

pV = nRT

for ideal gas it is assumed as

Ideal gas particles occupy negligible volume

Ideal gas has negligible intermolecular interactions

Ideal gas equation shows deviations from

Avogadro's Hypothesis

Boyle's Law

Charles' Law

So its called

Failures of ideal gas equation

---

14. Van der Waals Equation for real gases:

As the ideal gas equation deviates from gas laws

So van der Waals in 1873 modified the ideal-gas equation to give the van der Waals equation for real gases

Van der Waals:

Modified from ideal gas equation

Accounts for:

Non-zero volumes of gas particles (repulsive effect)

Attractive forces between gas particles (attractive effect)

Attractive effect

Pressure = Force per unit area of container exerted by gas molecules

Dependent on:

Frequency of collision

Force of each collision

Both factors affected by attractive forces

Each factor dependent on concentration (n/V)

Hence pressure changed proportional to (n/V)2

Letting a be the constant relating p and (n/V)

Pressure term, p, in ideal gas equation becomes

[p+a(n/V)2]

Repulsive effect:

Gas molecules behave like small, impenetrable spheres

Actual volume available for gas smaller than volume of container, V

Reduction in volume proportional to amount of gas, n

Let another constant, b, relate amount of gas, n, to reduction in volume

Volume term in ideal gas equation, V, becomes (V-nb)

Combining both derivations…

We get the Van der Waals Equation

$$\left[p + a\left(\frac{n}{V}\right)^2\right][V\text{-}nb] = nRT$$

OR

$$\left[p + \frac{a}{V_m^2}\right][V_m\text{-}b] = RT$$

15. Van der Waal's corrections:

Sir Johannes Diderik van Der Waals in 1873, modified the Ideal Gas Equation

He proposed the ideal gas equation with

"Van der Waal's corrections"

By adding the necessary Constants

Critical Constants

For intermolecular attractions (weak forces)

B. The volume occupied by the gas particles (themselves)

At higher pressure, the volume is much reduced and at this state the volume of gas molecules

Becomes “no more negligible” in comparison

with the total volume V occupied by the gas.

The “no more negligible” volume is generally denoted by “b” called effective volume.

Therefore the total (actual) volume available in which the molecules are free to move will be

= Total volume (V) — Effective volume (b).

i.e., Correct Volume (V – b)

Pressure correction:

The pressure of a gas is due to the hits of the molecules

on the walls of the container.

The weak attractive force (Van Der Waals’s forces)

between the molecules comes into play

when the molecules are brought close (under high pressure)

together during compression of the gas,

therefore an extra inward pull is observed on the molecules

Towards the center of the gas,

which ultimately decreases the total pressure.

Therefore the ideal pressure (Pi)

will be equal to (total) observed pressure (P)plus a pressure correction (Pa).

Pa depending upon the inwards pull (attractive forces) among the gas molecules.

I.e. P(Ideal) = P + Pa

Where

Pa=a/V2 Hence P(Ideal) = P +a/V2After adding necessary corrections,

the Ideal gas Equation can be used for the real gases as well.

It is known as Van Der Waals Equation

This equation explains the behavior of real gases

with great accuracy and also describes the

deviations of gas law from ideal behavior.

Ideal gas equation is PV=nRT After adding the necessary corrections by calculating critical constants
for additional pressure and subtracted

volume.

For 1 mole of a substance

$(P+a/V2)(V-b)=RT$

For “n” mole of a substance

$$\underbrace{\overset{\text{actual pressure}}{P}+a\left(\frac{n}{V}\right)^{2}}_{\text{ideal gas pressure}} \times \underbrace{(\overset{\text{actual volume}}{V}-nb)}_{\text{ideal gas volume}} = nRT$$

Critical Constants:

The Critical Volume: The volume occupied by a unit mass of a gas or vapors in its critical states.

The Critical Pressure: The pressure required to liquefy a gas at its critical temperature

The Critical Temperature

The temperature at and above which vapors of the substance cannot be liquefied, no matter how much pressure is applied.

For Van Der Waal’s critical constants,

the pressure required to liquefy the gas at critical temperature is called critical pressure

and the volume occupied by 1 mole of a gas under critical conditions is called the critical volume.

The relationship between critical constants of the gases and

their Van der Waal constants is as follows:

Vc = 3b, Pc = a/27b2, Tc = 8a/27Rb

Here, Pc, Vc, and Tc are the critical values for pressure,

molar volume, and temperature,

and Zc is the compressibility which is equal to P V /RT,

at the critical points.

It is so called because only after the first, second, and third laws of thermodynamics had been formulated was it realized that the Zeroth law is needed for the development of thermodynamics.

Statement of the Zeroth law logically precedes the other three laws of thermo dynamics

The Zeroth law allows us to assert the existence of temperature as a state function.

On putting above values

$Z_c = P_cV_c/RT_c$

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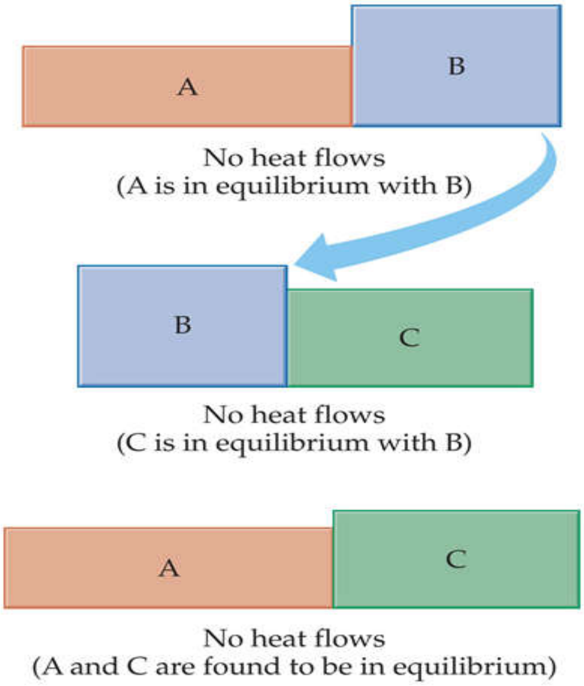
16. Zeroth Law of Thermodynamics:

Two systems that are each found to be in thermal equilibrium with a third system

will be found to be in thermal equilibrium with each other.

This generalization from experience is the Zeroth law of thermodynamics



17. First Law of Thermodynamics:

The first law of thermodynamics is a statement of the conservation of energy

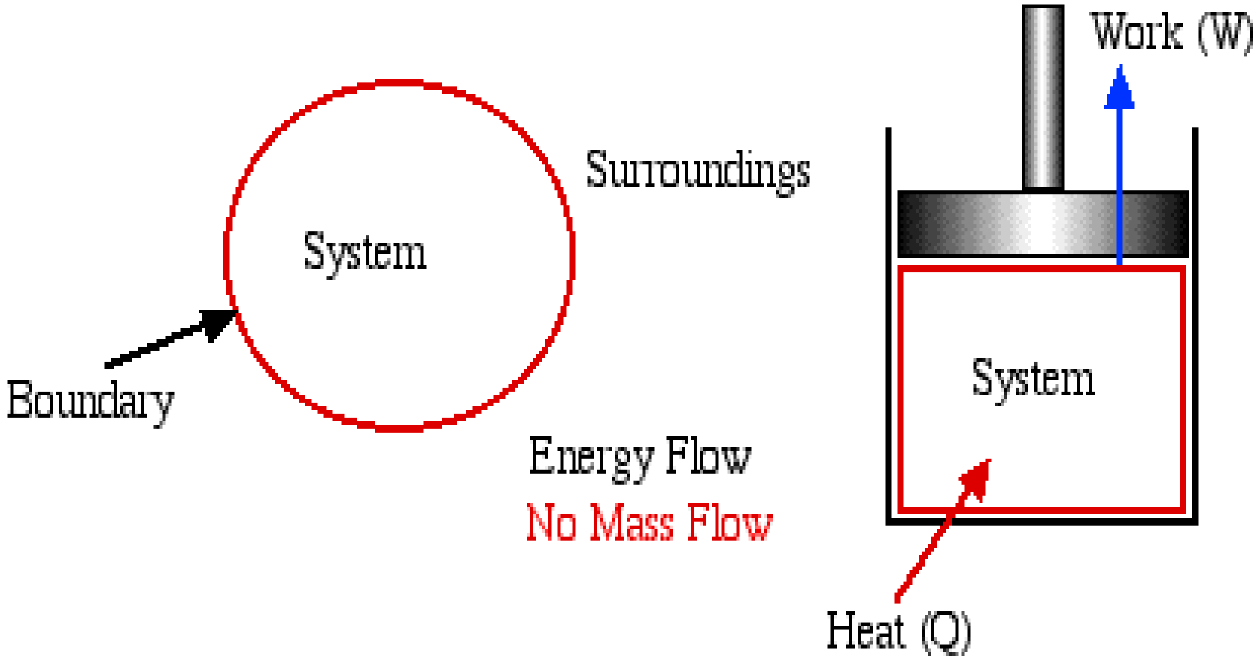
It is also called the Law of Conservation of Energy

Energy can be changed from one form to another, but it cannot be created or destroyed. The total amount of energy and matter in the Universe remains constant, merely changing from one form to another.

Heat and work changes:

- The energy of a system will change if heat is transferred to or from the system or work is done by the system
- 1st law stated that, if some amount of heat (Q) is added into the system, it must either do work or increase the total energy of the system

Heat and work changes:



If the capacity to do work is represented by the symbol "W" and "H" stands for heat content then the Ist law can be expressed as:

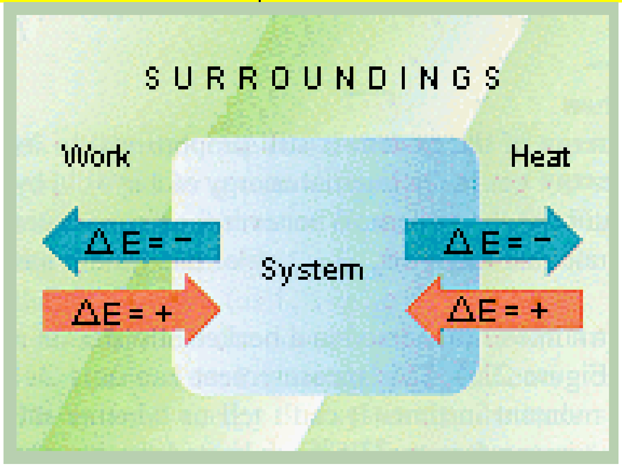
$$\Delta U = Q - W$$

Change in Internal energy

Heat added to the system

Work done by the system

q (heat)	+ system gain thermal energy	- System loses thermal energy
w (work)	+ work done on the system	- Work done by the system
ΔU (change in internal energy)	+ energy flows into the system	- Energy flows out of the system



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18. Enthalpy:

The energy change associated with a chemical reaction is called the enthalpy of reaction and abbreviated Δ H.

Δ H = E + PV

E = energy of the system

P = pressure of the system

V = volume of the system

- Enthalpy = Heat Transferred Recall our original definition of enthalpy:

$H = E + PV$

- Then for a change in enthalpy:

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

- If we set P constant, then:
- $\Delta H = \Delta E + P \Delta V$
- Since

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

- Then
- $\Delta H = q_p$
- The change in enthalpy, ΔH, is then equal to the heat transferred at constant pressure, q_p.

Enthalpy is a "State Function":

A "state function" is a value that is a function only of the initial and final states of the system, not the path you take to get there!

Entropy:

- Entropy (S): Can be thought of as a measure of the *disorder* of a system
- In general, greater disorder means greater entropy
- Entropy is a state function just as enthalpy

$\Delta S = S_{\text{final}} - S_{\text{initial}}$

Rewrite:

$$\Delta S = k \ln W_{\text{final}} - k \ln W_{\text{initial}}$$

- $W_f > W_i$ then $\Delta S > 0$ entropy increases

19.Second law of Thermodynamics:

The first law of thermodynamics is simple, general, but does not constitute a complete theory because certain processes it permits do not occur in nature!

The problems arise from:

1. Classical thermodynamics is connected with states of equilibrium and various processes connecting them.
2. The exact process by which a system reaches the final state from its initial state is immaterial. i.e. the transition is independent of the particular path taken

3. The theory emphasizes reversible processes! Yet, real processes are irreversible!

Two statements of the second law of thermodynamics:

Clausius Statement: It is impossible to construct a device that operates in a cycle and whose sole effect is to transfer heat from a cooler body to a hotter body.

Kevin-Planck Statement: It is impossible to construct a device that operates in a cycle and produces no other effects than the performance of work and the exchange of heat with a single reservoir.

Equivalence of the Two Statements:

- It can be shown that the violation of one statement leads to a violation of the other statement, i.e. they are equivalent.

Two statements of the second law of thermodynamics:

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Equivalence of the Two Statements:

- It can be shown that the violation of one statement leads to a violation of the other statement, i.e. they are equivalent.

The second law of thermodynamics states:

- that the total entropy of an isolated system can only increase over time. It can remain constant in ideal cases where the system is in a steady state (equilibrium) or undergoing a reversible process. The increase in entropy accounts for the irreversibility of natural processes, and the asymmetry between future and past.
- Entropy of the universe increases in a spontaneous process and remains unchanged in an equilibrium process.
- *Equilibrium process*: caused to occur by adding or removing energy from a system that is at equilibrium

Mathematically speaking:

Spontaneous process:

$\Delta S_{\text{universe}} = \Delta S_{\text{system}} + \Delta S_{\text{surroundings}} > 0$

Equilibrium process:

$\Delta S_{\text{universe}} = \Delta S_{\text{system}} + \Delta S_{\text{surroundings}} = 0$

---

20. Third Law of Thermodynamics

Entropy of a perfect crystalline substance is zero at absolute zero.

Importance of this law: it allows us to calculate absolute entropies for substances

"It is impossible to reach a temperature of absolute zero."

On the Kelvin Temperature Scale,

T = 0 K **is often referred to as**

"Absolute Zero"

The Third Law of Thermodynamics can mathematically be expressed as $\lim S_{T \to 0} = 0$

where

- S ***= entropy (J/K)***
- T ***= absolute temperature (K)***

Importance of Third law of Thermodynamics:

- **It helps in calculating the thermodynamic properties.**

- **It is helpful in measuring chemical affinity. Because of this it is known as Nernst theorem.**
- **It explains the behavior of solids at very low temperature.**
- **It helps in analyzing chemical and phase equilibrium.**

21..Thermochemistry:

The quantitative study and measurement of heat and enthalpy changes is known as thermochemistry.

The heat that flows across the boundaries of a system undergoing a change is a fundamental property that characterizes the process. It is easily measured, and if the process is a chemical reaction carried out at constant pressure, it can also be predicted from the difference between the enthalpies of the products and reactants.

Thermochemical equations and standard states:

In order to define the thermochemical properties of a process, it is first necessary to write a thermochemical equation that defines the actual change taking place, both in terms of the formulas of the substances involved and their physical states (temperature, pressure, and whether solid, liquid, or gaseous.

To take a very simple example, here is the complete thermochemical equation for the vaporization of water at its normal boiling point:

$H2O(l, 373\ K, 1\ atm) \rightarrow H2O(g, 373\ K, 1\ atm) \quad \Delta H = 40.7\ kJ\ mol–1$

The quantity 40.7 is known as the enthalpy of vaporization (often referred to as "heat of vaporization") of liquid water.

The following points should be kept in mind when writing thermochemical equations:

Any thermodynamic quantity such as ΔH that is associated with a thermochemical equation always refers to the number of moles of substances

Thermochemical equations for reactions taking place in solution must also specify the concentrations of the dissolved species.

In the case of dissolved substances, the standard state of a solute is that in which the "effective concentration", known as the activity, is unity.

22:

Standard enthalpy of formation:

The standard enthalpy of formation of a compound is defined as the heat associated with the formation of one mole of the compound from its elements in their standard states.

The enthalpy change for a chemical reaction is the difference

$\Delta H = H_{products} - H_{reactants}$

If the reaction in question represents the formation of one mole of the compound from its elements in their standard states, as in

$H_2(g) + \frac{1}{2} O_2(g) \rightarrow H_2O(l) \quad \Delta H = -286\ kJ$

then we can arbitrarily set the enthalpy of the elements to zero and write

$Hf^\circ = \Sigma Hf^\circ_{products} - \Sigma Hf^\circ_{reactants} = -286\ kJ - 0 = -268\ kJ\ mol^{-1}$

which defines the standard enthalpy of formation of water at 298K.

In general, the standard enthalpy change for a reaction is given by the expression

important $\Rightarrow \Delta\ \Sigma Hf^\circ_{products} - \Sigma Hf^\circ_{reactants}$ (2-1)

The thermochemical equation defining Hf ° is always written in terms of one mole of the substance.

The standard heat of formation of a compound is always taken in reference to the forms of the elements that are most stable at 25°C and 1 atm pressure.

The physical state of the product of the formation reaction must be indicated explicitly if it is not the most stable one at 25°C and 1 atm pressure.

Although the formation of most molecules from their elements is an exothermic process, the formation of some compounds is mildly endothermic.

The thermochemical reactions that define the heats of formation of most compounds cannot actually take place.

The standard enthalpy of formation of gaseous atoms from the element is known as the heat of atomization.

The standard enthalpy of formation of an ion dissolved in water is expressed on a separate scale in which that of $H^+(aq)$ is defined as zero.

Hess’ law and thermochemical calculations

Germain Henri Hess (1802-1850) was a Swiss-born professor of chemistry at St. Petersburg, Russia. He formulated his famous law, which he discovered empirically, in 1840.

The enthalpy of a given chemical reaction is constant, regardless of the reaction happening in one step or many steps.

Another way to state Hess' Law is:

If a chemical equation can be written as the sum of several other chemical equations, the enthalpy change of the first chemical equation equals the sum of the enthalpy changes of the other chemical equations.

For example, the standard enthalpy changes for the oxidation of graphite and diamond can be combined to obtain ΔH° for the transformation between these two forms of solid carbon, a reaction that cannot be studied experimentally.

C(graphite) + O2(g)→ CO2(g)   ΔH° = –393.51 kJ mol–1

C(diamond) + O2(g)→ CO2(g)   ΔH° = –395.40 kJ mol–1

Subtraction of the second reaction from the first (i.e., writing the second equation in reverse and adding it to the first one) yields

C(graphite) → C(diamond)   ΔH° = 1.89 kJ mol–1

This principle, known as Hess’ law of independent heat summation is a direct consequence of the enthalpy being a state function.

Hess’ law is one of the most powerful tools of chemistry, for it allows the change in the enthalpy (and in other thermodynamic functions) of huge numbers of chemical reactions to be predicted from a relatively small base of experimental data.

24:

Calorimetry

The measurement of q is generally known as Calorimetry.

OR

measuring ΔH in the laboratory is called Calorimetry

How are enthalpy changes determined experimentally?

First, We must understand that the only thermal quantity that can be observed directly is the heat q that flows into or out of a reaction vessel, and that q is numerically equal to ΔH° only under the special condition of constant pressure.

Moreover, q is equal to the standard enthalpy change only when the reactants and products are both at the same temperature, normally 25°C.

The most common types of calorimeters contain a known quantity of water which absorbs the heat released by the reaction. Because the specific heat capacity of water (4.184 J g–1 K–1) is known to high precision, a measurement of its temperature rise due to the reaction enables one to calculate the quantity of heat released.

The calorimeter constant

In all but the very simplest calorimeters, some of the heat released by the reaction is absorbed by the components of the calorimeter itself.

It is therefore necessary to "calibrate" the calorimeter by measuring the temperature change that results from the introduction of a known quantity of heat.

The calorimeter constant

calorimeter constant, expressed in J K–1, can be regarded as the

“heat capacity of the calorimeter”.

The known source of heat is usually produced by passing a known quantity of electric current through a resistor within the calorimeter, but it can be measured by other means.

25:

Types of Calorimeter:

Although calorimetry is simple in principle, its practice is a highly exacting art, especially when applied to processes that take place slowly or involve very small heat changes.

Calorimeters can be as simple as a foam plastic coffee cup. Research-grade calorimeters, able to detect minute temperature changes, are more likely to occupy table tops, or even entire rooms

The bomb calorimeter:

Most serious calorimetry carried out in research laboratories involves the determination of heats of combustion, since these are essential to the determination of standard enthalpies of formation of the thousands of new compounds that are prepared and characterized each month.

In order to ensure complete combustion, the experiment is carried out in the presence of oxygen above atmospheric pressure. This requires that the combustion be confined to a fixed volume.

Since the process takes place at constant volume, the reaction vessel must be constructed to withstand the high pressure resulting from the combustion process, which amounts to a confined explosion.

The vessel is usually called a “bomb”, and the technique is known as bomb calorimetry.

The reaction is initiated by discharging a capacitor through a thin wire which ignites the mixture.

Ice calorimeter:

The ice calorimeter is an important tool for measuring the heat capacities of liquids and solids, as well as the heats of certain reactions.

This simple yet ingenious apparatus is essentially a device for measuring the change in volume due to melting of ice.

To measure a heat capacity, a warm sample is placed in the inner compartment, which is surrounded by a mixture of ice and water.

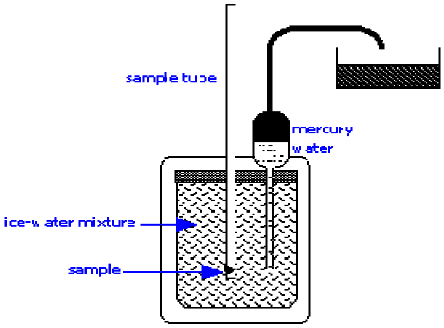
The heat withdrawn from the sample as it cools causes some of the ice to melt.

Since ice is less dense than water, the volume of water in the insulated chamber decreases.

This causes an equivalent volume of mercury to be sucked into the inner reservoir from the outside container.

The loss in weight of this container gives the decrease in volume of the water, and thus the mass of ice melted.

This, combined with the heat of fusion of ice, gives the quantity of heat lost by the sample as it cools to 0°C.



26:

Heat Capacity:

he heat capacity of a defined system is the amount of heat (usually expressed in calories, kilocalories, or joules) needed to raise the system's temperature by one degree (usually expressed in Celsius or Kelvin).

It is expressed in units of thermal energy per degree temperature.

The amount of heat needed to increase the temperature of one mole of a substance by one degree is the molar heat capacity.

It is expressed in joules per moles per degrees Celsius (or Kelvin).

Specific Heat Capacity:

The amount of heat needed to increase the temperature of one gram of a substance by one degree is the specific heat capacity.

It is expressed in joules per gram per degree Celsius.

Quantity of Heat:

The quantity of heat is a measurement of the amount of heat is present.

The formula of quantity of heat, q, is equal to the mass of substance, m, multiplied with the specific heat and the change in temperature, ΔT .

When the mass of substance is multiplied with the specific heat the product is equal to heat capacity, which is donated as C.

$q=\Delta T\times C\times m$

The total heat in a closed system must remain constant, which is represented by the equation

$qsystem+qsurroundings=0$

Specific Latent Heat:

There are two types of specific latent heat:

vaporization and fusion.

The specific latent heat of vaporization:

The specific latent heat of vaporization is defined as the quantity of heat energy that is necessary to raise one unit of weight (pounds or grams) with no change of temperature in the surroundings.

Like the name implies, this specific latent heat **quantifies the transfer of energy when a substance's state changes from liquid to gas or from gas to liquid.**

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Like the name implies, this specific latent heat quantifies the transfer of energy when a substance's state changes from liquid to gas or from gas to liquid.

Specific Latent heat of fusion:

The specific heat of fusion is the quantity of heat that is necessary to raise one unit of weight without any change in temperature.

This specific latent heat quantifies the transfer of energy when a substance's state changes from a solid to a liquid or from a liquid to a solid.

27:

Effect of Temperature on Heat Capacity:

Specific heat or Heat Capacity is a measure of the ability of the substance to absorb heat.

The heat goes first into increasing the kinetic energies of the molecules.

Molecules can also store energy in vibrations and rotations.

At low temperatures, collisions do not provide enough energy to get out of the ground states for rotation or vibration.

As the substance heats up, the average kinetic energy of the molecules increases.

The collisions impart enough energy to allow rotation to occur.

Rotation then contributes to the internal energy and raises the specific heat.

Effect of Pressure on Heat Capacity

Conventional thermodynamic expression predicts that the heat capacity decreases with increasing pressure.

In model calculations, heat capacity increases with pressure, decreases, or remains insensitive to pressure, depending on the model applied.

28.

Thermodynamic Processes:

Two Types

Reversible Process

Irreversible process

Reversible Process:

A reversible process is defined as a process that can be reversed without leaving any trace on the surroundings.

It means both system and surroundings are returned to their initial states at the end of the reverse process.

Reversible processes do not occur and they are only idealizations of actual processes.

We use reversible process concept because

They are easy to analyze (since system passes through a series of equilibrium states

They serve as limits (idealized models) to which the actual processes can be compared.

Internally reversible process:

If no irreversibilities occur within the boundaries of the system.

In these processes a system undergoes through a series of equilibrium states, and when the process is reversed, the system passes through exactly the same equilibrium states while returning to its initial state

Externally reversible process:

if no irreversibilities occur outside the system boundaries during the process.

Heat transfer between a reservoir and a system is an externally reversible process if the surface of contact between the system and reservoir is at the same temperature.

Totally reversible or simply reversible process means: both externally and internally reversible processes.

Examples:

Some examples of nearly reversible processes are:

Frictionless relative motion.

Expansion and compression of spring. (iii) Frictionless adiabatic expansion or compression of fluid.

Polytrophic expansion or compression of fluid.

Isothermal expansion or compression.

Electrolysis.

29:

Irreversible process:

An irreversible process is one in which heat is transferred through a finite temperature.

In summary, processes that are not reversible are called irreversible.

Some factors that cause a process to become irreversible:

Friction

Unrestrained expansion and compression

Mixing

Heat transfer (finite ΔT)

Inelastic deformation

Chemical reactions

Examples of irreversible process:

Relative motion with friction

Combustion

Diffusion

Free expansion

Throttling

Electricity flow through a resistance

Heat transfer

Plastic deformation.

Irreversibilities are of two types:

External irreversibilities.

These are associated with dissipating effects outside the working fluid.

Example: Mechanical friction occurring during a process due to some external source.

2. Internal irreversibilities.

These are associated with dissipating effects within the working fluid.

Example: Unrestricted expansion of gas, viscosity and inertia of the gas.

30:

Spontaneous Process:

Spontaneous processes do not require energy input to proceed, whereas nonspontaneous processes do.

A spontaneous process is capable of proceeding in a given direction without needing to be driven by an outside source of energy.

Spontaneous changes, also called natural processes, proceed when left to themselves, and in the absence of any attempt to drive them in reverse.

The sign convention of changes in free energy follows the general convention for thermodynamic measurements.

This means a release of free energy from the system corresponds to a negative change in free energy, but to a positive change for the surroundings.

The laws of thermodynamics govern the direction of a spontaneous process, ensuring that if a sufficiently large number of individual interactions (like atoms colliding) are involved, then the direction will always be in the direction of increased entropy.

Spontaneity does not imply that the reaction proceeds with great speed.

For example, the decay of diamonds into graphite is a spontaneous process that occurs very slowly, taking millions of years.

The rate of a reaction is independent of its spontaneity, and instead depends on the chemical kinetics of the reaction.

Every reactant in a spontaneous process has a tendency to form the corresponding product.

This tendency is related to stability.

Examples include:

A smell diffusing in a room

Ice melting in lukewarm water

Salt dissolving in water

Iron rusting.

31.

Nonspontaneous Processes:

A nonspontaneous process will not take place unless it is “driven” by the continual input of energy from an external source. A process that is spontaneous in one direction under a particular set of conditions is nonspontaneous in the reverse direction.

For example At room temperature and typical atmospheric pressure, ice will spontaneously melt, but water will not spontaneously freeze.

An endergonic reaction (also called a nonspontaneous reaction or an unfavorable reaction) is a chemical reaction in which the standard change in free energy is positive, and energy is absorbed.

Endergonic reaction is a reaction that absorbs energy from its surroundings.

The total amount of energy is a loss (it takes more energy to start the reaction than what is gotten out of it) so the total energy is a negative net result.

Endergonic reactions can also be pushed by coupling them to another reaction, which is strongly exergonic, through a shared intermediate.

Examples:

The oxidation of gold, mercury and osmium are excellent examples. Also, the burning of chlorine, fluorine and bromine require a large input of energy to make them go.

The oxidation of Nitrogen is another very good example. It's because the chemical energy of the products is greater than that of the reactants, so they need a big push.

32:

Equilibrium Constant:

A reversible reaction can proceed in both the forward and backward directions.

Equilibrium is when the rate of the forward reaction equals the rate of the reverse reaction.

All reactant and product concentrations are constant at equilibrium.

Equilibrium is the state in which the reactants and products experience no net change over time.

This occurs when the forward and reverse reactions occur at equal rates.

The equilibrium constant is used to determine the amount of each compound that present at equilibrium.

Consider a chemical reaction of the following form:

$aA+bB \rightleftharpoons cC+dD$

For the above equation, the equilibrium constant is defined as:

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

For reactions that are not at equilibrium, we can write a similar expression called the reaction quotient Q, which is equal to Kc at equilibrium.

Kc and Q can be used to determine if a reaction is at equilibrium, to calculate concentrations at equilibrium, and to estimate whether a reaction favors products or reactants at equilibrium.

33:

Equilibrium Constant:

There are some important things to remember when calculating Equilibrium Constant “Kc”.

Kc is a constant for a specific reaction at a specific temperature. If you change the temperature of a reaction, then Kc also changes.

Pure solids and pure liquids, including solvents, are not included in the equilibrium expression.

Kc is often written without units.

The reaction must be balanced with the coefficients written as the lowest possible integer values in order to get the correct value for Kc.

Homogeneous equilibrium:

A homogeneous equilibrium has everything present in the same phase.

The usual examples include reactions where everything is a gas, or everything is present in the same solution.

A good example of a gaseous homogeneous equilibrium is the conversion of sulphur dioxide to sulphur trioxide.

A commonly used liquid example is the esterification reaction between an organic acid and an alcohol.

Heterogeneous equilibrium:

A heterogeneous equilibrium has things present in more than one phase.

The usual examples include reactions involving solids and gases, or solids and liquids.

Typical examples of a heterogeneous equilibrium include:

The equilibrium established if steam is in contact with red hot carbon.

If you shake copper with silver nitrate solution, you get equilibrium involving solids and aqueous ions.

34:

Equilibrium Constant of Concentration:

The equilibrium constant of concentration gives the ratio of concentrations of products over reactants for a reaction that is at equilibrium.

This is usually used when the state of matter for the reaction is (aq).

The equilibrium constant expression is written as Kc as in the expression below:

If K>1 then equilibrium favors products

If K<1 then equilibrium favors the reactants

Notice the mathematical product of the chemical products raised to the powers of their respective coefficients is the numerator of the ratio and the mathematical product of the reactants raised to the powers of their respective coefficients is the denominator.

This is the case for every equilibrium constant.

Keep in mind that this expression was obtained by a homogeneous equilibrium reaction.

K represents an equilibrium constant and c represents concentration (e.g., Kc).

35:

Equilibrium Constant of Pressure:

Gaseous reaction equilibria are not expressed in terms of concentration, but instead in terms of partial pressures.

The equilibrium constant of pressure gives the ratio of pressure of products over reactants for a reaction that is at equilibrium (the concentrations of all species are raised to the powers of their respective concentrations).

The equilibrium constant is written as Kp, as shown below:

Where p can have units of pressure (e.g., atm or bar).

Conversion of Kc to Kp:

To convert Kc to Kp, the following equation is used:

where:

R=0.0820575 L atm mol-1 K-1 or 8.31447 J mol-1 K-1

T= Temperature in Kelvin

Δngas= Moles of gas (product) - Moles of Gas (Reactant)

36:

Applications of Equilibrium Constants:

1. The magnitude of the equilibrium constant, K, indicates the extent to which a reaction will proceed:

If K is a large number, it means that the equilibrium concentration of the products is large. In this case, the reaction as written will proceed to the right (resulting in an increase in the concentration of products)

If K is a small number, it means that the equilibrium concentration of the reactants is large. In this case, the reaction as written will proceed to the left (resulting in an increase in the concentration of reactants.

Knowing the value of the equilibrium constant, K, will allow us to determine:

The direction a reaction will proceed to achieve equilibrium

The ratios of the concentrations of reactants and products when equilibrium is reached

2. Predicting the Direction of a Reaction

If $Q = Kc$, then the system is already at equilibrium

If $Q > Kc$, then essentially we have too much product and the reaction will proceed to the left (to reduce the concentration of product and increase the concentration of product)

If $Q < Kc$, then essentially we have too little product and the reaction will proceed to the right (to produce more product and decrease the concentration of reactant)

. Calculation of the Equilibrium Concentration of a Reactant or Product

Many types of equilibrium problems deal with determining how much of a product (or reactant) we will have once a reaction reaches equilibrium.

4. Solving equilibrium concentrations of all components in a reaction

Sometimes an equilibrium problem will provide the value for the equilibrium constant and the initial concentration of all species.

37:

Gibbs Free Energy:

The Gibbs free energy of a system at any moment in time is defined as the enthalpy of the system minus the product of the temperature times the entropy of the system.

$G = H - TS$

The Gibbs free energy of the system is a state function because it is defined in terms of thermodynamic properties that are state functions.

The change in the Gibbs free energy of the system that occurs during a reaction is therefore equal to the change in the enthalpy of the system minus the change in the product of the temperature times the entropy of the system.

$\Delta G = \Delta H - \Delta(TS)$

If the reaction is run at constant temperature, this equation can be written as follows.

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

The change in the free energy of a system that occurs during a reaction can be measured under any set of conditions. If the data are collected under standard-state conditions, the result is the standard-state free energy of reaction (ΔGo).

$\Delta Go = \Delta Ho - T\Delta So$

The beauty of the equation defining the free energy of a system is its ability to determine the relative importance of the enthalpy and entropy terms as driving forces behind a particular reaction.

The change in the free energy of the system that occurs during a reaction measures the balance between the two driving forces that determine whether a reaction is spontaneous

The beauty of the equation defining the free energy of a system is its ability to determine the relative importance of the enthalpy and entropy terms as driving forces behind a particular reaction.

The change in the free energy of the system that occurs during a reaction measures the balance between the two driving forces that determine whether a reaction is spontaneous**.**

38:

Gibbs free energy with equilibrium constant:

Gibbs free energy relates to the equilibrium constant K in two ways.

The first is a qualitative relationship.

If ΔG is a negative number the said reaction is spontaneous.

This means that at equilibrium, the products dominate.

K would be a very large number.

On the other hand, if ΔG is a positive number the reaction is non-spontaneous and the reactants will dominate the equilibrium.

If the reactants dominate K is a small number.

Quantitatively Gibbs Free Energy can be calculated by using

$\Delta G = - RT\ln K$

At the standard condition, activities of all reactants and products are unity (all equal to 1).

In this system, $Q = 1$. If $K > 1$, the forward reaction is spontaneous,

Gibbs Free Energy Change, ΔG:

The generalized statement can be represented by a generalized Gibb's free energy change, ΔG, for a system not at standard condition, but whose reaction quotient is Q. Obviously, the formulation is

$\Delta G = \Delta Go + R\ T \ln Q$.

As the system strives to reach an equilibrium state, (no longer any net change),

$Q \to K$

we have the following results,

$\Delta Go = - R\ T \ln K$
$\Delta Go + R\ T \ln K = 0$
$\Delta G = 0$.

When ΔG is positive, the reverse reaction is spontaneous.

When ΔG is negative, the forward reaction is spontaneous,

When ΔG is zero, the system has reached an equilibrium state.

39:

Gibbs Helmholtz Equation:

The Gibbs-Helmholtz equation was first deduced by the German physicist Hermann von Helmholtz

In it, he introduced the concept of free energy and used the equation to demonstrate that the free energy, not heat production, was the driver of spontaneous change in isothermal chemical reactions,

The Gibbs-Helmholtz equation provides information about the temperature dependence of the Gibbs free energy

$$\left(\frac{\partial(G/T)}{\partial T}\right)_p = -\frac{H}{T^2}$$

where H is the enthalpy,

T the absolute temperature and

G the Gibbs free energy of the system, all at constant pressure p.

The equation states that the change in the G/T ratio at constant pressure as a result of an infinitesimally small change in temperature is a factor H/T2.

Applications of the Gibbs-Helmholtz equation:

Can Calculate ΔHrxn from ΔG and its variation with temperature at constant pressure

This application is useful particularly in relation to reversible reactions in electrochemical cells, where ΔG identifies with the electrical work done

2. Calculate ΔGrxn for a reaction at a temperature other than 298K

Usually varies slowly with temperature, and can with reasonable accuracy be regarded as constant.

Integration enables us to compute ΔGrxn for a constant-pressure process at a temperature T2 from a knowledge of ΔG and ΔH at temperature T1

3. Calculate the effect of a temperature change on the equilibrium constant Kp

ΔH usually varies slowly with temperature, and can with reasonable accuracy be regarded as constant. The integrated van ‘t Hoff equation (6) allows the equilibrium constant Kp at T2 to be calculated with knowledge of Kp and ΔH° at T1

Fugacity:

Fugacity Measures Nonideality of a Gas.

Fugacity is the effective pressure for a non-ideal gas.

The pressures of an ideal gas and a real gas are equivalent when the chemical potential is the same.

The equation that relates the non-ideal to the ideal gas pressure is:

$f = \phi P$

f represents fugacity,

P is the pressure for an ideal gas, and

ϕ is the fugacity coefficient.

The fugacity coefficient (Φi) is defined as the ratio of fugacity to its value at the ideal state.

The fugacity coefficient takes a value of unity when the substance behaves like an ideal gas.

Therefore, the fugacity coefficient is also regarded as a measure of non-ideality; the closer the value of the fugacity coefficient is to unity, the closer we are to the ideal state.

Activity:

Activity is a measure of the effective concentration of a species under non-ideal (e.g., concentrated) conditions. This determines the real chemical potential for a real solution rather than an ideal one.

Activities and concentrations can both be used to calculate equilibrium constants and reaction rates.

However, most of the time we use concentration even though activity is also a measure of composition, similar to concentration.

It is satisfactory to use concentration for diluted solutions, but when you are dealing with more concentrated solutions, the difference in the observed concentration and the calculated concentration in equilibrium increases.

This is the reason that the activity was initially created.

$$a = e^{\frac{\mu - \mu o}{RT}}$$

a =Activity

μ is chemical potential (dependent on standard state) which is Gibbs Energy per mole

μ0 is the standard chemical potential

R is the gas constant

T is the absolute Temperature

Activity is more accurate in more concentrated solutions

The Reaction Quotient:

The reaction quotient Q is a measure of the relative amounts of products and reactants present in a reaction at a given time.

This expression might look awfully familiar, because Q is a concept that is closely related to the equilibrium constant K.

Unlike K which is based on equilibrium concentrations, Q can be calculated whether we are at equilibrium or not

Using Q to predict the direction of reaction:

When a stress is applied that moves a reaction away from equilibrium, the reaction will try to adjust to get back to equilibrium.

By comparing Q and K, we can see how our reaction is adjusting

is it trying to make more product,

or is it consuming product to make more reactant?

Alternatively, are we at equilibrium already?

There are three possible scenarios to consider:

In the case where Q>K, this suggests that we have more product present than we would have at equilibrium. Therefore, the reaction will try to use up some of the excess product and favor the reverse reaction to reach equilibrium.

If Q<K, In this case, the ratio of products to reactants is less than that for the system at equilibrium. In other words, the concentration of the reactants is higher than it would be at equilibrium; you can also think of it as the product concentration being too low. In order to reach equilibrium, the reaction will favor the forward reaction and try to use up some of the excess reactant to make more product.

3. If Q=K3, The reaction is already at equilibrium! Our concentrations won't change since the rates of the forward and backward reactions are equal.

42:

Van’t Hoff Equation:

$$\frac{d \ln K}{dT} = \frac{\Delta H}{RT^2}$$

where K is the equilibrium constant, T is temperature, H is the enthalpy of the reaction and R is the gas constant. It provides the materials engineer a means to determine how the equilibrium constant for a reaction or process will vary with temperature.

From this form of the van't Hoff equation, we see that at constant pressure, a plot with lnKeq on the y-axis and 1/T on the x-axis has a slope given by $-\Delta H / R$.

This is the origin of LeChatelier's Principle for the heat absorbed or evolved during the course of a chemical reaction.

For an endothermic reaction, the slope is negative and so as the temperature increases, the equilibrium constant increases.

For an exothermic reaction, the slope is positive and so as temperature increases, the equilibrium constant decreases,

The van't Hoff equation provides information about the temperature dependence of the equilibrium constant.

The van't Hoff equation may be derived from the Gibbs-Helmholtz equation, which gives the temperature dependence of the Gibbs free energy.

43:

Le Chatelier's Principle:

If a dynamic equilibrium is disturbed by changing the conditions, the position of equilibrium moves to counteract the change.

An action that changes the temperature, pressure, or concentrations of reactants in a system at equilibrium stimulates a response that partially offsets the change while a new equilibrium condition is established.

Hence, Le Châtelier's principle states that any change to a system at equilibrium will adjust to compensate for that change.

In 1884 the French chemist and engineer Henry-Louis Le Châtelier proposed one of the central concepts of chemical equilibria, which describes what happens to a system when something briefly removes it from a state of equilibrium.

It is important to understand that Le Châtelier's principle is only a useful guide to identify what happens when the conditions are changed in a reaction in dynamic equilibrium; it does not give reasons for the changes at the molecular level (e.g., timescale of change and underlying reaction mechanism).

Le Chatelier's principle describes what happens to a system when something momentarily takes it away from equilibrium. We focuses on three ways in which we can change the conditions of a chemical reaction at equilibrium:

(1) changing the concentration of one of the components of the reaction

(2) changing the pressure on the system

(3) changing the temperature at which the reaction is run.

44:

Using Le Chatelier's Principle with a change of concentration:

Le Châtelier's principle states that if the system is changed in a way that increases the concentration of one of the reacting species, it must favor the reaction in which that species is consumed.

In other words, if there is an increase in products, the reaction quotient, Q_c , is increased, making it greater than the equilibrium constant, K_c .

Increasing the concentration

Consider an equilibrium established between four substances, A , B , C , and D :

$A+2B \rightleftharpoons C+D$

What happens if conditions are altered by increasing the concentration of A?

According to Le Châtelier, the position of equilibrium will move in such a way as to counteract the change.

In this case, the equilibrium position will move so that the concentration of A decreases again by reacting it with B to form more C and D.

The equilibrium moves to the right (indicated by the green arrow below).

Decreasing the concentration:

In the opposite case in which the concentration of A is decreased, according to Le Châtelier, the position of equilibrium will move so that the concentration of A increases again.

More C and D will react to replace the A that has been removed:

The position of equilibrium moves to the left.

This is essentially what happens if one of the products is removed as soon as it is formed.

If, for example, C is removed in this way, the position of equilibrium would move to the right to replace it.

If it is continually removed, the equilibrium position shifts further and further to the right, effectively creating a one-way, irreversible reaction.

45:

Using Le Chatelier's Principle with a change of pressure:

This only applies to reactions involving gases, although not necessarily all species in the reaction need to be in the gas phase.

A general homogeneous gaseous reaction is given below:

$A(g)+2B(g) \rightleftharpoons C(g)+D(g)$

Increasing the pressure:

According to Le Châtelier, if the pressure is increased, the position of equilibrium will move so that the pressure is reduced again.

Pressure is caused by gas molecules hitting the sides of their container.

The more molecules in the container, the higher the pressure will be.

The system can reduce the pressure by reacting in such a way as to produce fewer molecules.

Decreasing the pressure:

The equilibrium will move in such a way that the pressure increases again.

It can do that by producing more gaseous molecules.

In this case, the position of equilibrium will move towards the left-hand side of the reaction.

Summary of Pressure Effects:

Three ways to change the pressure of an equilibrium mixture are:

Add or remove a gaseous reactant or product,

Add an inert gas to the constant-volume reaction mixture, or

Change the volume of the system.

Adding products makes Qc greater than Kc.

This creates a net change in the reverse direction, toward reactants.

The opposite occurs when adding more reactants.

Adding an inert gas into a gas-phase equilibrium at constant volume does not result in a shift.

This is because the addition of a non-reactive gas does not change the partial pressures of the other gases in the container.

While the total pressure of the system increases, the total pressure does not have any effect on the equilibrium constant.

When the volume of a mixture is reduced, a net change occurs in the direction that produces fewer moles of gas.

When volume is increased the change occurs in the direction that produces more moles of gas.

46:

Using Le Chatelier's Principle with a change of temperature:

To understand how temperature changes affect equilibrium conditions, the sign of the reaction enthalpy must be known.

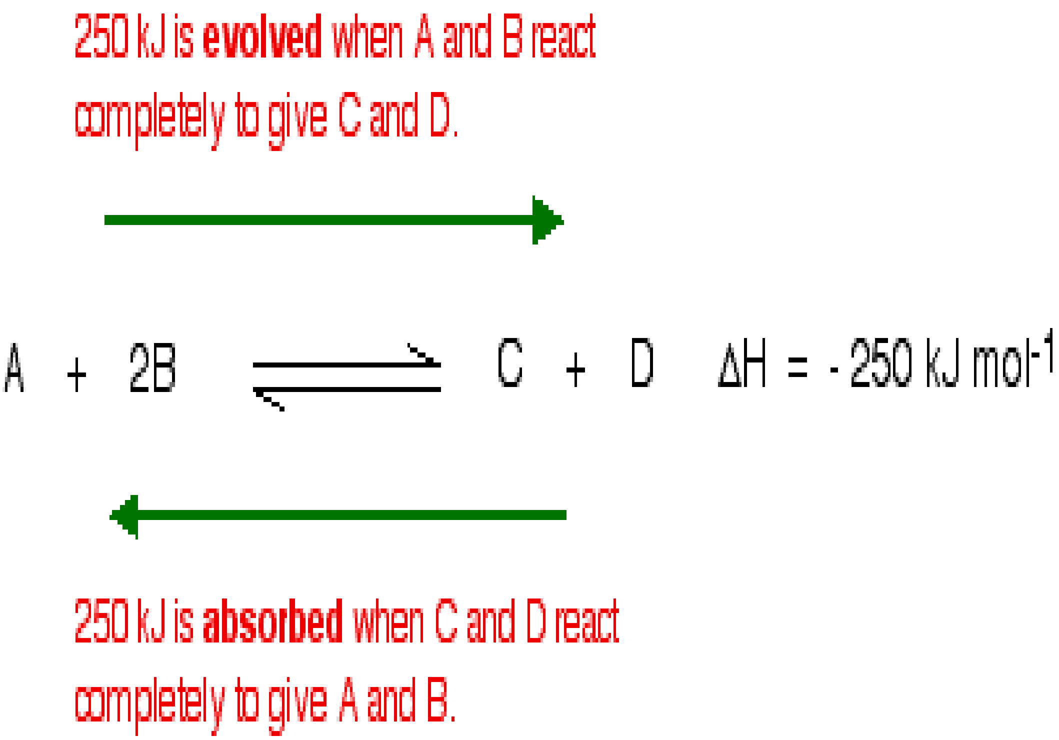
Assume that the forward reaction is exothermic (heat is evolved):

$A+2B \rightleftharpoons C+D \quad \Delta H= -250$ KJ per mol

In this reaction, 250 kJ is evolved (indicated by the negative sign) when 1 mole of A reacts completely with 2 moles of B.

For reversible reactions, the enthalpy value is always given as if the reaction was one-way in the forward direction.

The back reaction (the conversion of C and D into A and B) would be endothermic, absorbing the same amount of heat.



250 kJ is **evolved** when A and B react completely to give C and D.

$$A + 2B \rightleftharpoons C + D \quad \Delta H = -250 \text{ kJ mol}^{-1}$$

250 kJ is **absorbed** when C and D react completely to give A and B.

Increasing the temperature

If the temperature is increased, then the position of equilibrium will move so that the temperature is reduced again.

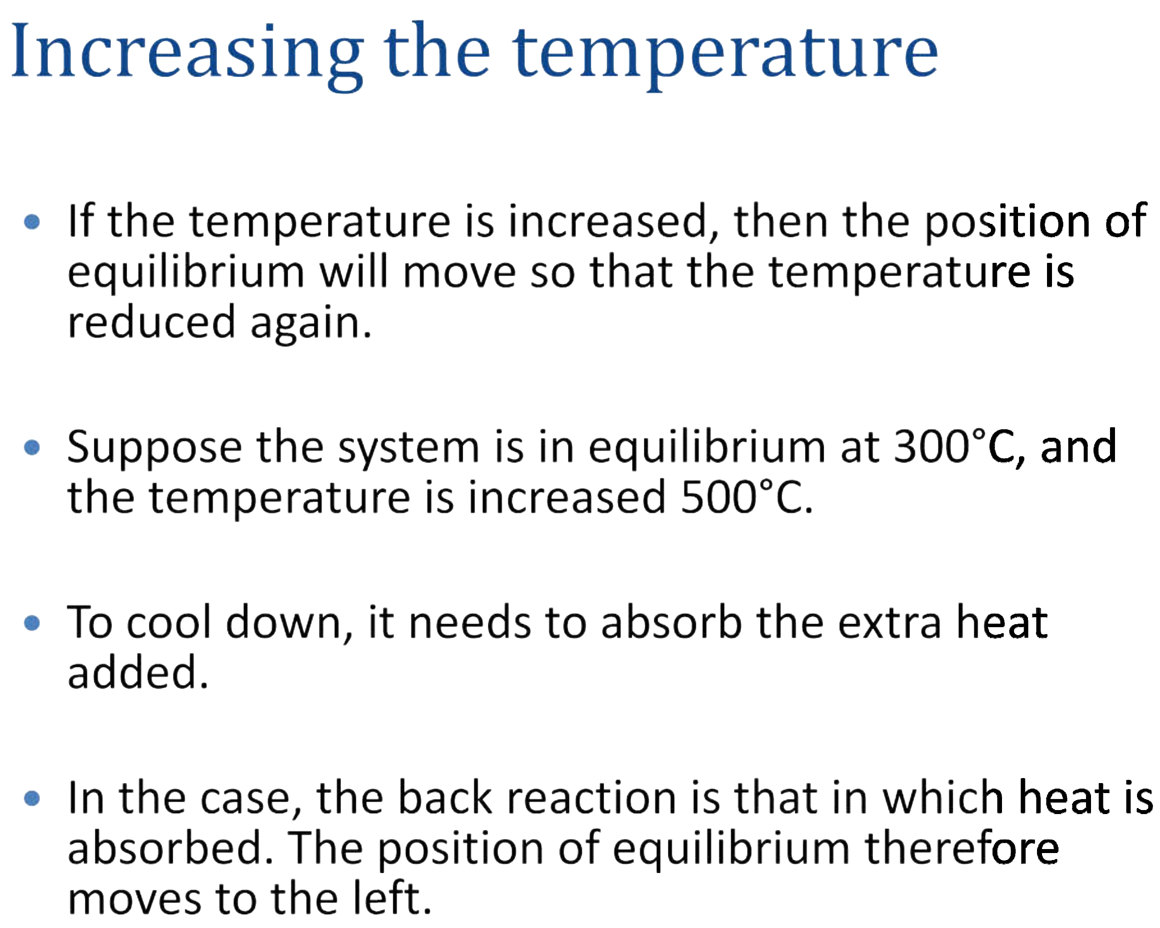
Suppose the system is in equilibrium at 300°C, and the temperature is increased 500°C.

To cool down, it needs to absorb the extra heat added.

In the case, the back reaction is that in which heat is absorbed. The position of equilibrium therefore moves to the left.

The new equilibrium mixture contains more A and B, and less C and D.

If the goal is to maximize the amounts of C and D formed, increasing the temperature on a reversible reaction in which the forward reaction is exothermic is a poor approach.



Increasing the temperature

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- To cool down, it needs to absorb the extra heat added.
- In the case, the back reaction is that in which heat is absorbed. The position of equilibrium therefore moves to the left.

Decreasing the temperature:

The equilibrium will move in such a way that the temperature increases again.

Suppose the system is in equilibrium at 500°C and the temperature is reduced to 400°C.

The reaction will tend to heat itself up again to return to the original temperature by favoring the exothermic reaction.

The position of equilibrium will move to the right with more A and B converted into C and D at the lower temperature:

Summary of Temperature Effects:

Increasing the temperature of a system in dynamic equilibrium favors the endothermic reaction. The system counteracts the change by absorbing the extra heat.

Decreasing the temperature of a system in dynamic equilibrium favors the exothermic reaction. The system counteracts the change by producing more heat**.**

47:

Properties of Liquids:

The intermolecular attractive forces are strong enough to hold molecules close together

Liquids are more dense and less compressible than gasses

Liquids have a definite volume, independent of the size and shape of their container

The attractive forces are not strong enough, however, to keep neighboring molecules in a fixed position and molecules are free to move past or slide over one another

Physical properties of liquids:

The physical properties of a substance depends upon its physical state.

Water vapor, liquid water and ice all have the same chemical properties, but their physical properties are considerably different.

Intermolecular forces (non-covalent bonds) influence the physical properties of liquids

In a gas, the distance between molecules is very large compared with the size of the molecules; thus gases have a low density and are highly compressible.

In contrast, the molecules in liquids are very close together, with essentially no empty space between them.

As in gases, however, the molecules in liquids are in constant motion, and their kinetic energy (and hence their speed) depends on their temperature.

The properties of liquids can be explained using a modified version of the kinetic molecular theory of gases.

This model explains the higher density, greater order, and lower compressibility of liquids versus gases; the thermal expansion of liquids; why they diffuse; and why they adopt the shape (but not the volume) of their containers.

A kinetic molecular description of liquids must take into account both the nonzero volumes of particles and the presence of strong intermolecular attractive forces.

Solids and liquids have particles that are fairly close to one another, and are thus called "condensed phases" to distinguish them from gases.

Physical properties of liquids, Examples

- Density
- Compressibility
- Thermal Expansion
- Diffusion
- Viscosity/Fluidity
- Surface tension
- Capillary action

Surface Tension:

Surface tension is the energy required to increase the surface area of a liquid by a unit amount.

Or

The magnitude of the force that controls the shape of the liquid is called the surface tension.

The surface tension of a liquid results from an imbalance of intermolecular attractive forces, the cohesive forces between molecules:

A molecule in the bulk liquid experiences cohesive forces with other molecules in all directions.

A molecule at the surface of a liquid experiences only net inward cohesive forces.

In a sample of water, there are two types of molecules.

Those that are on the outside, exterior, and those that are on the inside, interior.

The interior molecules are attracted to all the molecules around them, while the exterior molecules are attracted to only the other surface molecules and to those below the surface.

This makes it so that the energy state of the molecules on the interior is much lower than that of the molecules on the exterior.

Because of this, the molecules try to maintain a minimum surface area, thus allowing more molecules to have a lower energy state.

49:

Viscosity:

Viscosity is defined as a liquid’s resistance to flow.

Viscosity is also often referred as the thickness of a fluid.

You can think of water (low viscosity) and honey (high viscosity).

At a molecular level, viscosity is a result the interaction between the different molecules in a fluid.

This can be also understood as friction between the molecules in the fluid.

Just like in the case of friction between moving solids, viscosity will determine the energy required to make a fluid flow.

Measuring Viscosity:

There are numerous ways to measure viscosity.

One of the most elementary ways is to allow a sphere, such as a metal ball, to drop through a fluid and time the fall of the metal ball:

The slower the sphere falls, the lower the viscosity that is measured.

Another more advanced design of measuring viscosity known as the Ostwald Viscometer that is much more accurate than dropping a metal ball.

An Ostwald Viscometer consists of two reservoir bulbs and a capillary tube.

The viscometer is filled with liquid until the liquid reaches the mark A with the aid of a pipette to accurately measure out the volume of needed liquid.

The viscometer is then put into a water bath which equilibrates the temperature of the test liquid.

As noted before, the equilibration is important to maintain a constant temperature as to not affect the viscosity otherwise.

The liquid is then drawn through the side 2 of the U-tube by use of suction and lastly, the flow is time between marks C and B.

The viscosity is calculated with Equation

nu=Kt

Where K is the value of a liquid with known viscosity and density such as water. Once the value of K is known, the viscosity can be determined by measuring the amount of time the test liquid flows between the two graduated marks.

50. Refractive Index:

The refractive index is a ratio of the speed of light in a medium relative to its speed in a vacuum.

This change in speed from one medium to another is what causes light rays to bend.

This is because as light travels through another medium other than a vacuum, the atoms of that medium constantly absorb and reemit the particles of light, slowing down the speed light travels at.

The refractive index can be calculated by measuring the angle of incidence and the angle of refraction and applying the formula:

$n = \sin(\theta i) / \sin(\theta r)$

(where n is the index of refraction)

The two factors which affect the value of the refractive index are:

Temperature

Wavelength of light

Temperature:

Refractive index values are usually determined at standard temperature.

A higher temperature means the liquid becomes less dense and less viscous, causing light to travel faster in the medium. This results in a smaller value for the refractive index due to a smaller ratio.

A lower temperature means the liquid becomes denser and has a higher viscosity, causing light to travel slower in the medium. This results in a larger value for the refractive index due to a larger ratio.

Wavelength of light”

The refractive index varies with wavelength linearly because different wavelengths interfere to different extents with the atoms of the medium.

It is important to use monochromatic light to prevent dispersion of light into different colors.

The chosen wavelength should not be absorbed by the medium.

The sodium D line at 598 nm is the most frequently used wavelength of light for a refractometer.

51:

Dipole Moment:

When atoms in a molecule share electrons unequally, they create what is called a dipole moment.

This occurs when one atom is more electronegative than another, resulting in that atom pulling more tightly on the shared pair of electrons, or when one atom has a lone pair of electrons and the difference of electronegativity vector points in the same way.

One of the most common examples is the water molecule, made up of one oxygen atom and two hydrogen atoms. The differences in electronegativity and lone electrons give oxygen a partial negative charge and each hydrogen a partial positive charge.

Dipole moment (μ) is the measure of net molecular polarity, which is the magnitude of the charge Q at either end of the molecular dipole times the distance r between the charges.

$\mu = Q \times r$

Dipole moments tell us about the charge separation in a molecule.

The larger the difference in electronegativities of bonded atoms, the larger the dipole moment.

For example, NaCl has the highest dipole moment because it has an ionic bond

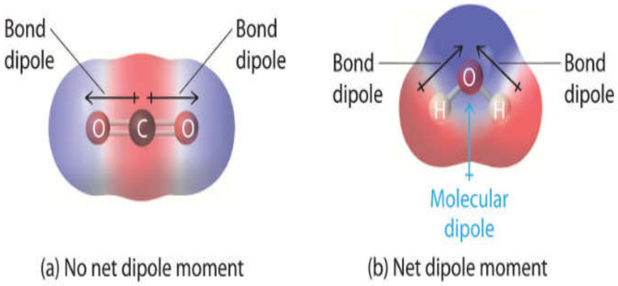
Polarity and Structure of Molecules:

The shape of a molecule and the polarity of its bonds determine the OVERALL POLARITY of that molecule.

If these centers lie at the same point in space, then the molecule has no overall polarity (and is non polar).

If a molecule is completely symmetric, then the dipole moment vectors on each molecule will cancel each other out, making the molecule nonpolar.

A molecule can only be polar if the structure of that molecule is not symmetric.



Charge distributions of CO2 and H2O .
Blue and red colored regions are negative and positively signed regions, respectively.A molecule that contains polar bonds, might not have any overall polarity, depending upon its shape. The simple definition of whether a complex molecule is polar or not depends upon whether its overall centers of positive and negative charges overlap .

A good example of a nonpolar molecule that contains polar bonds is carbon dioxide.

This is a linear molecule and the C=O bonds are, in fact, polar.

The central carbon will have a net positive charge, and the two outer oxygens a net negative charge.

However, since the molecule is linear, these two bond dipoles cancel each other out (i.e. the vector addition of the dipoles equals zero) and the overall molecule has a zero dipole moment ($\mu=0\mu=0$).

52:

Dipole Dipole Interactions:

Dipole-Dipole interactions result when two dipolar molecules interact with each other.

When this occurs, the partially negative portion of one of the polar molecules is attracted to the partially positive portion of the second polar molecule.

This type of interaction between molecules accounts for many physically and biologically significant phenomena such as the elevated boiling point of water.

Molecular dipoles occur due to the unequal sharing of electrons between atoms in a molecule.

Those atoms that are more electronegative pull the bonded electrons closer to themselves.

The buildup of electron density around an atom or discreet region of a molecule can result in a molecular dipole in which one side of the molecule possesses a partially negative charge and the other side a partially positive charge.

Molecules with dipoles that are not canceled by their molecular geometry are said to be polar.

Biological Importance of Dipole Interactions:

The potential energy from dipole interactions is important for living organisms.

The biggest impact dipole interactions have on living organisms is seen with protein folding.

Every process of protein formation, from the binding of individual amino acids to secondary structures to tertiary structures and even the formation of quaternary structures is dependent on dipole-dipole interactions.

A prime example of quaternary dipole interaction that is vital to human health is the formation of erythrocytes.

Erythrocytes, commonly known as red blood cells, are comprised of four protein subunits and a heme molecule.

For an erythrocyte to form properly, multiple steps must occur, all of which involve dipole interactions.

The four protein subunits-two alpha chains, two beta chains-and the heme group, interact with each other through a series of dipole-dipole interactions which allow the erythrocyte to take its final shape.

Any mutation that destroys these dipole-dipole interactions prevents the erythrocyte from forming properly, and impairs their ability to carry oxygen to the tissues of the body.

So we can see that without the dipole-dipole interactions, proteins would not be able to fold properly and all life as we know it would cease to exist.

53.

Unusual Properties of Water:

With 70% of our earth being ocean water and 65% of our bodies being water, it is hard to not be aware of how important it is in our lives.

There are 3 different forms of water, or H2O: solid (ice), liquid (water), and gas (steam). Because water seems so ubiquitous, many people are unaware of the unusual and unique properties of water, including:

Boiling Point and Freezing Point

Surface Tension, Heat of Vaporization, and Vapor Pressure

Viscosity and Cohesion

Solid State

Liquid State

Gas State

Boiling Point and Freezing Point:

we all know that the boiling point of water is 100°C. So despite its small molecular weight, water has an incredibly big boiling point. This is because water requires more energy to break its hydrogen bonds before it can then begin to boil. The same concept is applied to freezing point as well.

The boiling and freezing points of water enable the molecules to be very slow to boil or freeze, this is important to the ecosystems living in water.

If water was very easy to freeze or boil, drastic changes in the environment and so in oceans or lakes would cause all the organisms living in water to die.

This is also why sweat is able to cool our bodies.

Surface Tension, Heat of Vaporization, and Vapor Pressure:

Besides mercury, water has the highest surface tension for all liquids.

Water's high surface tension is due to the hydrogen bonding in water molecules.

Water also has an exceptionally high heat of vaporization.

Vaporization occurs when a liquid changes to a gas, which makes it an endothermic reaction.

Water's heat of vaporization is 41 kJ/mol.

Vapor pressure is inversely related to intermolecular forces, so those with stronger intermolecular forces have a lower vapor pressure.

Water has very strong intermolecular forces, hence the low vapor pressure, but it's even lower compared to larger molecules with low vapor pressures.

54.

Unusual Properties of Water 2:

3. Viscosity and Cohesion

Viscosity is the property of fluid having high resistance to flow.

We normally think of liquids like honey or motor oil being viscous, but when compared to other substances with like structures, water is viscous.

Liquids with stronger intermolecular interactions are usually more viscous than liquids with weak intermolecular interactions.

Cohesion is intermolecular forces between like molecules; this is why water molecules are able to hold themselves together in a drop.

Water molecules are very cohesive because of the molecule's polarity.

This is why you can fill a glass of water just barely above the rim without it spilling.

Solid State (Ice)

All substances, including water, become less dense when they are heated and more dense when they are cooled.

So if water is cooled, it becomes more dense and forms ice.

Water is one of the few substances whose solid state can float on its liquid state! Why? Water continues to become more dense until it reaches 4°C.

After it reaches 4°C, it becomes LESS dense

When freezing, molecules within water begin to move around more slowly, making it easier for them to form hydrogen bonds and eventually arrange themselves into an open crystalline, hexagonal structure.

Because of this open structure as the water molecules are being held further apart, the volume of water increases about 9%.

So molecules are more tightly packed in water's liquid state than its solid state.

This is why a can of soda can explode in the freezer.

Liquid State (Liquid Water):

It is very rare to find a compound that lacks carbon to be a liquid at standard temperatures and pressures.

So it is unusual for water to be a liquid at room temperature!

Water is liquid at room temperature so it's able to move around quicker than it is as solid, enabling the molecules to form fewer hydrogen bonds resulting in the molecules being packed more closely together.

Each water molecule links to four others creating a tetrahedral arrangement, however they are able to move freely and slide past each other, while ice forms a solid, larger hexagonal structure.

Gas State (Steam):

As water boils, its hydrogen bonds are broken.

Steam particles move very far apart and fast, so barely any hydrogen bonds have the time to form. So, less and less hydrogen bonds are present as the particles reach the critical point above steam. The lack of hydrogen bonds explains why steam causes much worse burns that water.

Steam contains all the energy used to break the hydrogen bonds in water, so when steam hits your face you first absorb the energy the steam has taken up from breaking the hydrogen bonds it its liquid state.

Then, in an exothermic reaction, steam is converted into liquid water and heat is released.

This heat adds to the heat of boiling water as the steam condenses on your skin.

55.

Water as the Universal Solvent:

Because of water's polarity, it is able to dissolve or dissociate many particles.

Oxygen has a slightly negative charge, while the two hydrogens have a slightly positive charge. The slightly negative particles of a compound will be attracted to water's hydrogen atoms, while the slightly positive particles will be attracted to water's oxygen molecule; this causes the compound to dissociate.

Besides the explanations above, we can look to some attributes of a water molecule to provide some more reasons of water's uniqueness:

Forgetting fluorine, oxygen is the most electronegative non-noble gas element, so while forming a bond, the electrons are pulled towards the oxygen atom rather than the hydrogen. This creates 2 polar bonds, which make the water molecule more polar than the bonds in the other hydrides in the group.

A 104.5° bond angle creates a very strong dipole.

Water has hydrogen bonding which probably is a vital aspect in waters strong intermolecular interaction

Why is unusual properties of water important for the real world?

The properties of water make it suitable for organisms to survive in during differing weather conditions.

Ice freezes as it expands, which explains why ice is able to float on liquid water.

During the winter when lakes begin to freeze, the surface of the water freezes and then moves down toward deeper water; this explains why people can ice skate on or fall through a frozen lake.

If ice was not able to float, the lake would freeze from the bottom up killing all ecosystems living in the lake.

However ice floats, so the fish are able to survive under the surface of the ice during the winter.

The surface of ice above a lake also shields lakes from the cold temperature outside and insulates the water beneath it, allowing the lake under the frozen ice to stay liquid and maintain a temperature adequate for the ecosystems living in the lake to survive.

56.

Colligative Properties:

Colligative properties are the physical changes that result from adding solute to a solvent.

Colligative Properties depend on how many solute particles are present as well as the solvent amount, but they do NOT depend on the type of solute particles, although do depend on the type of solvent. Colligative Properties are the properties of solutions that rely only on the number(concentration) of the solute particles, and not on the identity/type of solute particles, in an ideal solution (e.g., vapor pressure lowering, freezing point depression, boiling point elevation and osmotic pressure).

There is a direct relationship between the concentration and the effect that is recorded.

Therefore, the colligative properties are helpful when characterizing the nature of a solute after it is dissolved in a solvent.

Anomalous Colligative Properties:

Anomalous colligative properties are colligative properties that deviate from the normal.

Chemist Jacobus van't Hoff was the first to describe anomalous colligative properties, but it was Svante Arrhenius who succeeded in explaining anomalous values of colligative properties.

57:

Ideal and non ideal solutions:

In chemistry, an ideal solution or ideal mixture is a solution with thermodynamic properties analogous to those of a mixture of ideal gases.

The solutions which obey Raoult’s law at all compositions of solute in solvent at all temperature are called ideal solution.

An ideal solution or ideal mixture is a solution in which the enthalpy of solution ($\Delta H_{solution} = 0$) is zero; with the closer to zero the enthalpy of solution, the more "ideal" the behavior of the solution becomes.

Since the enthalpy of mixing (solution) is zero, the change in Gibbs energy on mixing is determined solely by the entropy of mixing (ΔSsolution).

Ideal solutions can be obtained by mixing two components with identical molecular size, structure and they should have almost same inter molecular attraction e.g., two liquids A and B form and ideal solution when A – A and B – B molecular attractions will be same and hence A-B molecular attraction will be almost same as A-A and B-B molecular attraction.

Raoult's Law only works for ideal solutions.

An ideal solution is defined as one which obeys Raoult's Law. "An ideal solution shows thermodynamic mixing characteristics identical to those of ideal gas mixtures [except] ideal solutions have intermolecular interactions equal to those of the pure components."

Examples of Ideal solutions :

Ethyl chloride and ethyl bromide

n-hexane and n-heptane

CCl_4 and $SiCl_4$

Non ideal solution:

The solution which deviate from ideal behavior are called non ideal solution or real solutions and they do not obey Raoult’s law over entire range of composition.

It has been found that on increasing dilution, a non ideal solution tend to be ideal.

58:

Raoult's Law:

Raoult's law states that the vapor pressure of a solvent above a solution is equal to the vapor pressure of the pure solvent at the same temperature scaled by the mole fraction of the solvent present:

$P_{solution} = X_{solvent} P^o_{solvent}$

In the 1880s, French chemist François-Marie Raoult discovered that when a substance is dissolved in a solution, the vapor pressure of the solution will generally decrease.

This observation depends on two variables:

1. The mole fraction of the amount of dissolved solute present and

2. The original vapor pressure (pure solvent).

At any given temperature for a particular solid or liquid, there is a pressure at which the vapor formed above the substance is in dynamic equilibrium with its liquid or solid form.

This is the vapor pressure of the substance at that temperature.

At equilibrium, the rate at which the solid or liquid evaporates is equal to the rate that the gas is condensing back to its original form.

All solids and liquids have a vapor pressure, and this pressure is constant regardless of how much of the substance is present.

Raoult's Law only works for ideal solutions.

Like many other concepts explored in Chemistry, Raoult's Law only applies under ideal conditions in an ideal solution.

However, it still works fairly well for the solvent in dilute solutions.

In reality though, the decrease in vapor pressure will be greater than that calculated by Raoult's Law for extremely dilute solutions.

Limitations on Raoult's Law:

Ideal solutions satisfy Raoult's Law.

In an ideal solution, it takes exactly the same amount of energy for a solvent molecule to break away from the surface of the solution as it did in the pure solvent.

The forces of attraction between solvent and solute are exactly the same as between the original solvent.

Why Raoult's Law works

Adding a solute lowers vapor pressure because the additional solute particles will fill the gaps between the solvent particles and take up space.

This means less of the solvent will be on the surface and less will be able to break free to enter the gas phase, resulting in a lower vapor pressure.

There are two ways of explaining why Raoult's Law works - a simple visual way, and a more sophisticated way based on entropy.

59:

Vapor Pressure Lowering:

The vapor pressure of a solvent in a solution is always lower than the vapor pressure of the pure solvent.

The vapor pressure lowering is directly proportional to the mole fraction of the solute.

This is Raoult's Law

$\mathrm{Psolution} = \mathrm{XsolventPosolvent}$

where Po is the vapor pressure of the pure solvent and Xsolvent is the mole fraction of the solvent.

Since this is a two-component system (solvent and solute), then

$\mathrm{Xsolvent} + \mathrm{Xsolute} = 1$

where Xsolute is the mole fraction of the solvent or solute. The change in vapor pressure (ΔP) can be expressed

$\Delta P = \mathrm{P\ solution} - \mathrm{P\ o\ solvent} = \mathrm{XsolventPosolvent} - \mathrm{Posolvent}$

Or

$\Delta P = (\mathrm{Xsolvent}\ -1)\ \mathrm{Posolvent} = \mathrm{Xsolute\ Posolven}$

60.

Freezing Point Depression:

Freezing point depression is a colligative property observed in solutions that results from the introduction of solute molecules to a solvent.

The freezing points of solutions are all lower than that of the pure solvent and is directly proportional to the molality of the solute.

$\Delta \mathrm{Tf} = \mathrm{Tf(solvent)} - \mathrm{Tf(solution)} = \mathrm{Kf} \times \mathrm{m}$

Where ΔTf is the freezing point depression,

Tf (solution) is the freezing point of the solution

Tf(solvent) is the freezing point of the solvent,

Kf is the freezing point depression constant,

and m is the molality.

Adding solutes to an ideal solution results in a positive ΔS, an increase in entropy

Because of this, the newly altered solution's chemical and physical properties will also change.

The properties that undergo changes due to the addition of solutes to a solvent are known as colligative properties.

These properties are dependent on the amount of solutes added, not on their identity.

Two examples of colligative properties are boiling point and freezing point: due to the addition of solutes, the boiling point tends to increase and freezing point tends to decrease.

Freezing point is reached when the chemical potential of the pure liquid solvent reaches that of the pure solid solvent.

Again, since we are dealing with mixtures with decreased chemical potential, we expect the freezing point to change.

Unlike the boiling point, the chemical potential of the impure solvent requires a colder temperature for it to reach the chemical potential of the solid pure solvent.

Therefore, a freezing point depression is observed.

Applications:

Road salting takes advantage of this effect to lower the freezing point of the ice it is placed on.

Lowering the freezing point allows the street ice to melt at lower temperatures.

The maximum depression of the freezing point is about −18 °C (0 °F), so if the ambient temperature is lower, NaCl will be ineffective.

Under these conditions, CaCl2 can be used since it dissolves to make three ions instead of two for NaCl.

61.

Boiling Point Elevation:

The boiling points of solutions are all higher than that of the pure solvent. Difference between the boiling points of the pure solvent and the solution is proportional to the concentration of the solute particles:

$\Delta T_b = T_b(\text{solution}) - T_b(\text{solvent}) = K_b \times m$

The colligative properties of a solution depend on the relative numbers (concentration) of solute and solvent particles, they do not depend on the nature of the particles.

Colligative properties change in proportion to the concentration of the solute particles.

We distinguish between four colligative properties:

vapor pressure lowering,

freezing point depression,

boiling point elevation,

and osmotic pressure.

All four colligative properties fit the relationship

property = solute concentration x constant

Property	Symbol	Solute Concentration	Proportionality Constant
Vapor pressure	ΔP	mole fraction	Po (vapor pressure of pu solvent)
Boiling Point	ΔTb	molal	Kb (boiling point consta
Freezing Point	ΔTf	molal	Kf (freezing point consta
Osmotic Pressure	P	molar	RT

The determination of colligative properties allows us to determine the concentration of a solution and calculate molar masses of solutes

---

62.

Osmotic Pressure:

Osmosis is the diffusion of a fluid through a semipermeable membrane.

When a semipermeable membrane separates a solution from a solvent, then only solvent molecules are able to pass through the membrane.

The osmotic pressure of a solution is the pressure difference needed to stop the flow of solvent across a semipermeable membrane.

The osmotic pressure of a solution is proportional to the molar concentration of the solute particles in solution.

$II=nRT / V=MMRT$

where

II is the osmotic pressure,

R is the ideal gas constant (0.0821 L atm / mol K),

T is the temperature in Kelvin,

n is the number of moles of solute present,

V is the volume of the solution (nV is then the molar concentration of the solute), and

MM is the molar mass of the solute.

Semipermiable membranes do not let the solute pass through.

A solvent will move to the side that is more concentrated to try to make each side more similar! Since there is a flow of solvents, the height of each side changes, which is osmotic pressure.

When we work with aqueous solutions, we use mm of H2O to describe the difference.

63.

Henry's Law:

Henry's law is one of the gas laws formulated by William Henry in 1803 and states:

"At a constant temperature, the amount of a given gas that dissolves in a given type and volume of liquid is directly proportional to the partial pressure of that gas in equilibrium with that liquid."

An equivalent way of stating the law is that the solubility of a gas in a liquid is directly proportional to the partial pressure of the gas above the liquid:

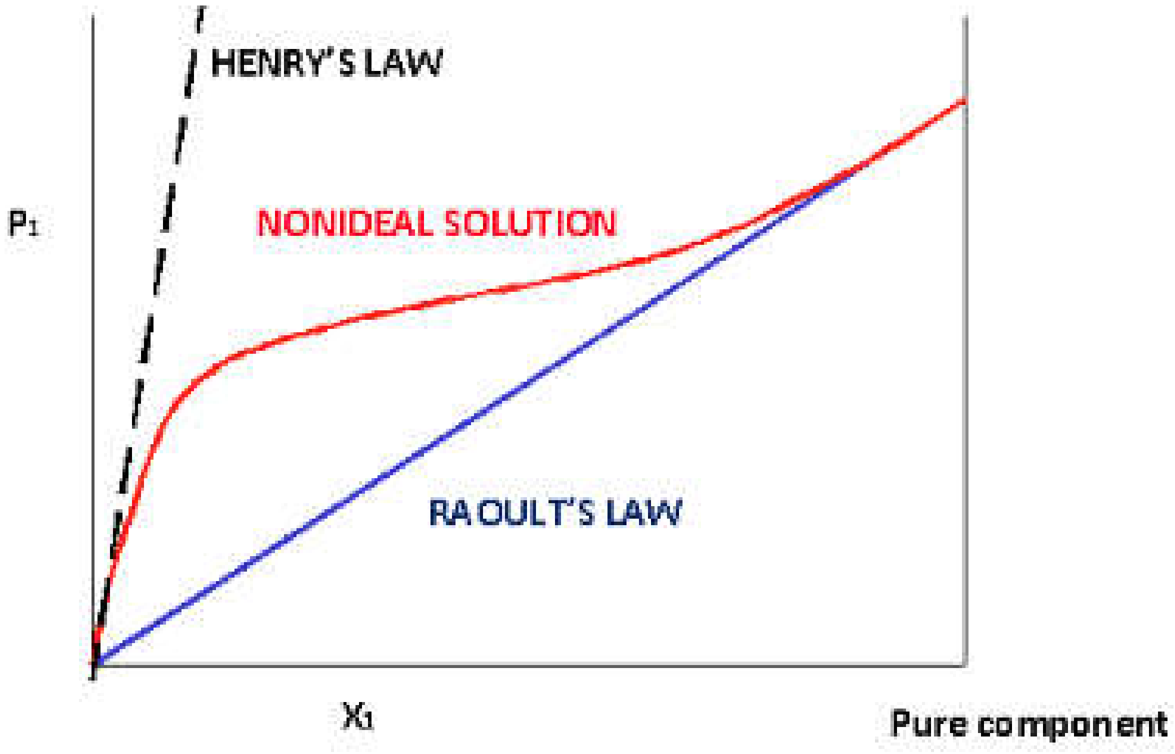
$C=kPgas$

where

C is the solubility of a gas at a fixed temperature in a particular solvent (in units of M or mL gas/L)

k is Henry's law constant (often in units of M/atm)

Pgas is the partial pressure of the gas (often in units of Atm)



Positive non-ideal behavior of the vapor pressure of a solution follows Henry's Law at low concentrations and Raoult's Law at high concentrations (pure).

Applicability of Henry's Law:

Henry's law only works if the molecules are at equilibrium.

Henry's law does not work for gases at high pressures (e.g., N2(g) at high pressure becomes very soluble and harmful when in the blood supply).

Henry's law does not work if there is a chemical reaction between the solute and solvent (e.g., HCl(g) reacts with water by a dissociation reaction to generate H3O and Cl− ions).

64.

Electrolyte Solutions:

Solutions are homogeneous mixtures containing one or more solutes in a solvent.

The solvent that makes up most of the solution, whereas a solute is the substance that is dissolved inside the solvent.

An electrolyte solution is a solution that generally contains ions, atoms or molecules that have lost or gained electrons, and is electrically conductive.

For this reason they are often called ionic solutions, however there are some cases where the electrolytes are not ions.

For this discussion we will only consider solutions of ions.

A basic principle of electrostatics is that opposite charges attract and like charges repel.

It also takes a great deal of force to overcome this electrostatic attraction.

The general form of Coulomb's law describes the force of attraction between charges:

$F = kq1mq2 / r2$

However, we must make some changes to this physics formula to be able to use it for a solution of oppositely charged ions. In Coulomb's Law, the constant

$k=1/4\pi\varepsilon0$

Where $\varepsilon0$ is the permittivity of free space, such as in a vacuum.

However, since we are looking at a solution, we must consider the effect that the medium (the solvent in this case) has on the electrostatic force, which is represented by the dielectric constant ε:

$F=q1q2 / 4\pi\varepsilon0\varepsilon r2$

Polar substances such as water have a relatively high dielectric constant.

65.

Ionic Solutions:

Using the rule "like dissolves like" with the formation of ionic solutions, we first assess two things:

The strength of the ion-dipole forces of attraction between water and the ionic compound and

The strength of the interionic bond of the ionic compound.

For an ionic compound to form a solution, the ion-dipole forces between water and ionic compound must be greater than the interionic bonds.

Therefore, to form a compound:

ion-dipole forces > interionic bonds

When the ionic compound is surrounded by water, the water dipoles surround the crystal's clustered structure.

The water's negative ends of the dipole will be attracted to the positive dipoles of the ion and the positive ends of the water's dipole will be attracted to the negative dipoles of the ion.

If the force of this attraction is stronger than the interionic bonds, the crystal's interionic bonds will be broken, then surrounded by the water molecules or hydrated .

There is a 3-step process that we can use to approach the energy involved in ionic solution formation.

Breaking apart the ionic compound is endothermic and requires energy.

Hydrating cation is exothermic and therefore releases energy.

Hydrating the anion is exothermic and also releases energy.

The sum of these 3 steps will then give us the enthalpy of the solution.

66.

Enthalpy of Solution 1:

A solution can either be in the gas phase, the liquid phase, the solid phase, or in a combination of these phases.

The enthalpy change of solution refers to the overall amount of heat which is released or absorbed during the dissolving process (at constant pressure).

The enthalpy of solution can either be positive (endothermic reaction) or negative (exothermic reaction).

The enthalpy of solution is commonly referred to as ΔHsolution.

When understanding the enthalpy of solution, it is easiest to think of three processes happening between two substances.

One substance is the solute, let’s call that A.

The other substance is the solvent, let's call that B.

The first process that happens deals only with the solute, A.

A has to break apart from the intramolecular forces holding it together.

This means the solute molecules separate from each other.

The enthalpy of this process is called ΔH1. This is an endothermic process because energy is required for this reaction, so ΔH1 > 0.

The second process is very similar to the first step.

Much like how the solute, A, needed to break apart from itself, the solvent, B, also needs to overcome the intermolecular forces holding it together.

This causes the solvent molecules separate from each other.

The enthalpy of this process is called ΔH2.

Like the first step, this reaction is an endothermic one and ΔH2 > 0 because energy is required to break the forces between the B molecules.

67.

Enthalpy of Solution 2:

Summary the last lesson is

The solute, A, has broken from the intermolecular forces holding it together and the solvent, B, has broken from the intermolecular forces holding it together as well.

It is at this time that the third process happens.

We also have two values ΔH1 and ΔH2. Both of these values are greater than zero (again, because both processes are endothermic)

The third process is when substance A and substance B mix.

The separated solute molecules and the separated solvent molecules join together to form a solution.

This solution will contain one mole of the solute A in an infinite amount of the solvent B.

The enthalpy of combining these two substances to form the solution is called ΔH3.

This is an exothermic reaction, because energy is given off as the two substances bond together; therefore, ΔH3 < 0.

The final value for the enthalpy of solution can either be endothermic or exothermic (so ΔHsolution can either be greater than zero or less than zero), depending on how much energy is required or given off in each step.

The enthalpy of solution can be written as a formula;

ΔHsolution = ΔH1 + ΔH2 + ΔH3.

If ΔHsolution = 0, then these solutions are called ideal solutions.

If ΔHsolution > 0 or ΔHsolution < 0, then these solutions are called non-ideal solutions.

The enthalpy of solution depends on the intermolecular forces of the solute and solvent.

If the solution is ideal, and ΔHsolution = 0, then that means ΔH1 added to ΔH2 is equal to ΔH3.

This means the forces of attraction between like (the solute-solute and the solvent-solvent) and unlike (solute-solvent) molecules are the same.

If the solution is non-ideal, then either ΔH1 added to ΔH2 is greater than ΔH3 or ΔH3 is greater than the sum of ΔH1 and ΔH2.

The first case means the forces of attraction of unlike molecules is greater than the forces of attraction between like molecules.

The second case means the forces of attraction between like molecules is greater than the forces of attraction between unlike molecules.

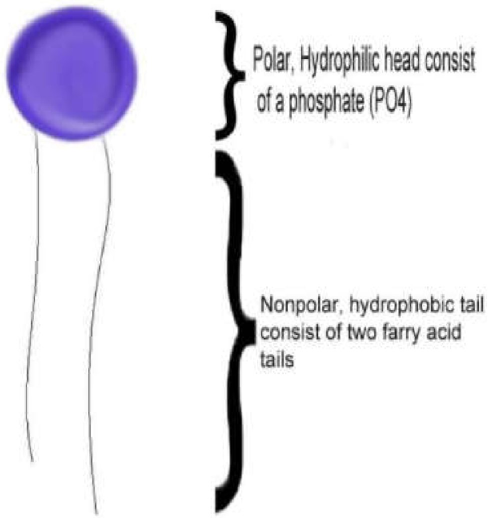
If ΔH3 is much greater than the sum of ΔH1 and ΔH2, then a heterogeneous mixture occurs.

68.

Intermolecular Forces in Solutions:

The epitome of intermolecular forces in solution is the miracle of solubility, because when a matter precipitates it no longer interacts with the solvent.

So what is the attraction between "like" molecules that makes them attract to each other?



How can a single molecule be both polar molecule loving and polar molecule disliking at the same time?

This is because at the polar head, the phosphate has a net negative charge thus attracting the partial positive charge of the hydrogen molecules of water.

Its nonpolar tails on the other hand, is a very organized form of hydrocarbon, consisting of no net charges.

The tail is then repelled by water as it struggles to fit between the partial positive and partial negative of the water molecule.

Another side effect of the interactions of molecules is reflected by the use of the activity coefficient during thermodynamic equilibrium constant calculations.

This constant differentiates ideal and nonideal solutions so that interactions for solution equilibrium can be more accurately estimated.

Most versions of the equilibrium constant K utilizes activity instead of concentration so that the units would disappear more fluently.

For an ideal solution, the activity coefficient is 1 [x]/ oCelcius, thus when the concentration is dived by it to yield activity, it is unaltered.

69.

Interionic Attractions:

This theory was discovered due to Arrhenius's theory having deficiencies.

Arrhenius's theory states that ions exist in a solid substance and dissociated from each other once the solid dissolves.

Arhennius's theory did not take into account the fact that strong electrolytes are not as great as he originally thought and the values of the van't Hoff factor i relied on the concentration of the solution.

The theory of electrolyte solution was brought about by Peter Debye and Erich Huckel in 1923.

Interionic Attractions are when an ion is surrounded by an ionic atmosphere which has a net charge opposite for its own.

For example an anion would be completely surrounded by ions mostly composed of cations and a cation would mostly be surrounded by ions of anions.

The ionic atmosphere decreases the mobility of each ion by exerting a drag on it, which in turn also decreases the magnitude of colligative properties.

The ionic atmosphere cannot created nor destroyed.

In solutions with weak electrolytes the number of ions is not large, therefore the effect of the interionic attraction is small.

In a concentrated solution of strong electrolytes the ion count is large, and therefore the interionic attraction will be apparent.

The reason behind the differences in the interionic attraction is that in concentrated solutions ions are closer together due to the large ion count, while in less concentrated solutions they are further apart.

70.

Units of Concentration 1:

Relative Concentration Units

Concentrations are often expressed in terms of relative unites (e.g. percentages) with three different types of percentage concentrations commonly used.

1. **Mass Percent**: The mass percent is used to express the concentration of a solution when the mass of a solute and the mass of a solution is given:

$$\text{Mass Percent} = \frac{\text{Mass of Solute}}{\text{Mass of Solution}} \times 100\%$$

2. **Volume Percent**: The volume percent is used to express the concentration of a solution when the volume of a solute and the volume of a solution is given:

$$\text{Volume Percent} = \frac{\text{Volume of Solute}}{\text{Volumeof Solution}} \times 100\%$$

3.

Mass/Volume Percent: Another version of a percentage concentration is mass/volume percent, which measures the mass or weight of solute in grams (e.g., in grams) vs. the volume of solution (e.g., in mL).

An example would be a 0.9%(w/v) NaCl solution in medical saline solutions that contains 0.9 g of NaCl for every 100 mL of solution.

The mass/volume percent is used to express the concentration of a solution when the mass of the solute and volume of the solution is given.

Since the numerator and denominator have different units, this concentration unit is not a true relative unit (e.g. percentage), however it is often used as an easy concentration unit since volumes of solvent and solutions are easier to measure than weights

- Moreover, since the density of dilute aqueous solutions are close to 1 g/mL, if the volume of a solution in measured in mL (as per definition), then this well approximates the mass of the solution in grams {making a true relative unit (m/m)}.

$$Mass/VolumePercent = \frac{Mass\ of\ Solute(g)}{Mass\ of\ Solution(mL)} \times 100\%$$