Central University of Haryana

Toxic and Hazardous substances

PROFESSOR DEEPAK PANT
CENTRAL UNIVERSITY OF HARYANA
MAHENDRAGARH
DPANT2003@YAHOO.COM

TOXIC PROPERTIES OF CHEMICAL SUBSTANCES

A **hazardous waste** is a solid waste or a combination of solid wastes, which because of its quantity, concentration, or physical, chemical, or infectious characteristics may cause, or significantly contribute to, an increase in mortality or cause an increase in serious irreversible illness; or pose a substantial present or potential hazard to human health and the environment when improperly treated, stored, transported, or disposed of, or otherwise managed.

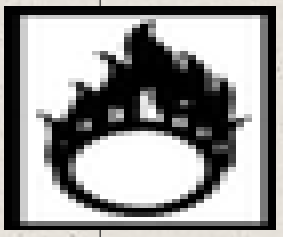
- Different states:
  - Solid
  - Semi-solid
  - Liquid
  - Contained gas

- Different characteristics:
  - Ignitability
  - Corrosivity
  - Reactivity
  - Toxicity

1. CATEGORIES

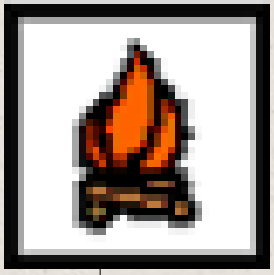
- Waste hazard codes
  - Ignitable waste — Type I
  - Corrosive waste — Type C
  - Reactive waste — Type R
  - Toxicity Characteristic Waste — Type E
  - Acute Hazardous Waste — Type H
  - Toxic Waste — Type T

Identification of Hazardous Waste Common Symbols



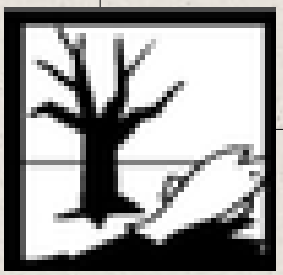
Oxidizer

Explosive



Flammable

Poison or toxic



Environmental Hazard

Corrosive

GHS Pictograms and Hazard Classes		
 • Oxidizers	 • Flammables • Self Reactives • Pyrophorics • Self-Heating • Emits Flammable Gas • Organic Peroxides	 • Explosives • Self Reactives • Organic Peroxides
 • Acute toxicity (severe)	 • Corrosives	 • Gases Under Pressure
 • Carcinogen • Respiratory Sensitizer • Reproductive Toxicity • Target Organ Toxicity • Mutagenicity • Aspiration Toxicity	 • Environmental Toxicity	 • Irritant • Dermal Sensitizer • Acute toxicity (harmful) • Narcotic Effects • Respiratory Tract Irritation

WHAT ARE IGNITABLE WASTES?

- A liquid with flash point less than 60°C (140°F);
- A solid is capable, under standard temperature and pressure, of causing fire through friction, absorption of moisture or spontaneous chemical changes and, when ignited, bums so vigorously and persistently ;
- A material that may, generally by yielding oxygen, cause or enhance the combustion of other materials”.

CORROSIVE WASTES (TYPE C)

Corrosive wastes are solid wastes that exhibit either of the following properties:

- It is aqueous and has a pH less than or equal to 2 or greater than or equal to 12.5,
- It is a liquid and corrodes steel at a rate greater than 6.35 mm (0.250 inch) per year at a test temperature of 55°C (130°F)."

REACTIVE WASTES (TYPE R)

Reactive wastes are solid wastes that exhibit any of the following properties:

- It is normally unstable and readily undergoes violent change without detonating,
- It reacts violently with water,
- It forms potentially explosive mixtures with water. When mixed with water, it generates toxic gases, vapors or fumes in a quantity sufficient to present a danger to human health or the environment,
- It is a cyanide or sulfide bearing waste which, when exposed to pH conditions between 2 and 12.5, can generate toxic gases, vapors or fumes in a quantity sufficient to present a danger to human health or the environment,
- It is capable of detonation *or* explosive reaction if it is subjected to a strong initiating source or if heated under confinement,
- It is readily capable of detonation or explosive decomposition or reaction at standard temperature and pressure.

INCOMPATIBLE WASTES

Incompatible wastes are hazardous wastes which, if placed together, could result in potentially dangerous consequences. An "incompatible waste" is a hazardous waste which is unsuitable for:

- Placement in a particular device or facility because it may cause corrosion or decay of containment materials (e.g., container inner liners or tank walls)"; or
- Commingling with another waste or material under uncontrolled conditions because the commingling might produce heat or pressure, fire or explosion, violent reaction, toxic dusts, mists, fumes, or gases, or flammable fumes or gases."

Question:1

Which of the following hazard warning labels are shown on the reagent bottle of benzene?

(1) Oxidizing

(2) Carcinogenic

(3) Flammable

a) (1) and (2) only

b) (1) and (3) only

c) (2) and (3) only

d) (1), (2) and (3)

Question:2

Toxic synthetic organic compounds frequently found in chemical waste dumps have been shown to cause

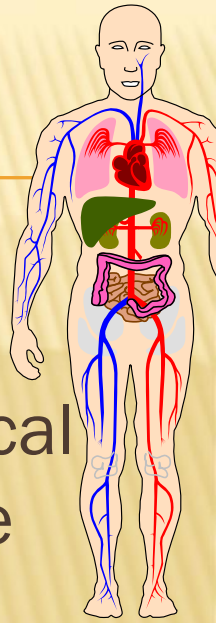
(a) birth defects.

(b) cancer.

(c) nervous system disorders.

(d) all of the above

PATHWAY OF ENTRY



- A toxicant can cause injury at the site of contact (local effects) such as skin, by damaging or destroying the tissues.
- The absorption of a chemical can occur through the lungs, skin, gastrointestinal tract, and several minor routes. The nature and the intensity of the toxicity of a substance would depend on its concentration in the target organs. Most toxicants are absorbed in the gastrointestinal tract upon ingestion.

The route of entry of many toxicants is inhalation. Such substances include gases, vapors of volatile liquids, and particulate matter. The main site of absorption is the alveoli in the lungs,

Many chemicals can be absorbed through the skin to produce a systemic effect. Although skin is relatively impermeable and acts as a barrier, certain chemicals can diffuse through the epidermis.

A chemical can bind in a tissue or organ. Such binding can result in its accumulation or higher concentration in the tissue.

Many chlorinated pesticides and polychlorinated biphenyl (PCBs) are soluble in lipid and remain stored in the adipose tissue.

Metal ions, such as lead, cadmium, and strontium, exchange with calcium in the bone and deposit.

Fluoride and other anions undergo ion exchange with hydroxide and accumulate in the bone. Such ion exchange takes place between ions of similar charges and radii.

After being absorbed and distributed in the organism, chemicals may be excreted, either as the parent compounds or as their metabolites and/or their conjugate adducts. The principal excretory organs are the kidney, liver, and lungs.

DETOXICATION AND BIOACTIVATION

Many chemicals absorbed into various parts of the body may undergo metabolic transformation. This process, also known as *biotransformation,* occurs in the organs and tissues. The most important site is the liver. Other sites of such reactions are the lungs, stomach, intestine, kidneys, and skin. The detoxication process involves the conversion of the toxicants to their metabolites, which in many cases are less toxic than the parent compounds.

Detoxication or biotransformation of toxicants involves two types of reactions:
(1) degradation, and
(2) addition or conjugation reactions.

Some biotransformation processes produce metabolites that are more toxic than the parent chemicals. Such reactions are also catalyzed by enzymes in a process as *bioactivation.*

Thus, bioactivation increases the toxicity of a compound.

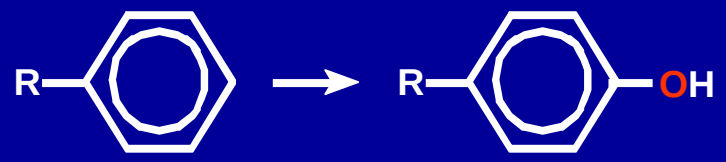
Some examples of degradative and conjugation reactions:

OXIDATION:

Aliphatic hydroxylation

$$R - CH_2 - CH_2 - CH_3 \longrightarrow R - CH_2 - CHOH - CH_3$$

Aromatic hydroxylation



Epoxidation

$$R - CH = CH - R' \longrightarrow R - \overset{O}{\overset{\diagup\diagdown}{CH - CH}} - R'$$

N-, O-, or S-dealkylation

$$R - \overset{H}{(N, O, S)} - CH_3 \longrightarrow R - (NH_2, OH, SH) + CH_2O$$

Deamination

$$R - CH_2 - NH_2 \longrightarrow R - \overset{O}{\overset{\|}{C}} - H + NH_3$$

N - hydroxylation

$$R - NH - \overset{O}{\overset{\|}{C}} - CH_3 \longrightarrow R - NOH - \overset{O}{\overset{\|}{C}} - CH_3$$

Sulphur oxidation

$$R - S - R' \longrightarrow R - \underset{\underset{O}{\|}}{S} - R'$$

De-sulphurnation

$$R_1R_2P - \overset{S}{\overset{\|}{X}} \longrightarrow R_1R_2P - \overset{O}{\overset{\|}{X}} + S$$

Oxidative dehalogenation

$$R - \underset{\underset{H}{|}}{\overset{\overset{X}{|}}{C}} - H \longrightarrow R - \underset{\underset{H}{|}}{\overset{\overset{X}{|}}{C}} - OH \longrightarrow R - \overset{O}{\overset{\|}{C}} - H + HX$$

Question:3

Detoxification or biotransformation of toxin involves which types of reactions:

(a) degradation, and addition

(b) degradation, and conjugation

(c) Both

(d)None of these

PHYSICAL PROPERTIES OF COMPOUNDS AND HAZARDOUS CHARACTERISTICS

Certain physical properties of a substance determine its hazard and the risk of human exposure.

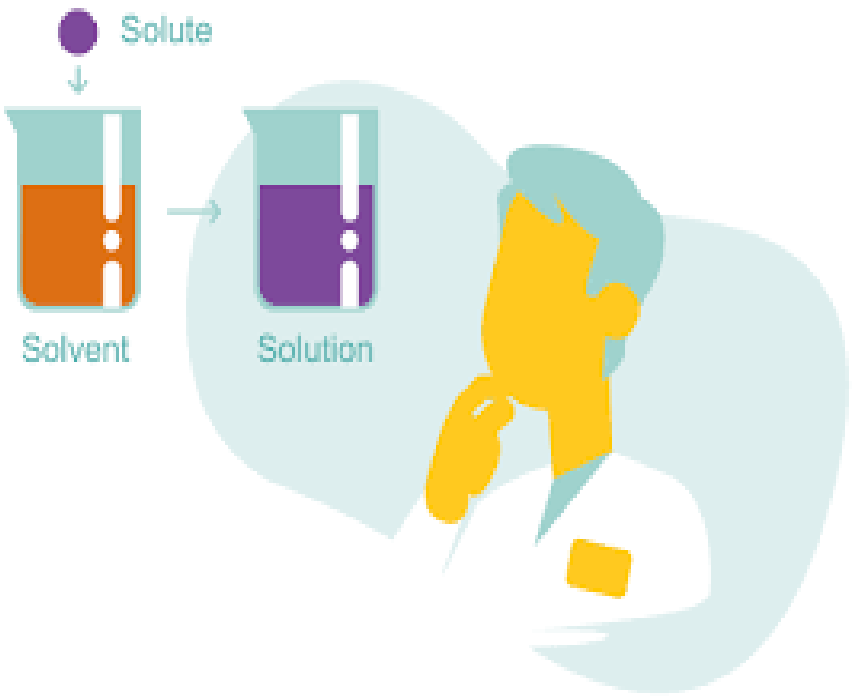
(1)Solubility
(2)Vapor Pressure
(3)Vapor density

Solubility

Solubility of a substance in water and other solvents is a very important physical property in toxicity studies. The fate of a pollutant, its oxidation, hydrolysis, biodegradation, groundwater contamination, and overall persistence in the environment depend on the water solubility.

Solubility

- the ability to be dissolved, especially in water.
- **Solubility** is the ability of a substance (the solute), to mix into a liquid (the solvent).[1]
- Solubility is the property of solid, liquid or gaseous chemical substance called solute to dissolve in a solid, liquid or gaseous solvent.



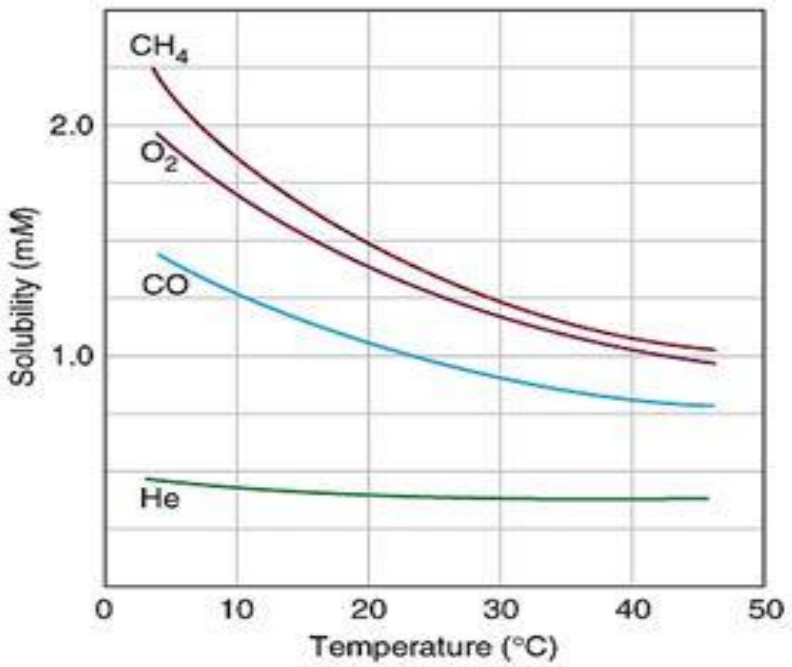
1. *Atkins' Physical Chemistry*, 7th Ed. by Julio De Paula, P.W. Atkins ISBN 0-19-879285-9

Solubility of any substance depends on:-

- temperature,
- pressure
- presence of other chemicals (including changes to the pH) of the solution.
- Nature of solvent & solute.

- The **solubility** of most solid and liquid solutions increases as the temperature increases. This is not true for gases; rather the solubility of gases decreases as the temperature increases.

Since an increase in temperature contributes to a decline in the solubility of gases in water; water that is of a higher temperature lacks oxygen.



Solubility product constant:-

- Every substance is soluble to some extent. Even the so-called insoluble salt may exhibit slight solubility at the ppm level. The solubility of a salt in water may be readily calculated from its solubility product constant (K_{SP}) value. The higher the K_{SP}, the greater the solubility.

Solubility-Product Constants, K_{sp}, at 25 °C

Fluorides	
BaF_2	2.4×10^{-6}
MgF_2	8×10^{-8}
PbF_2	4×10^{-8}
SrF_2	7.9×10^{-10}
CaF_2	3.9×10^{-11}
Chlorides	
$PbCl_2$	1.6×10^{-5}
$AgCl$	1.7×10^{-10}
Hg_2Cl_2[a]	1.1×10^{-18}
Bromides	
$PbBr_2$	4.6×10^{-6}
$AgBr$	5.0×10^{-13}
Hg_2Br_2[a]	1.3×10^{-22}
Iodides	
PbI_2	8.3×10^{-9}
AgI	8.5×10^{-17}
Hg_2I_2[a]	4.5×10^{-29}
Sulfates	
$CaSO_4$	2.4×10^{-5}
Ag_2SO_4	1.2×10^{-5}
$SrSO_4$	7.6×10^{-7}
$PbSO_4$	1.3×10^{-8}
$BaSO_4$	1.5×10^{-9}
Chromates	
$SrCrO_4$	3.6×10^{-5}
Hg_2CrO_4[a]	2×10^{-9}
$BaCrO_4$	8.5×10^{-11}
Chromates (*cont.*)	
Ag_2CrO_4	1.9×10^{-12}
$PbCrO_4$	2×10^{-16}
Carbonates	
$NiCO_3$	1.4×10^{-7}
$CaCO_3$	4.7×10^{-9}
$BaCO_3$	1.6×10^{-9}
$SrCO_3$	7×10^{-10}
$CuCO_3$	2.5×10^{-10}
$ZnCO_3$	2×10^{-10}
$MnCO_3$	8.8×10^{-11}
$FeCO_3$	2.1×10^{-11}
Ag_2CO_3	8.2×10^{-12}
$CdCO_3$	5.2×10^{-12}
$PbCO_3$	1.5×10^{-15}
$MgCO_3$	1×10^{-15}
Hg_2CO_3[a]	9.0×10^{-15}
Hydroxides	
$Ba(OH)_2$	5.0×10^{-3}
$Sr(OH)_2$	3.2×10^{-4}
$Ca(OH)_2$	1.3×10^{-6}
$AgOH$	2.0×10^{-8}
$Mg(OH)_2$	8.9×10^{-12}
$Mn(OH)_2$	2×10^{-13}
$Cd(OH)_2$	2.0×10^{-14}
$Pb(OH)_2$	4.2×10^{-15}
$Fe(OH)_2$	1.8×10^{-15}
$Co(OH)_2$	2.5×10^{-16}
Hydroxides (*cont.*)	
$Ni(OH)_2$	1.6×10^{-16}
$Zn(OH)_2$	4.5×10^{-17}
$Cu(OH)_2$	1.6×10^{-19}
$Hg(OH)_2$	3×10^{-26}
$Sn(OH)_2$	3×10^{-27}
$Cr(OH)_3$	6.7×10^{-31}
$Al(OH)_3$	5×10^{-33}
$Fe(OH)_3$	6×10^{-38}
$Co(OH)_3$	2.5×10^{-43}
Sulfides	
MnS	7×10^{-16}
FeS	4×10^{-19}
NiS	3×10^{-21}
CoS	5×10^{-22}
ZnS	2.5×10^{-22}
SnS	1×10^{-26}
CdS	1.0×10^{-28}
PbS	7×10^{-29}
CuS	8×10^{-37}
Ag_2S	5.5×10^{-51}
HgS	1.6×10^{-54}
Bi_2S_3	1.6×10^{-72}
Phosphates	
Ag_3PO_4	1.8×10^{-18}
$Sr_3(PO_4)_2$	1×10^{-31}
$Ca_3(PO_4)_2$	1.3×10^{-32}
$Ba_3(PO_4)_2$	6×10^{-39}
$Pb_3(PO_4)_2$	1×10^{-54}

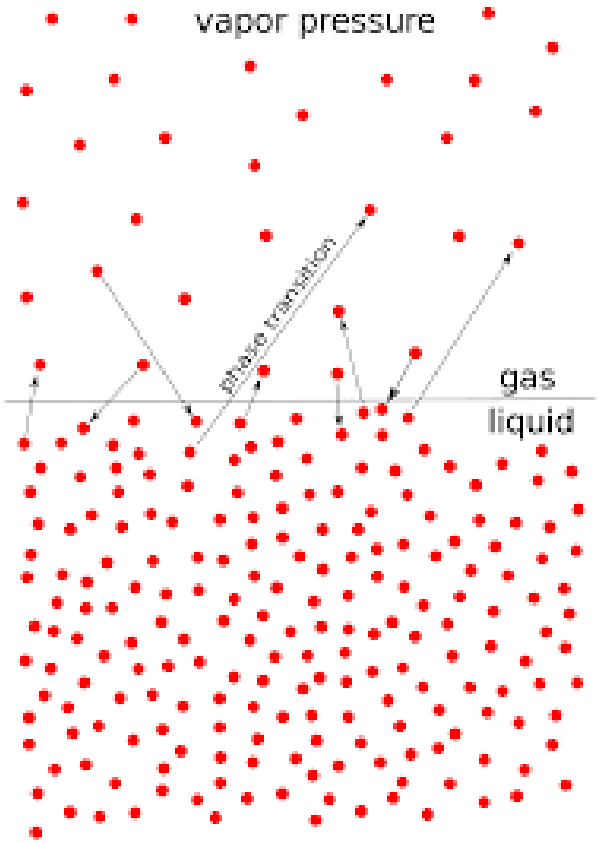
[a] As Hg_2^{2+} ion, $K_{sp} = [Hg_2^{2+}][X^-]^2$

Solubility cont.

- Solubility of a substance in water or lipid can indicate whether the water-soluble toxic metabolite is susceptible to excrete out from the body or a high lipid soluble substance would be retained in the body fat.[2]
- water solubility of a compound should be a decisive factor in extinguishing a fire, or diluting or cleaning up a spill.[4]
- .Many lipid soluble substances, such as dichloro diphenyl trichloro ethane (DDT) and polychlorinated biphenyl(PCBs),are stored in the body tissues and are not excreted readily.[9]

Vapour pressure

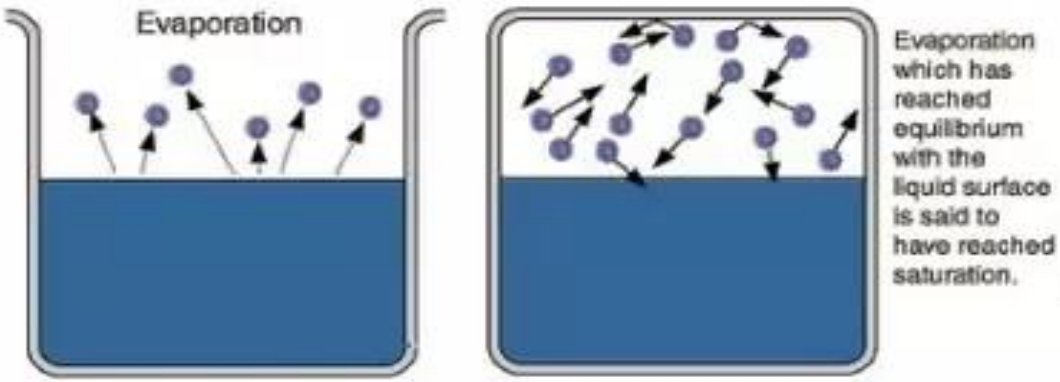
- The pressure of a vapour in contact with its liquid or solid form
- **Vapour pressure** is defined as the pressure exerted by a vapor in thermodynamic equilibrium with its condensed phases (solid or liquid) at a given temperature in a closed system.

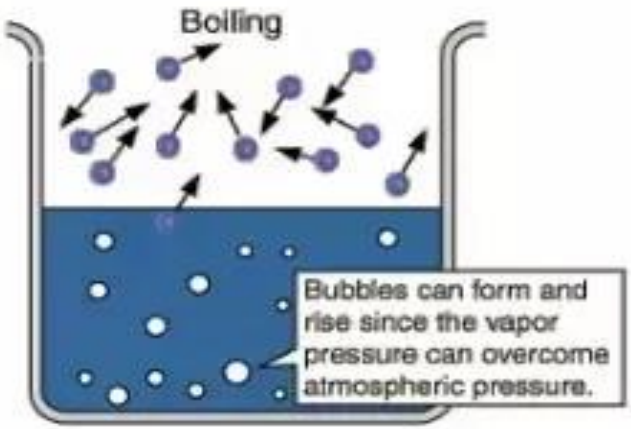


- The volatility of a substance can be assessed from its vapor pressure and boiling point.
- The latter is defined as the temperature at which the vapor pressure of a liquid is equal to the atmospheric pressure.
- The higher the temperature, the higher the vapor pressure.
- Similarly , the weaker the intermolecular forces, the higher the vapor pressure.

Section 14.2

Vapor Pressure and Boiling Point





At the boiling point, saturated vapor pressure equals atmospheric pressure.

Vapor Pressure

Inhalation toxicity and the level of exposure to liquid substances may depend on their volatility. The more volatile a substance, the greater the risk of exposure of inhaling its vapors.

The volatility of a substance can be assessed from its vapor pressure and boiling point.

Vapor pressure is related to the temperature and the intermolecular forces. The higher the temperature, the higher the vapor pressure. Similarly, the weaker the intermolecular forces, the higher the vapor pressure.

- **Inhalation toxicity** and the **level of exposure** to such liquid substances may depend on their volatility.
- The more volatile a substance, the greater the risk of exposure of inhaling its vapors.
- The vapors of many flammable substances form explosive mixtures with air.
- Therefore, knowledge on volatility of a substance is essential to assess itsfire,explosion,and toxic hazard and the risk of exposures, especially in confined places.
- Substances of low molecular weights have vapor pressures and water solubilites greater than those of high-molecular-weight compounds in the same family.

The **relationship between the vapor pressure and temperature** can be mathematically expressed in the following equation:

$$\ln P = \frac{-\Delta Hvap}{R}\left(\frac{1}{T}\right) \pm C$$

where, lnP is the natural logarithm of the vapor pressure P; ΔHvap is the heat of vaporization of the liquid. T is the temperature in K; R is the universal gas constant (8.31 J/mol); and C is a constant. This is known as the Clausius–Clapeyron equation.

Vapour density

- Vapour density is the **density of vapour in relation to that of hydrogen** .It may be defined as mass of a certain volume of a substance divided by mass of same volume of hydrogen.
- It is often necessary to know whether the vapors of a hazardous substance is heavier than air. For example, vapors of a flammable liquid, such as, diethyl ether are heavier than air and can present a “flashback” fire hazard. Being heavier than air, they remain longer near their sources and do not dissipate up or vent out readily into the air. Also, this may present a relatively high-level exposure and occupational health problem.

- It may be noted that **the vapor density is different from the gas density**. While the latter is defined as the mass of a gas per unit volume, usually expressed as grams per liter (g/L) at a specific temperature,the vapor density simply indicates how many times the vapor of a substance is heavier than air. It does not have a unit .

odour

- Odour is probably the most sensitive of the human perceptory organs(sense organs). Many chemicals can be identifie at trace levels from their odor. Odour may serve as an indicator to warn of the presence of highly odorous hazardous substances. Odour is another physical property of great significance. Many hazardous substances such as hydrogen sulfide or ammonia can be readily identified from their odour.unit of odour is “oif” derived from latin word “olfactus” which means smell.

Classification of odour:-

Odors have been quantified in several different ways:-

(1) threshold odour concentration (TOC),

(2) odor recognition threshold,

(3) Threshold odour number (TON) and

(4) odour index (OI)

- **(1) Threshold odor concentration**:- The TOC may be defined as the absolute

perception threshold (at which the odor

is barely identifiable, but too faint)

- **(2) Odour recognition threshold**:- the recognition threshold (100%) means the

threshold concentration of the odorant whose odor may be defined (or accepted) by 100% odor panel as being representative odor of the substance being studied. By contrast, when 50% odor panel define the odor that is representative of the substance, then the above term becomes “50% recognition threshold

(3) Threshold odour number (TON):–The TON is the number of times a given volume of the gaseous sample is to be diluted in clean air to bring it to the threshold odor level determined by 50% of a panel of observers. Its intensity is expressed in odor units.

(4) Odour index (OI):–The OI, is the ratio of vapor pressure to 100% odor recognition threshold. Both the terms, that is, the vapor pressure and the odor recognition threshold, are expressed in ppm. Therefore, the OI becomes a dimensionless term.

$$OI = \frac{vapor\ pressure(ppm)}{100\%odar\ recognisation\ threshold(ppm)}$$

Chemical pollutant oxidation

- Chemical oxidation is a process involving the transfer of electrons from an oxidizing reagent to the chemical species being oxidized.
- The aim of chemical oxidation is to oxidize organic pollutants to less dangerous or harmless substances. In the best case scenario, complete oxidization of organic substances will result in CO2 and H2O. This technique can also be used to remove inorganic components (e.g. oxidization of cyanide).

Assignment:

- Explore physical properties of compounds and hazardous characteristics of some common substance around us in terms of (i) Vapour Pressure; (ii) Vapour density and (iii) Solubility

- Define each of the following terms in our daily life: (i) Ignitable waste; (ii) Corrosive waste; (iii) Reactive waste and (iv) Toxic waste

THANK YOU