

*EQUILIBRIUM, MASS  
CONSERVATION,  
AND KINETICS*

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# *1 Concentration*

The subject of mass transfer involves movement of one mass species through one or more other species.

The quantity of a certain species is described by its concentration, which is defined as the amount of substance per unit mass or volume.

$$\rho_A = \text{mass concentration} = \frac{\text{mass of } A}{\text{unit volume}} = \frac{\text{kg of } A}{\text{m}^3}$$

$$c_A = \text{molar concentration} = \frac{\text{moles of } A}{\text{unit volume}} = \frac{\text{mol of } A}{\text{m}^3}$$

Thus, the two concentrations can be interchanged using the relation

$$\rho_A = c_A M_A$$

Where  $M_A$  is the molecular weight of component A.

# *Concentration in a Gaseous Mixture*

In a mixture of perfect gases, the concentrations of individual gases can be calculated from their partial pressures. Using the ideal gas law for a mixture of gases of total volume  $V$  at temperature  $T$ , we can write for the component  $A$

$$p_A V = n_A R_g T$$

Where  $P_A$  is the partial pressure of gas  $A$  for which there is  $n_A$  moles are present and  $R_g$  is the gas constant.

$$c_A = \frac{n_A}{V} = \frac{p_A}{R_g T}$$

Thus, concentration of any gas species  $i$  can be written as

$$c_i = \frac{p_i}{R_g T}$$

The total concentration  $c$  is written as

$$c = \frac{P}{R_g T}$$

## ***Example 1 Concentration of Individual Gases in air***

Consider an air-water vapor mixture at a total pressure of 1 atm and a temperature of 60°C having 20% water vapor, 17% oxygen, and 63% nitrogen. Calculate the molar and mass concentrations of each of the three gases in air.

Analysis: *Molar* concentration as

$$c_{\text{vapor}} = \frac{p_{\text{vapor}}}{R_g T} = \frac{0.2 \times 1.013 \times 10^5 \text{ N/m}^2}{8.315 \text{ J/mol} \cdot \text{K} \times 333 \text{ K}} = 7.32 \frac{\text{mol}}{\text{m}^3}$$

$$c_{\text{oxygen}} = \frac{p_{\text{oxygen}}}{R_g T} = \frac{0.17 \times 1.013 \times 10^5 \text{ N/m}^2}{8.315 \text{ J/mol} \cdot \text{K} \times 333 \text{ K}} = 6.22 \frac{\text{mol}}{\text{m}^3}$$

$$c_{\text{nitrogen}} = \frac{p_{\text{nitrogen}}}{R_g T} = \frac{0.63 \times 1.013 \times 10^5 \text{ N/m}^2}{8.315 \text{ J/mol} \cdot \text{K} \times 333 \text{ K}} = 23.05 \frac{\text{mol}}{\text{m}^3}$$

Mass concentration as

$$\rho_{vapor} = 7.32 \times 18 \times 10^{-3} \frac{kg}{m^3} = 0.1317 \frac{kg}{m^3}$$

$$\rho_{oxygen} = 6.22 \times 32 \times 10^{-3} \frac{kg}{m^3} = 0.1990 \frac{kg}{m^3}$$

$$\rho_{nitrogen} = 23.05 \times 28 \times 10^{-3} \frac{kg}{m^3} = 0.6454 \frac{kg}{m^3}$$

The total molar concentration of gases is given by

$$\begin{aligned} c &= c_{vapor} + c_{oxygen} + c_{nitrogen} \\ &= 7.32 + 6.22 + 23.05 \frac{mol}{m^3} = 36.59 \frac{mol}{m^3} \end{aligned}$$

and the total mass concentration of gases is given by

$$\begin{aligned} \rho &= \rho_{vapor} + \rho_{oxygen} + \rho_{nitrogen} \\ &= 0.1317 + 0.1990 + 0.6454 \frac{kg}{m^3} = 0.9761 \frac{kg}{m^3} \end{aligned}$$

# *2 Species Mass Balance*

## *(Mass Conservation)*

Like total energy, total mass is conserved. For example, though chemical reactions.

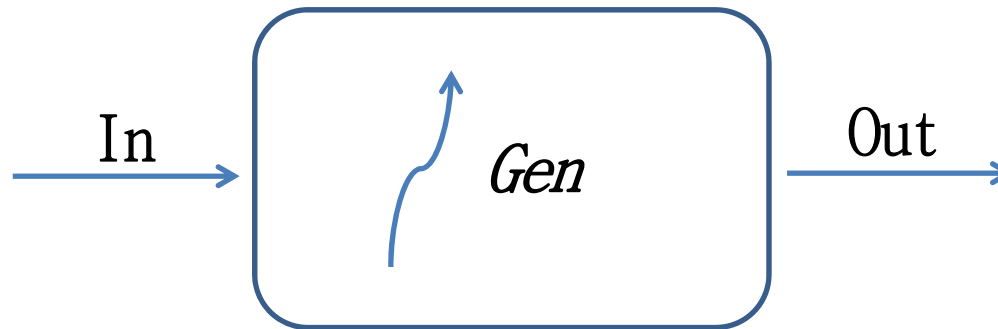


Figure 1. A control volume for mass conservation showing different components.

A word equation for mass conservation of a species can be written from this figure as

$$\underbrace{\text{Rate of Mass In}}_{\text{species } i} - \underbrace{\text{Rate of Mass Out}}_{\text{species } i} + \underbrace{\text{Rate of Mass Generation}}_{\text{species } i} = \underbrace{\text{Rate of Mass Storage}}_{\text{species } i}$$

# *3 Equilibrium*

The transfer of mass within a phase or between two phases requires a departure from equilibrium.

## *Equilibrium Between a Gas and a Liquid*

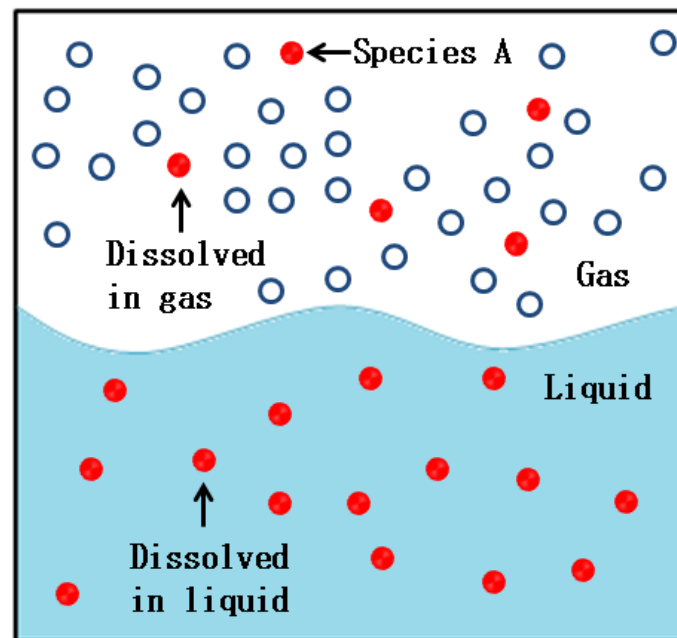


Figure 2. Schematic of equilibrium between a gas and a liquid phase.



An example of equilibrium between gas and liquid is water saturated with dissolved oxygen in contact with air, as shown in Figure 9.3. Such equilibrium between a gas and a liquid phase can be described by the well known Henry' s law:

$$p_A = Hx_A$$

Where  $p_A$  is the partial pressure of species  $A$  in gas phase at equilibrium.  $x_A$  is the concentration of species  $A$  in liquid phase at equilibrium, and  $H$  is the Henry' s constant. Equation 9.6 is illustrated in Figure 9.5

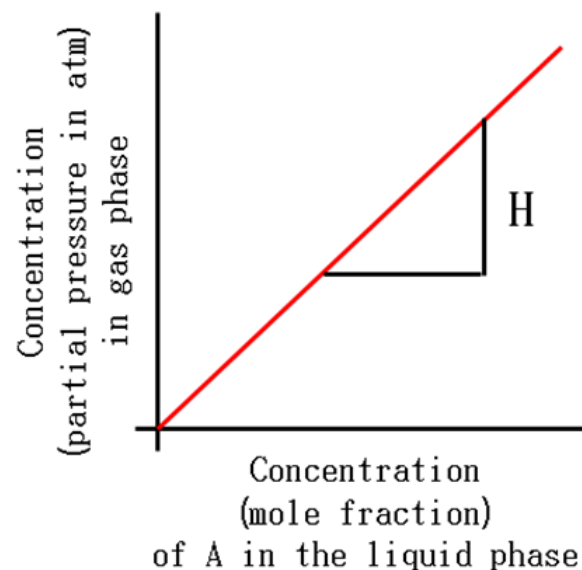


Figure 3. Equilibrium relationship between a gas phase and a liquid phase following Henry' s law.

$$x_A = \frac{p_A}{H}$$

Henry's constant for several gases in water are given in Figure 9.4.

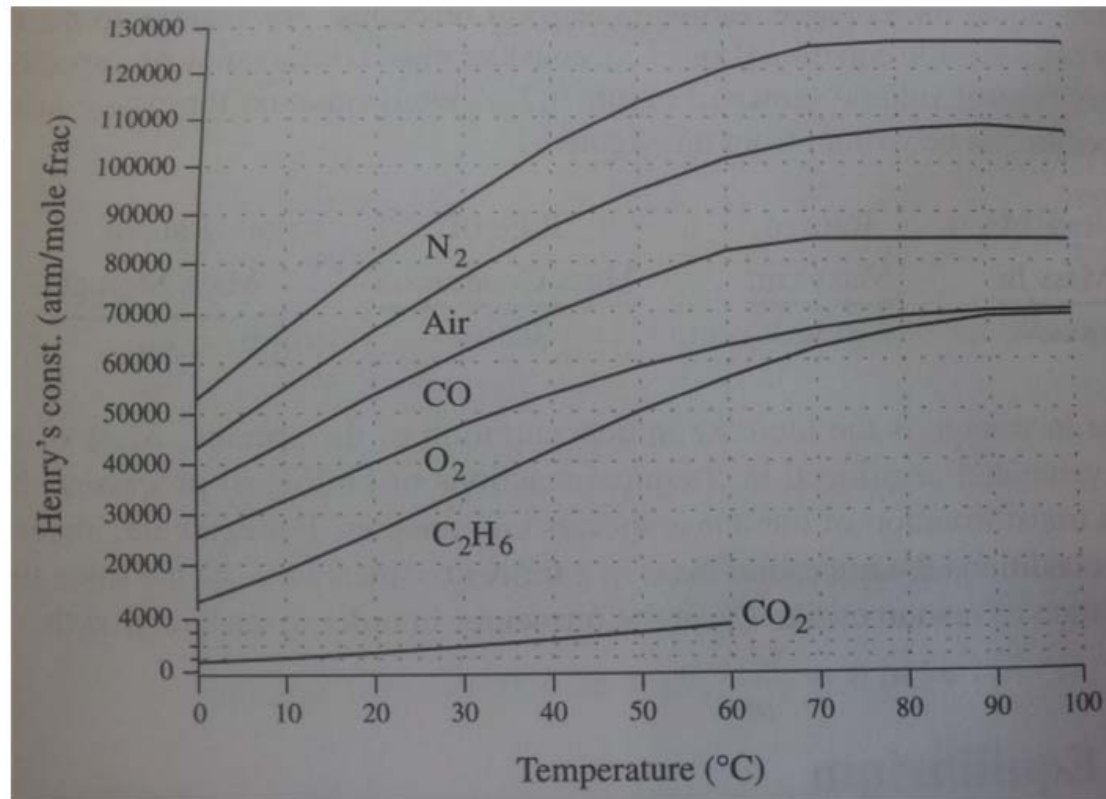


Figure 4. Henry's constant,  $H$ , for gases slightly soluble in water. Data abridged from Foust et al.(1960)

## ***Example 2 Oxygen Concentration in Water in Equilibrium with Air***

Water at 5°C is in contact with a large volume of ordinary air at a total pressure of 1 atmosphere 1)How much oxygen is dissolved in the water in mgO<sub>2</sub>/liter of water? 2)What is the new amount of oxygen dissolved in the same units? 3)What happens is water at 25°C and having initially an amount of oxygen 10mg O<sub>2</sub>/liter of water?

Analysis:

1)  $p_{O_2} = 0.21\text{atm}$ . Using Henry's law to find the concentration of oxygen in the water,  $x_{O_2}$ , at equilibrium at 5°C:

$$\begin{aligned}
x_{O_2} &= \frac{p_{O_2}}{H} \\
&= \frac{0.21 \text{ atm}}{2.9 \times 10^4 \text{ atm/mole fraction}} \\
&= 7.241 \times 10^{-6} [\text{mol } O_2 / \text{mol solution}] \\
&\approx 7.241 \times 10^{-6} [\text{mol } O_2 / \text{mol water}] \\
&= 7.241 \times 10^{-6} \times \frac{32}{18} [\text{g } O_2 / \text{mol water}] \\
&= 12.87 [\text{mg } O_2 / \text{liter of water}]
\end{aligned}$$

2) Similarly, the amount of oxygen dissolved in water at 25°C is

$$\begin{aligned}
x_{O_2} &= \frac{p_{O_2}}{H} \\
&= \frac{0.21 \text{ atm}}{4.45 \times 10^4 \text{ atm/mole fraction}} \\
&= 4.719 \times 10^{-6} [\text{mol } O_2 / \text{mol solution}] \\
&= 8.39 [\text{mg } O_2 / \text{liter of water}]
\end{aligned}$$

# *Equilibrium Between a Gas and a Solid (with Adsorbed Liquid)*

The common example of a solid coming in equilibrium with a gas is the potato chip typically becoming soggy when left out of the package. The moisture in the potato chip comes to equilibrium with typically higher amount of water vapor in the outside air than inside the package.

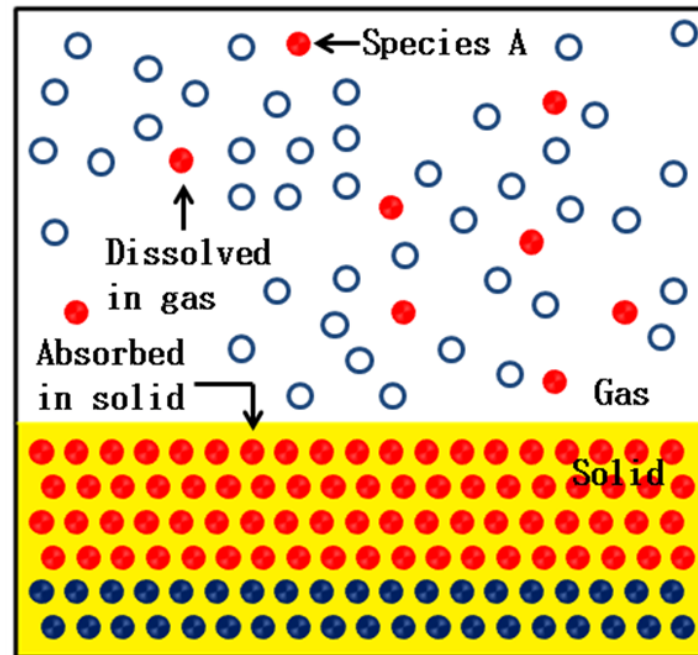


Figure 5. Schematic of equilibrium between a gas and a solid phase.

The relationship between the concentration of moisture in air and the corresponding equilibrium moisture content of a solid can be expressed as an equilibrium moisture curve. A typical curve is Figure 6.

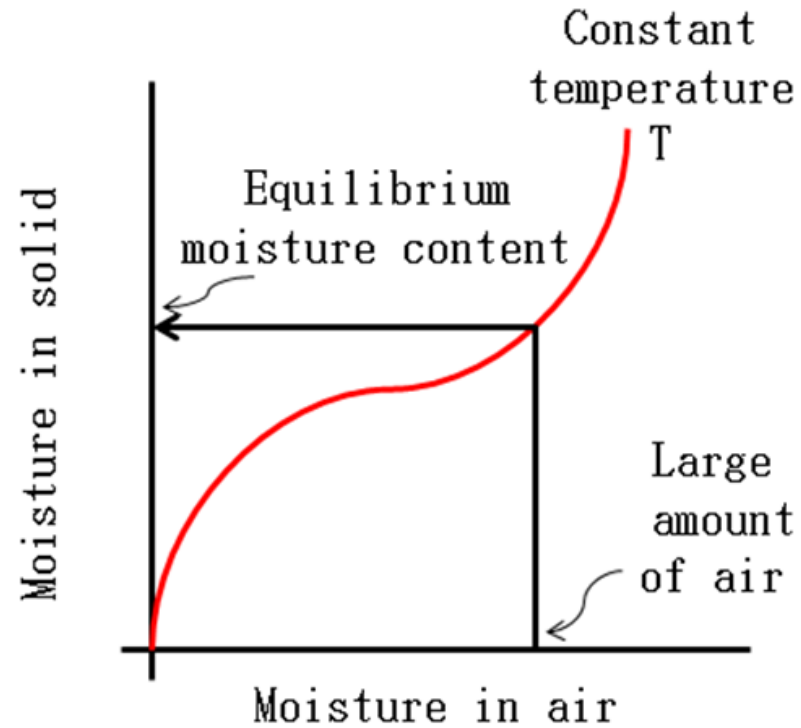


Figure 6. Typical equilibrium moisture isotherm.

Example of an empirical equation used to represent the equilibrium moisture content curve is:

$$1 - RH = b_1 \exp(-b_2 w)$$

Where RH is the relative humidity,  $b_1$  and  $b_2$  are constants, and  $w$  is the equilibrium moisture content(%).

## ***Hygroscopic and non-hygroscopic solids***

The moisture in air would come to equilibrium with moisture in the solid, as illustrated in Figure 6. This equilibrium relative humidity of the air is also called the *water activity* of the solid at its moisture content.

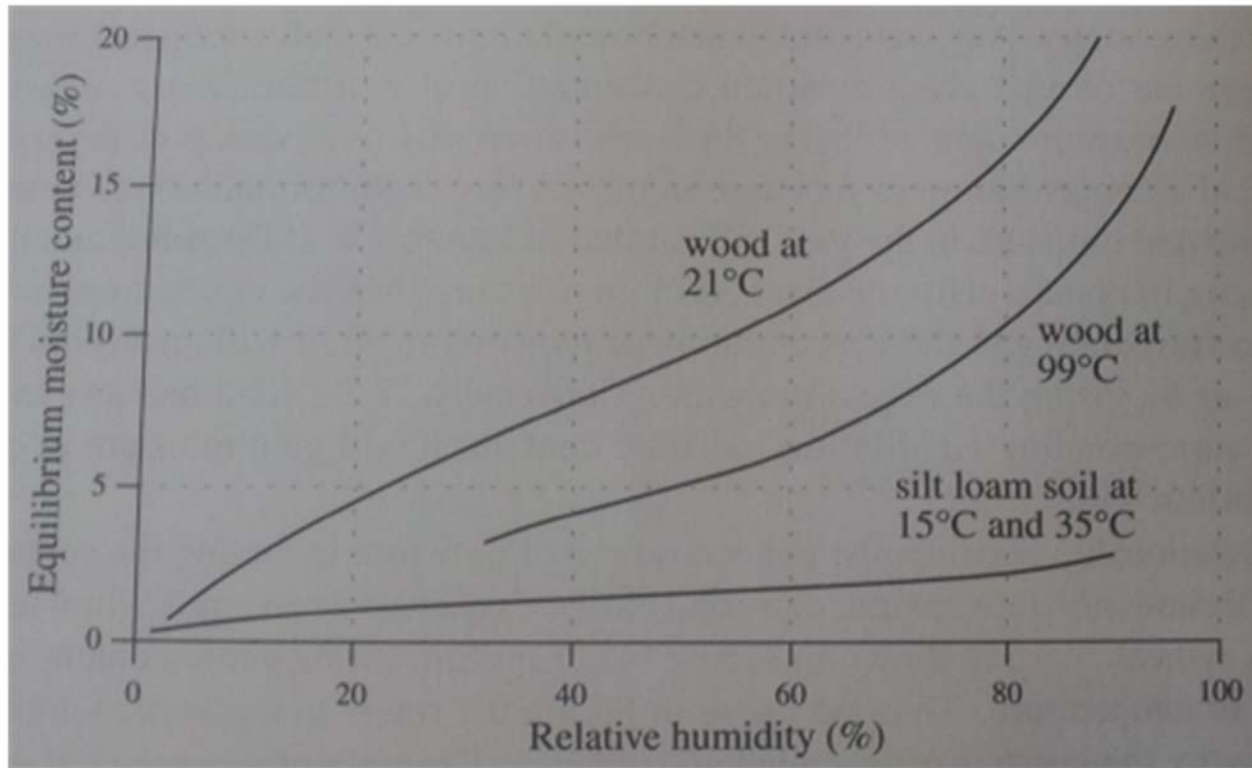


Figure 7. Moisture isotherm.

The equilibrium moisture isotherms in Figure 7 show that the relative humidity and therefore the vapor pressure of air surrounding a solid in a closed system is function of both moisture content and temperature of the solid.



The vapor pressure above the surface as a function of temperature is given by the Clausius-Clapeyron equation:

$$\frac{d \ln p_v}{dT} = \frac{\Delta H_{vap}}{RT^2}$$

# *Equilibrium Between a Solid and a liquid in Adsorption*

Consider a solid surface in contact with a liquid that has a dissolved species. As illustrated in Figure 9.10, some of the dissolved solute will bind to the solid surface, instead of remaining in solution.

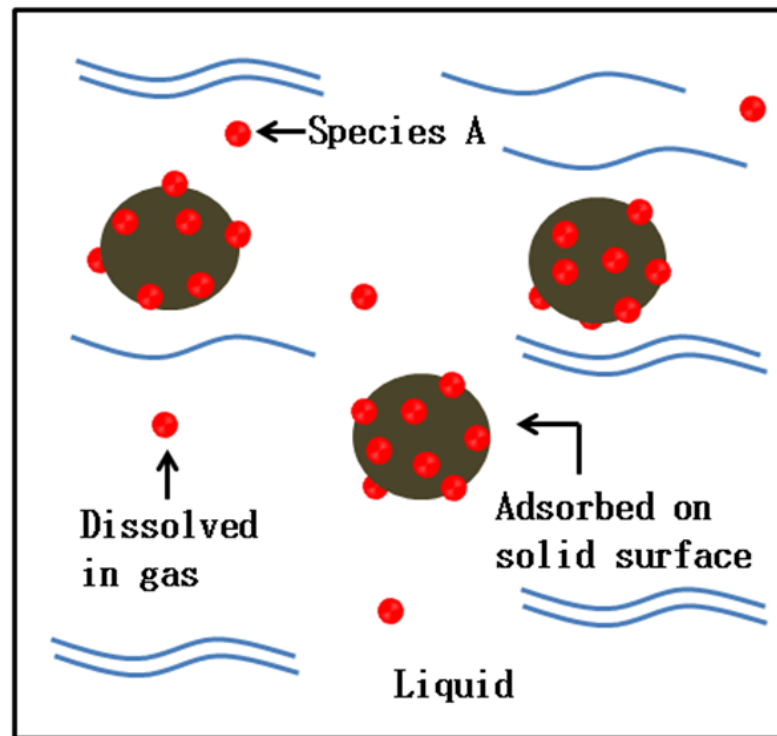


Figure 8. Equilibrium between dissolved and surface adsorbed species.

The isotherm shown in Figure 10 can be represented mathematically as

$$c_{A,adsorbed} = K^* c_A^n$$

Where  $c_{A,adsorbed}$  is the concentration of adsorbed A,  $c_A$  is the concentration of solute A in solution, and  $K$  and  $n$  are empirical constants.

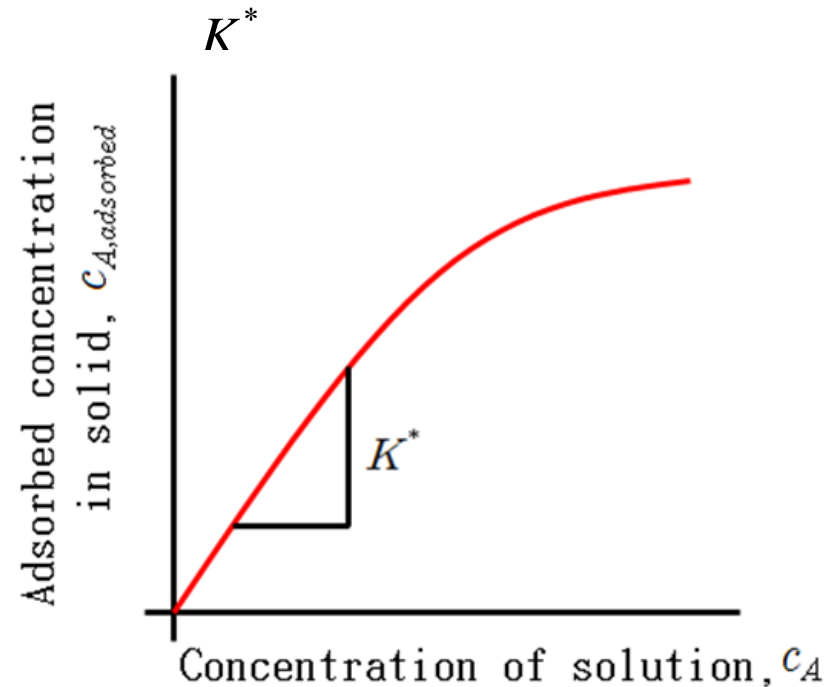


Figure 10. Freundlich isotherm.

# *4 Chemical Kinetics:*

## *Generation of Depletion of a Mass Species*

**Chemical Kinetics** is the study of the rate and mechanism by which one chemical species is converted to another species.

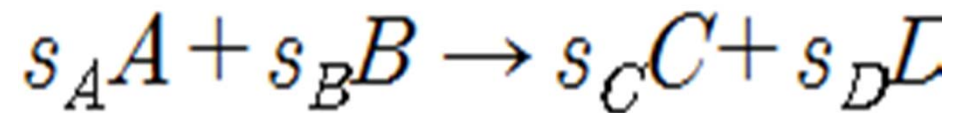
The rate of a chemical reaction is defined by

$$\text{Rate} = \frac{\text{Mass of product produced or reactant consumed}}{(\text{Unit volume})(\text{Time})}$$

# *Rate law of Homogeneous Reactions*

Rate laws describe the dependence of the reaction rates on concentration.

Consider an irreversible reaction:



<  $s_A, s_B, s_C, s_D$  are stoichiometric coefficient >

The rate of disappearance of A

$$r_A = - \frac{dc_A}{dt} = k'' c^{\alpha_A} c^{\beta_B}$$

a : the order of reaction with respect to A

b : the order of reaction with respect to B

a+b : the overall order of reaction

k'' : the reaction rate constant

✘ While many variables may affect the reaction, temperature is the most important.

## *Zeroth Order Reaction*

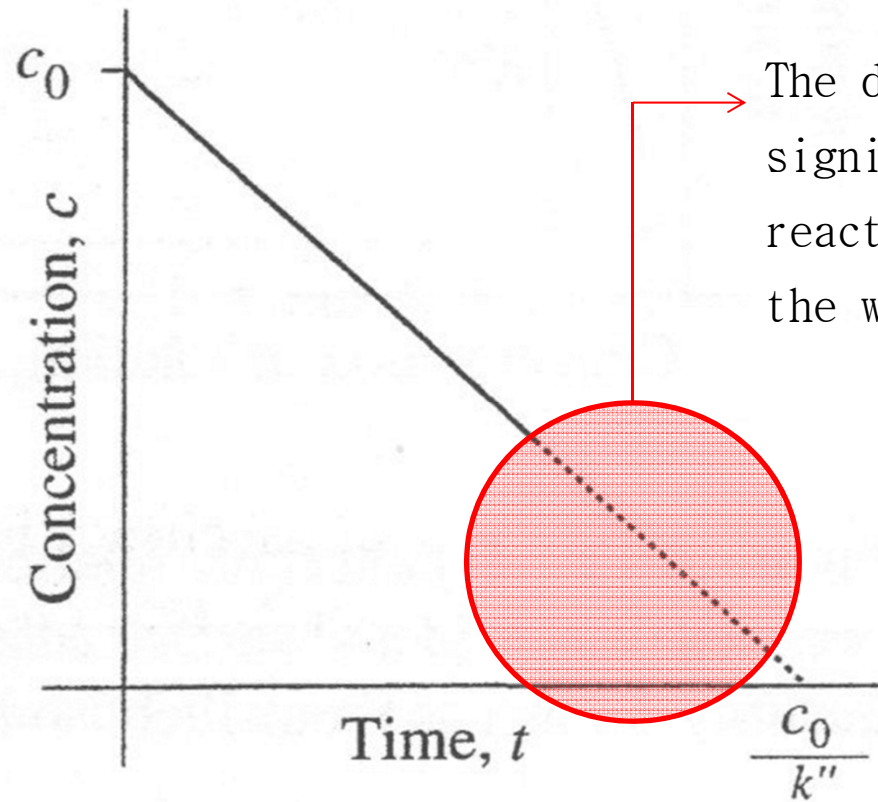
A reaction is of zeroth order when the rate of reaction is independent of the concentration of the species

$$r_A = -\frac{dc}{dt} = k''$$

Integrating, and noting that  $c$  can never becoming negative

$$c_0 - c = k'' t \quad \text{for } t \leq \frac{c_0}{k''}$$

Linear change in concentration for a zeroth order reaction..



The dashed line in the figure signifies that the zeroth order reaction may not continue all the way.



# *First Order Reaction*

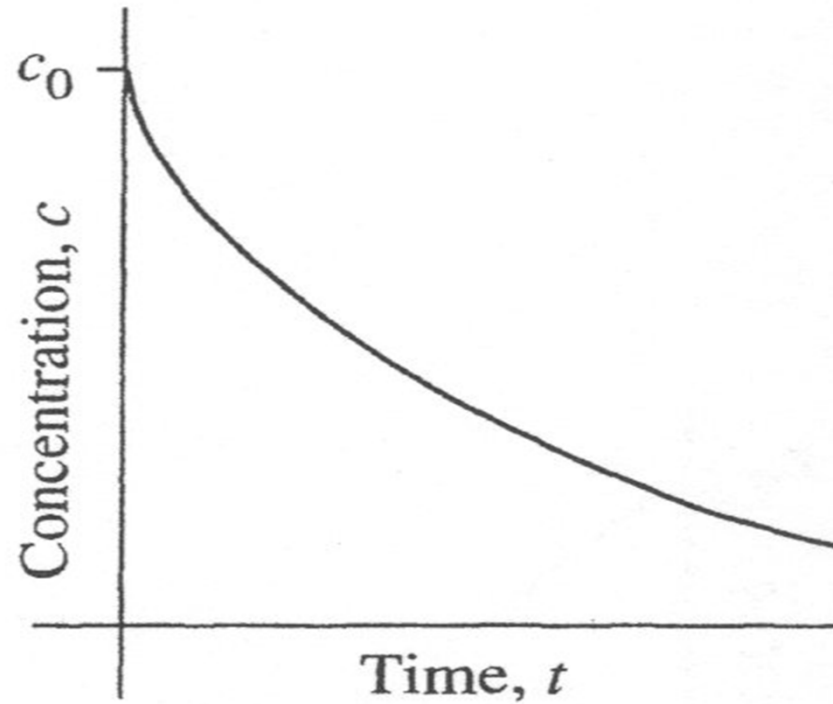
A reaction is first order when the rate of reaction is linearly related to the concentration of the species.

$$r_A = -\frac{dc}{dt} = k''c$$

$$-\frac{dc}{c} = k''dt$$

$$-\int_{c_0}^c \frac{dc}{c} = \int_0^t k'' dt$$

$$-\ln \frac{c}{c_0} = k''t \quad \longrightarrow \quad c = c_0 e^{-k''t}$$



✧ Exponential change in concentration for a first order reaction.

✧ The concentration never actually reaches zero even though it becomes very small.

Half life for a first order reaction is a convenient alternative description of reaction rate that is used widely in practice.

※ **Half-life** :

defined as the time to change concentration by 50%.

$$0.5c_0 = c_0 e^{-k'' t_{1/2}}$$

$$-k'' t_{1/2} = \ln(0.5)$$

$$= -0.693$$



$$c = c_0 e^{-\frac{0.693}{t_{1/2}} t}$$

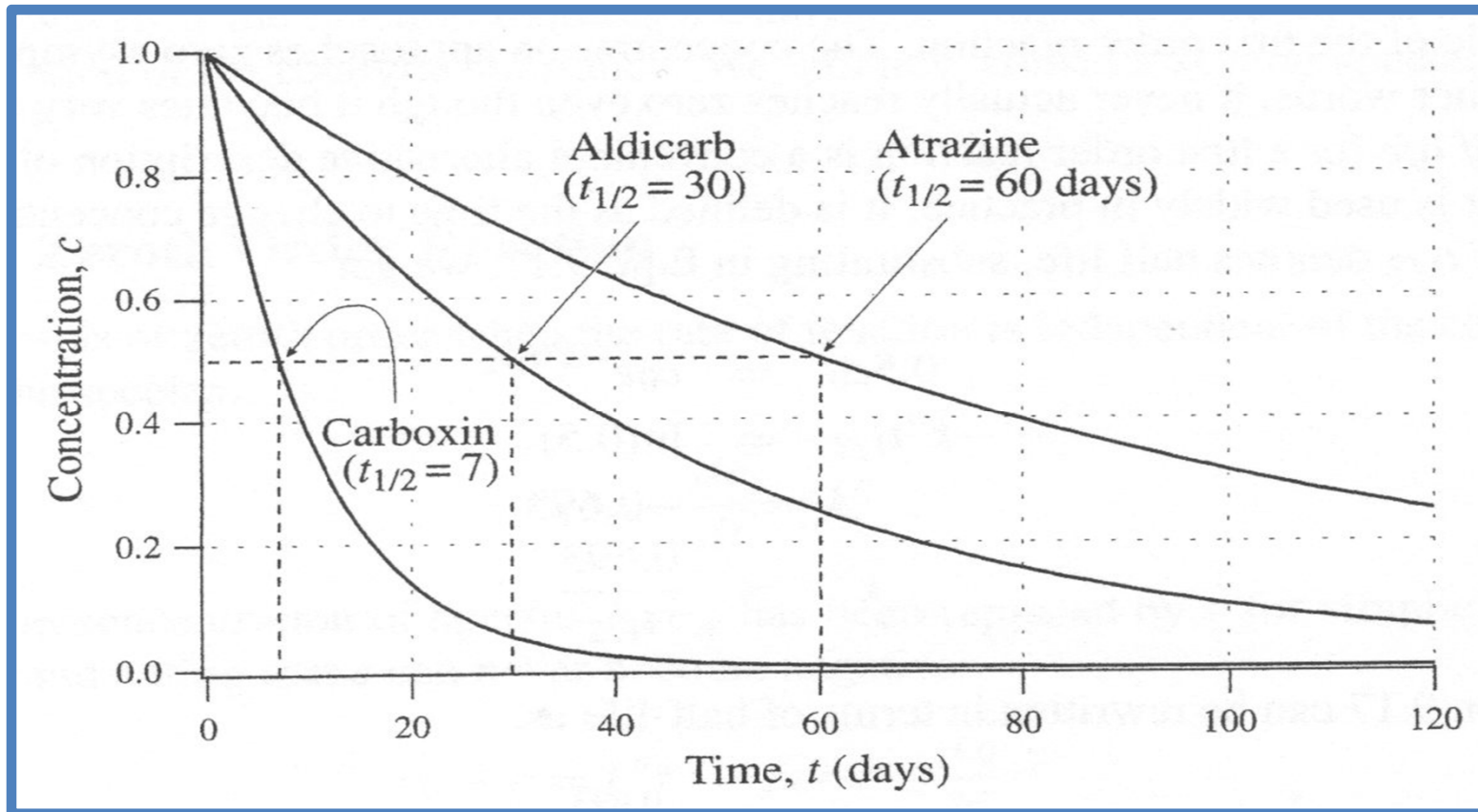
$$k'' = \frac{0.693}{t_{1/2}}$$

## For example )

Pesticide	t <sub>1/2</sub> in soil (days)	Health advisory level ( μ g/L or ppb)
Aldicarb	30	10
Atrazine	60	3
Carboxin	7	700

→ Half life of some important pesticides.

Here the health advisory level is the concentration level of a substance which is considered safe to be consumed daily throughout a person' s lifetime.



Concentration change with time (due to decay) for the pesticides listed in Table.

## ***nth Order Reaction***

When the mechanism of a reaction is not known, we often attempt to fit the data with an nth order rate equation of the form

$$r_A = -\frac{dc}{dt} = k'' c^n$$

Integrating :

$$\int_{c_0}^c \frac{dc}{c^n} = -\int_0^t k'' dt$$

$$\frac{c^{-n+1} \Big|_{c_0}^c}{-n+1} = -k'' t$$

Putting the limits and rearranging :

$$c^{1-n} - c_0^{1-n} = (n-1)k'' t, \quad n \neq 1$$

which provides concentration  $c$  as a function of time,  $t$ , for a nth order reaction.

## *Effects of Temperature.*

$$k'' = k_0'' e^{-E_a / (RT)}$$

※ Higher temperature speeds up most reactions.

※  $k_0''$  is called the frequency factor,  $E_a$  is called the activation energy (J/mole),  $R_g$  is the gas constant (J/mole · K),  $T$  is the absolute temperature in K.

# *Chapter Summary – Equilibrium, Mass Conservation, and Kinetics*

## ▲ Equilibrium

1. Equilibrium between a gas and a liquid is described by Henry's law.
2. Equilibrium between gas and a solid is described by isotherms.
3. Equilibrium between a solid and liquid in absorption.

## ▲ Kinetics of Chemical Reactions

1. A reaction where the rate is constant is called a zeroth order reaction.
2. A reaction is called first order whenever the reaction rate is proportional to the concentration of a single reactant.
3. temperature dependency of reaction rate for most reactions is given by Eqn.