

Polymer Process Engineering
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Lecture – 25



Mass transfer phenomenon in polymers: Diffusivity and solubility of gases in polymers

Hello friends, welcome to the diffusivity and solubility of the gases in polymers under the edges of mass transfer phenomena in polymers. In the previous lecture, we discussed the mass transfer coefficient in the laminar flow. We discussed the mass transfer in the falling film and briefly described the laminar falling film in the inclined surface where the angle theta. We described the mass transfer coefficient in the turbulent flow. We discussed the boundary layer theory concept and the film theory concept. In this particular segment, we are going to discuss the diffusion aspects in polymers.

Table of content

- **Diffusion in polymers**
- **Gas diffusivities in molten polymers**
- **Gas solubility's in molten polymers**
- **Examples**



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We will discuss the gas diffusivities in molten polymer. We will describe the gas solubility in the molten polymer with certain examples. Now, usually, we will go for different laws which we studied in previous chapters. So, when we talk about the diffusion and solution in the polymers, this is a very integral part of different types of aspects, especially when we try to synthesize the specialty polymers.

Diffusion and Solution in polymers

- **Fick's first law** gives the simplest representation of **the molecular diffusion of a species in a system**.
- This expression relates **the molar flux J_A** of species A to a **gradient dC_A/dy** by means of a transport or diffusion coefficient D_{AB}

$$J_A = -D_{AB} \frac{dC_A}{dy}$$

- D_{AB} is a **property** of the system in much the same way that thermal conductivity is for the transfer of heat.
- **Diffusivity** is the **ratio of molar flux** to concentration gradient whereas thermal conductivity is the ratio of heat flux to temperature gradient.



Molar flux J_A

$$J_A = -D_{AB} \frac{dC_A}{dy}$$

Now, in this aspect, Fick's first law gives the simplest representation of the molecular diffusion of a species in a system. Now, this expression relates the molar flux j_A of species A to a gradient dC_A over dy by means of a transport or diffusion coefficient d_{AB} . So, this can be represented as j_A , and this is the molar flux is equal to minus $d_{AB} dC_A$ over dy where d_{AB} is a property of the system in much of the same way, and the thermal conductivity is for the transfer of E . Now, diffusivity is the ratio of molar flux to concentration gradient and thermal conductivity is the ratio of the heat flux to temperature gradient. Now, for the diffusion of molecules into a liquid semi-solid or solid system, there is an important limiting case, which is the solution.

Diffusion and Solution in polymers

- A **third coefficient** of some importance is the **permeability**, which is defined as **the amount of a diffusing** molecule that passes through a **polymer film of unit thickness** per second per unit area and a unit difference of pressure.
- **Diffusivity, solubility, and permeability** are related by the following:

$$P = D \times H$$

Where, **D is diffusivity** and **H the Henry's law constant** obtained from the relationship

$$H P_i = X_i$$

Where, **P_i is the partial pressure** of the diffusing component and **X is the gas concentration** in the polymer.

The analogy to this particular situation is a chemical reaction, which is a kinetic process, and the chemical equilibrium ultimately limits that. So, all these things are very important in this particular aspect. Now, both the diffusivities and solubilities of small molecules are important in the polymer processing operation, and the rate of transport of small molecules within the polymer being processed, which is related to the diffusivity and solubility, can be fixed or can fix the retention of molecules in the system for a given temperature and pressure. A third coefficient is of some importance and is called the permeability, which is defined as the amount of a diffusing molecule that passes through a polymer film or a unit thickness per second per unit area and a unit difference of pressure. So, the diffusivity, solubility, and permeability are related by this particular equation that is P is equal to D into H where D is the diffusivity, and H is Henry's law constant.

Diffusion and Solution in polymers

- **Permeabilities** apply mainly to **molecular transport in solid polymers**, particularly **polymer films**.
- **Diffusivities** are usually obtained **in conjunction with permeability** measurements.
- The **principal role of processing** with respect to **permeabilities and diffusivities in solid polymers** is development of **the material's structural characteristics**.
- **Mass transport** of gaseous molecules **in molten or thermally softened polymer systems** is a particularly pertinent area. This is so because **polymer processing operations** generally involve gases diffusion systems.

This can be obtained from this particular relationship that is $H P_i$ is equal to x_i where P_i is the partial pressure of the diffusing component and x is the gas concentration in the polymer. Another thing is that this permeability applies mainly to the molecule transport in the solid polymer, particularly polymer films and diffusivities are usually obtained in conjunction with the permeability measurements. So, the principal role of processing with respect to the permeability and diffusivity in the solid polymer is usually developed by developed for the material structure characteristics and mass transport of gaseous molecule in molten or thermally softened polymer system is a particularly pertinent area and this is so because the polymer processing operation generally involve gases diffusive system.

Diffusion and Solution in polymers

- Measurement of solubilities and diffusivities have been accomplished by various techniques as shown in table.

Method	Used for diffusivity	Used for solubility
Movement of a color boundary	Yes	Yes
Gas chromatography	Yes	No
Piezoelectric	Yes	Yes
Special diffusion cell	Yes	Yes

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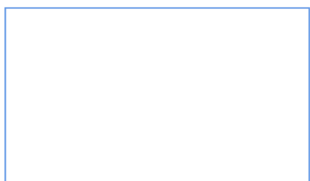

J. A. Woodcock and R. Krishna, Mass Transfer in Multicomponent Mixtures, Delhi Academic Press, Edition 1st, 2000.

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Now, if we talk about the measurement of solubilities and diffusivities, they have been accomplished by the various techniques which we have represented over here like the methods, there are different methods for measurement like movement of a colour boundary, if we can use it for diffusivity as well as we can use for the solubilities and a gas chromatography we can use for the diffusivity but we cannot use for the solubility. Apart from this the piezoelectric which can be used for the both the purpose and special diffusion cells again it can utilise for the both diffusivity and solubility.

Now, usually when we talk about the gas diffusivity in the polymer system, there is some experimental demonstration. So, a listing of experimentally determined diffusivities for a variety of gases and a polymer is given in this particular table at a given temperature of 188 degrees Celsius. Here, these are the various gases that can be utilized in several times in with respect to the polymeric system and there are so many polymeric systems like polyethylene, polypropylene, and polystyrene. So, we have enlisted helium, argon, methane, nitrogen, and carbon dioxide, so all the diffusivities is given with respect to three different polymer matrix: polyethylene, polypropylene and polystyrene. Now, the diffusivities of the gas in polymers are related to a variety of parameters like temperature, pressure, the nature of gases, and the nature of the polymer.

Gas diffusivities in polymer systems

- The **diffusivities of gases** in polymers are related to a variety of parameters: **temperature, pressure, the nature of the gas, and the nature of the polymer.**
- In order to deal properly with processing operations, it is necessary to be able to take these parameters into account, which means that **correlations are needed.**
- Diffusivities can be related to temperature by an **exponential function** given by:
Where, $D = D_0 \exp(-E_d / RT)$ 
- E_d is the **activation energy of diffusion** (kcal/mole).
 D_0 is the **pre-exponential function** (an empirical constant; its units are cm^2/s)

The diffusivities can be related to temperature by an exponential function

$$H = H_0 \exp\left(\frac{-E_s}{RT}\right)$$

Where,

- E_d is the **activation energy of diffusion** (kcal/mole).
- D_0 is the **pre-exponential function** (an empirical constant; its units are cm^2/s)

Now, in order to deal properly with the processing operation, it is necessary to be able to take these parameters into account which means that correlations are needed because some of things are needed you can measure directly and some of thing you need to have some correlations so that we can establish the complete profile.

Gas diffusivities in polymer systems

- Experimentally determined values of E_d and D_0 are given in Table below:

Polymer	Gas	E_d (kcal/mol)	$D_0 \times 10^5$ cm ² /s	Temp (°C)
Polyethylene	N ₂	2.0	53.414	125-188
	CO ₂	4.4	688.13	188-224
Polypropylene	CO ₂	3.0	111.76	188-224
Polystyrene	H ₂	10.1	218.06	120-188
	N ₂	9.6	21.11	119-188
	CH ₄	3.6	21.24	125-188

So, diffusivities this can be related to the temperature by an exponential function and that is equal to D is equal to $D_0 \exp(-E_d/RT)$ where E_d is the activation energy of a diffusion which is usually represented in kilo calorie per mole and D_0 is the pre-exponential function. This is an empirical constant and is having the units of centimetre square per second. So, if we take the things into consideration then experimentally determined values of E_d and D_0 is given in this particular table for the different polymer matrix like polyethylene, polypropylene, polystyrene and we used different gases like nitrogen, carbon dioxide, carbon dioxide with respect to the polypropylene and then polystyrene, hydrogen, nitrogen, methane all these things. So, E_d in kilo calorie per mole and D_0 and at a given temperature because temperature plays a very vital role.

Gas diffusivities in polymer systems

- Values of E_d and D_0 can be estimated for other gases and polymers by using Figs 1 and 2.

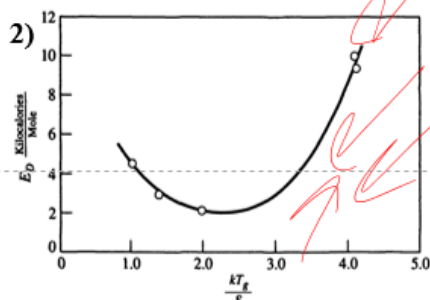


Fig 2: **Logarithm of D_0 vs. activation energy divided by gas constant**

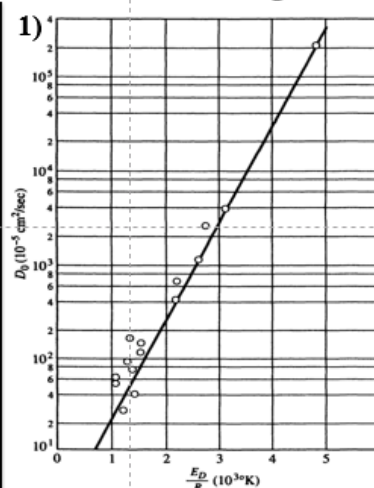


Fig 1: **Logarithm of D_0 vs. activation energy divided by gas constant**

Now, if we talk about the various values of E_d and D_0 this can be estimated for other gases too and polymers by using these two figures. This is the logarithmic of the D_0 versus activation

energy divided by gas constant and this is the logarithmic of D naught versus activation energy divided by the gas constant. So, all these things can be utilised. Now, in this particular figure, figure 1 the logarithmic of D naught is plotted against E_d over R and this particular plot, this gives the plot of E_d versus the function of polymers gas temperature and ϵ/k a gas molecule parameter. Now, in order to use the data of these two figures, figure 1 and figure 2, first establish the E_d value from this figure number 2 for a given polymer by using the polymers glass transition temperature and ϵ/k for the gas next to obtain the D naught value from this figure number 1.

Gas diffusivities in polymer systems

- The polymer's glass temperature and ϵ/k** for the gas is used from the table below

Gas	Collision diameter, σ (Å ^o)	ϵ/k , K
H ₂	2.915	380
He	2.576	10.2
N ₂	3.681	91.5
CO	3.590	110
CO ₂	3.996	190
CH ₄	3.822	137
C ₂ H ₄	4.232	205

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So, the polymeric the glass transition temperature and ϵ/k for the gas is used from the table like we have enlisted different gases like hydrogen, helium, nitrogen, carbon monoxide, carbon dioxide, methane, all these gases and then a collision diameter which is given in the angstrom which is given and ϵ/k in Kelvin is also given. Now, the smaller the molecule, the larger the diffusivity. This becomes apparent when a parameter that is the logarithmic of the diffusivity divided by the square of the diameter of the gas molecule. Now, the diffusivity decreases with increasing polymer weight which is evident from the correlation and the plot this is developed by Lindberg in 1969. So, in this particular figure, we have represented the diffusivities of the gases versus polymer weight.

Gas diffusivities in polymer systems

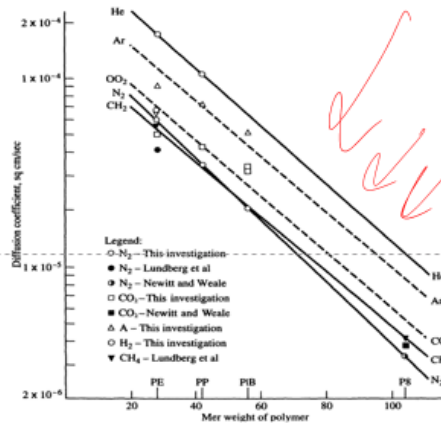


Fig 3: Diffusivities of gases versus polymer mer weight

- **The smaller the molecule, the larger the diffusivity.** This becomes apparent when a parameter (the logarithm of the diffusivity divided by the square of the diameter of the gas molecule).
- **The diffusivity decreases** with increasing polymer weight, which is evident from a **correlation and plot** developed by Lundberg et al., (1969)

Now, if we talk if we go for the explanation of this particular figure, the chain flexibility is not an appropriate explanation as the glass transition temperature of the polyisobutylene lies between the polyethylene and polypropylene. At the same time, the correct correlation shows that polyisobutylene diffusivity data is lower than either of the two other polymers. Now, diffusivity is to be related directly to the mobility of the diffusing species, and the material could be arranged in order to increase in consistency or decrease in diffusing species mobility as polyethylene, polypropylene, polyisobutylene, and polyacetylene. Now, the relation in this particular figure indicates between the diffusivity and polymer weight which is actually between the diffusivity and the mobility of the diffusing species. These polymers differ structurally in the pendant group attached to the basic polyethylene chain.

Gas diffusivities in polymer systems

- The relation indicated in Fig. 3 between **diffusivity and mer weight** is actually **between the diffusivity and mobility of the diffusing species** since these **polymers differ structurally** in the pendant groups attached to the basic polyethylene chain.
- There are actually **two relations between the diffusion coefficient** and the reciprocal of the absolute temperature. **One of the relations** holds up to **150°C**, and the **second from 150 to 170°C**.

Now, there are actually two relations between the diffusion coefficient and the reciprocal of absolute temperature. One is one of the relations that holds up to, say, 150 degrees Celsius, and the second is

in between 150 to 170 degrees Celsius. So, the resultant correlation involves the two complex equations with the diffusivity equation. In order to use the correlation, it is necessary to know the polymer density, the data as a function of temperature, the density data for the pure solvent as a function of temperature, several values of the polymer-solvent system diffusivity for at least two temperatures, sorption equilibrium data for the polymer-solvent system, rheological flow data for the polymer and solvent viscosity data. So, all these things are quite essential.

Gas diffusivities in polymer systems

- **The resultant correlation** involves **two complex equations** with **diffusivity equation**. In order to use the correlation, it is necessary to know:
 1. **Polymer density** data as a function of temperature
 2. **Density data for the pure solvent** as a function of temperature
 3. **Several values of the polymer-solvent** system diffusivity for at least two temperatures
 4. **Sorption equilibrium** data for the polymer solvent system
 5. **Rheological flow data** for the polymer
 6. **Solvent viscosity** data



Now, usually if we number them 1 to 6 these are then used to calculate the number of quantities such as solvent free volume parameters, a polymer free volume parameter and a molar volume at 0 Kelvin for the polymer and solvent. Now, these quantities are then used with the three continuity equations as to calculate the diffusivity. Now, this method this has been applied not to the semi crystalline molten polymer like polyethylene, but rather to amorphous polymers too like polystyrene and poly methyl methacrylate and then that which are the thermally soft. It appears that the simpler generalized technique they are adequate for the higher temperature range for both polystyrene and polyvinyl acetate PVA. Now, above say 420 Kelvin for polystyrene and 358 Kelvin for polyvinyl acetate.

Now, these temperatures are respectively 1.1 and 1.2 times the polymer glass transition temperatures. Now, it is therefore suggested that the free volume model to be used in the region from the glass transition temperature up to 1.1 to 1.2 times of its value.

Problem - 1

Question: What are the diffusivities at 220°C for the following systems:

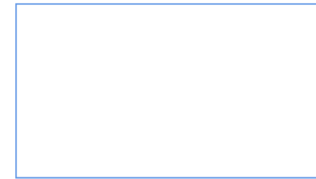
Methane-polyethylene

Nitrogen-polypropylene

Krypton-polyisobutylene

Given: $D_0 = 2.2 \times 10^{-5} \text{ cm}^2/\text{s}$; $-E_d$ (polyethylene) = 3 kcal/mol ; $-E_d$

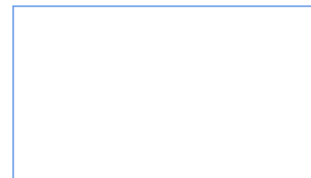
(polypropylene) = 2.78 kcal/mol ; $-E_d$ (polyisobutylene) = 5.4 kcal/mol



Put these values in
 $D = D_0 \exp\left(\frac{-E_d}{Rt}\right)$

$D_0 = 2.2 \times 10^{-5} \text{ cm}^2/\text{s}$
 $-E_d$ (poly ethylene) = 3 kcal/mol
 $-E_d$ (poly propylene) = 2.78 kcal/mol
 $-E_d$ (poly isobutylene) = 5.4 kcal/mol
 $T = 220^\circ\text{C}$ (493.16 K)
 $R = 1.987 \times 10^{-3} \text{ kcal/mol K}$

① Methane poly ethylene
 $D = 2.2 \times 10^{-5} \left(\frac{\text{cm}^2}{\text{s}}\right) \left(\frac{3 \text{ (kcal/mol)}}{1.987 \times 10^{-3} \text{ kcal/mol K}}\right)^{493.16 \text{ K}}$
 $D = 6.7 \times 10^{-5} \text{ cm}^2/\text{s}$



Let us solve one problem and that is what are the diffusivities at 220 degrees Celsius for the following system like methane, polyethylene, nitrogen, polypropylene, krypton, polyisobutylene. Now, given that D_0 is equal to $2.2 \times 10^{-5} \text{ cm}^2/\text{s}$, E_d that is for the polyethylene is equal to minus 3 kilo calorie per mole, E_d for polypropylene 2.78 kilo calorie per mole and polyisobutylene given as 5.4 kilo calorie per mole. So, putting these values in equation which is $D = D_0 \exp\left(\frac{-E_d}{RT}\right)$ which is $D = D_0 \exp\left(\frac{-E_d}{RT}\right)$. Now, D_0 is equal to $2.2 \times 10^{-5} \text{ cm}^2/\text{s}$ and the E_d values for polyethylene 3 kilo calorie per mole and polyethylene 3 kilo calorie per mole E_d for polypropylene 2.78 kilo calorie per mole and E_d for polyisobutylene which is equal to 5.4 kilo calorie per mole and T is given as 220 degrees Celsius that is 493.16 Kelvin and R is equal to $1.987 \times 10^{-3} \text{ kcal/mol K}$. See the consistency of the unit. Now, if we solve separately then for the first system methane polyethylene the D is equal to $6.7 \times 10^{-5} \text{ cm}^2/\text{s}$.

into 10 to the power minus 5 centimeter square per second into 3 into per 3 kilo calorie per mole over 1.987 into 10 to the power minus 3 mole into 493 kilo calorie per mole.

Handwritten calculations for the diffusion coefficient D for three different systems:

- Nitrogen - Polypropylene:**

$$D = 2.2 \times 10^{-5} \left(\frac{\text{cm}^2}{\text{s}} \right) \left(\frac{2.78 \text{ (kcal/mol)}}{1.987 \times 10^3 \text{ kcal/mol} \cdot (493.16 \text{ K})} \right)$$

$$D = 4.275 \times 10^{-5} \text{ cm}^2/\text{s} \quad \text{Ans}$$
- Krypton - polyisobutylene:**

$$D = 2.2 \times 10^{-5} \left(\frac{\text{cm}^2}{\text{s}} \right) \left(\frac{5.4 \text{ (kcal/mol)}}{1.987 \times 10^3 \text{ kcal/mol} \cdot (493.16 \text{ K})} \right)$$

$$D = 10.69 \times 10^{-5} \text{ cm}^2/\text{s} \quad \text{Ans}$$
- Krypton - polyisopropyl alcohol:**

$$D = 2.2 \times 10^{-5} \left(\frac{\text{cm}^2}{\text{s}} \right) \left(\frac{5.4 \text{ (kcal/mol)}}{1.987 \times 10^3 \text{ kcal/mol} \cdot (493.16 \text{ K})} \right)$$

$$D = 10.69 \times 10^{-5} \text{ cm}^2/\text{s} \quad \text{Ans}$$

So, $5.993.16$ Kelvin. Now, this comes out to be D is equal to 6.7 into 10 to the power 5 centimeter square per second and this is answer for the first segment. Now, if we talk about nitrogen and polypropylene D is equal to 2.2 into 10 to the power minus 5 centimeter square 2.78 , 1.987 into 10 to the power minus 3 into 493.16 Kelvin. So, So, this comes out to be D is equal to 4.275 into 10 to the power 5 centimetre square per second. This is answer to the second segment. Now, let's talk about the Krypton poly isopropyl alcohol. This is our third segment that is Krypton poly isobutylene that is D is equal to 2.2 into 10 to the power minus 5 into cm^2 per second into 5.4 kilo calorie per mole, 1.987 into 10 to the power minus 3 -kilo calorie per mole Kelvin into 493.16 and then D comes out to be 10.69 into 10 to the power 5 centimeter square per second. This is our answer.

Problem - 2

Questions: Estimate a value of diffusivity for the system carbon dioxide-polyvinyl chloride at 200°C (473.16 K) ?

Given $-E_d$ (polyvinyl chloride) = 2.84 kcal/mol and D_0 (461.16 K) = $2.2 \times 10^{-5} \text{ cm}^2/\text{s}$

Q9.

$$D_{473.16K} = D_{461.16K}$$

→ Can be written as

$$D_{473.16K} = 2.2 \times 10^{-5} \text{ (cm}^2\text{/s)}$$

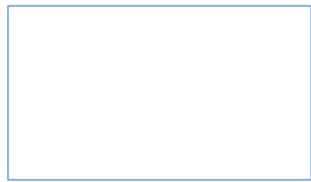
$$D_{473.16K} = 2.38 \times 10^{-5} \text{ cm}^2\text{/s}$$

$$\exp\left(\frac{-E_d}{R(461.16K)}\right)$$

$$\exp\left(\frac{-E_d}{R(473.16K)}\right)$$

$$\exp\left(\frac{-E_d}{R} \frac{(473.16 - 461.16)}{(473.16)(461.16)}\right)$$

Ans



Now, let us take up another problem that is you need to estimate a value of diffusivity for the system carbon dioxide polyvinyl chloride at 200 degrees Celsius that is 473.16 Kelvin. Now, it is given that ED for the polyvinyl chloride is 2.84 kilo calorie per mole and D naught at 461.16 is equal to 2.2 into 10 to the power minus 5 centimeter square per second. So, let us solve this problem. Now, we we can establish the equation D at 473.16 Kelvin is equal to D 461.16 Kelvin, then exponential ED over R 461.16 Kelvin over minus ED over R 473.16 Kelvin. So, this this equation can be written as D 473.16 Kelvin is equal to 2.2 into 10 to the power minus 5 centimeter square minus ED over R into 473.16 minus 461.16 over 473.16 into 461.16. So, if we solve then it can become D 473.16 Kelvin is equal to 2.38 into 10 to the power minus 5 centimeters, and this is our answer. Now, let us talk about the limiting effect. Now, the limiting effect of the diffusion of a gas into a molten or thermally softened polymer is its solution.

Gas solubilities in polymer systems

- **The limiting effect** of the diffusion of a gas into a molten or thermally softened **polymer is its solution.**
- **Such behavior can be expressed** in the form of **Henry's law.**
Experimentally determined values of H, the Henry's law constant are given in Table below:



Such behavior can be expressed in the form of Henry's law. Now, experimentally determined the values of H the Henry's laws constant are given in this particular table. This table shows the Henry law constant for various gas polymer systems and usual units of Henry law constant is centimeter cube per gram atom.

Gas solubilities in polymer systems

Table shows henry's law constants for various **gas-polymer systems**.
Henry's Law Constant: **cm³/g atm**

Polymer	Nitrogen	Carbon dioxide	Argon	Helium
Polyethylene	0.111	0.275	0.113	0.038
Polypropylene	0.133	0.228	0.176	0.086
<u>Polyisobutylene</u>	0.057	0.210	0.102	0.043
Polystyrene	0.049	0.220	0.093	0.029
Polymethyl methacrylate	0.045	0.260	0.105	0.066

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Now, here in this particular segment you see that we have enlisted different polymers like polyethylene, polypropylene, polyisobutylene, polystyrene, polymethyl methacrylate and then the different gases like nitrogen, carbon dioxide, argon, helium all these things are enlisted and their respective Henry's law constant is being given in this particular table. Now, as with the diffusion the solution is a function of a number of parameters including temperature, pressure and the nature of gases and the polymer involved.

Gas solubilities in polymer systems

- **As with diffusion**, solution is a function of a **number of parameters, including temperature, pressure, and the nature of the gases** and polymers involved.
- **The relation of the Henry's law constant** to temperature is an exponential one, represented by:

$$H = H_0 \exp\left(\frac{-E_s}{RT}\right)$$

where **E_s** is the **heat of solution** in **kcal/ mole**.

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Relation of Henry's Las Constant

$$H = H_0 \exp\left(\frac{-E_S}{RT}\right)$$

So, the relation of Henry's law constant to a temperature is an exponential expression which is represented by H is equal to H naught exponential of minus ES over RT where ES is the heat of a solution and which is having the units of a kilo calorie per mole.

Gas solubilities in polymer systems

- Experimental values of E_S are given in table below:

Polymer	Gases			
	H ₂	CO ₂	N ₂	CH ₄
Polyethylene	-	0.80	0.95	-
Polypropylene	-	1.7	-	-
polystyrene	1.9	-	1.7	1.05

So, various experimental values being determined by the different scientists and these some of the experimental values which are in use in the common polymers is given as polyethylene, polypropylene and polystyrene with respect to the different gases like hydrogen, carbon dioxide, nitrogen, methane all these things. Now, it is evident from this particular table that the heat of a solution changes with the gas structure for a given polymer. Now, these phenomena usually was observed in a solid amorphous polyethylene and natural rubber where the heats of solution move from endothermic to exothermic as the gas collision diameter increases. Now, in this particular figure, this demonstrate or compares the data for the molten polyethylene to data for solid amorphous polyethylene.

Gas solubilities in polymer systems

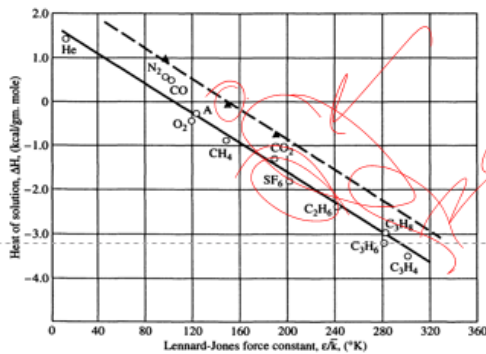
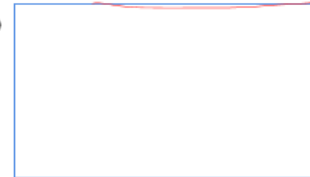


Fig 4: Heats of solution for gases in solid amorphous (solid line, circles) polyethylene and for molten polyethylene (dotted line, triangles)

- **The dotted line** of Fig. 4 can be used to **estimate heats of solution for gases** other than nitrogen or carbon dioxide in polyethylene.
- References in the literature indicate that the Henry's law constant is **independent at pressures** up to at least **1.01×10^7 Pa** and possibly up to **3.03×10^7 Pa**



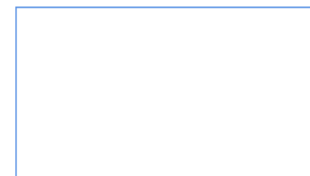
Now, the dotted lines this one, this can be used to estimate the heats of solution for gases other than the nitrogen or carbon dioxide in the polyethylene. References in this particular literature we have already included this that Henry law constant is independent of pressure up to at least 1.01 into 10 to the power 7 Pascal and possibly up to 3.03 into 10 to the power 7 Pascal. So, in this particular figure, where you see that heats of solution of a gas in the solid amorphous that is a solid lines with circle and polyethylene for a molten polyethylene that is a dotted line and we have represented the notation in triangle.

Problem -3

Question: What are the Henry's law constants for nitrogen, helium, argon, carbon dioxide in solid amorphous polyethylene at 461.16 K?

Given

$$\begin{aligned}
 H_0(\text{N}_2) &= 0.0351 \text{ cm}^3/\text{g. atm}; & -E_s(\text{N}_2) &= 950 \text{ kcal/mol} \\
 H_0(\text{He}) &= 0.0102 \text{ cm}^3/\text{g. atm}; & -E_s(\text{He}) &= 2300 \text{ kcal/mol} \\
 H_0(\text{A}) &= 0.0878 \text{ cm}^3/\text{g. atm}; & -E_s(\text{A}) &= 500 \text{ kcal/mol} \\
 H_0(\text{CO}_2) &= 0.384 \text{ cm}^3/\text{g. atm}; & -E_s(\text{CO}_2) &= 800 \text{ kcal/mol}
 \end{aligned}$$



$H = H_0 \exp\left(\frac{-E_s}{RT}\right)$
 $R = 1.987 \times 10^{-3} \text{ kcal/mol K}$
 $H_0(\text{N}_2) = 0.0351 \text{ cm}^3/\text{g atm}$
 $E_s(\text{N}_2) = 950 \text{ kcal/mol}$
 $H_0(\text{He}) = 0.0102 \text{ cm}^3/\text{g atm}$
 $E_s(\text{He}) = 2300 \text{ kcal/mol}$
 $H_0(\text{Ar}) = 0.0878 \text{ cm}^3/\text{g atm}$
 $E_s(\text{Ar}) = 500 \text{ kcal/mol}$
 $H_0(\text{CO}_2) = 0.384 \text{ cm}^3/\text{g atm}$
 $E_s(\text{CO}_2) = 800 \text{ kcal/mol}$

For N_2
 $H = 0.0351 \left(\frac{\text{cm}^3}{\text{g atm}}\right) \left(\frac{950 \text{ (kcal/mol)}}{1.987 \times 10^{-3} \text{ kcal/mol K} \times 461.16 \text{ K}}\right)$
 $H = 0.043 \text{ cm}^3/\text{g atm}$

Now, let us take up another problem that is you need to calculate the Henry's law constant for nitrogen, helium, argon, carbon dioxide in solid amorphous polyethylene at 461.16 Kelvin. Here the H naught nitrogen is given as Henry's law initial energy law constant is given for nitrogen, helium, argon and carbon dioxide like 0.0351, 0.0102, 0.0878 centimetres centimetre cube per gram atmosphere and 3.384 centimetre cube per gram atmosphere. Apart from this the ES values is given for nitrogen, helium, argon, carbon dioxide like this. So, we are having the equation with us like H is equal to H naught exponential minus ES over RT.

Now, here R is equal to 1.987 into 10 to the power minus 3 kilo calorie per mole Kelvin, H naught for nitrogen is given that is 0.0351 centimetre cube per gram atom, ES for nitrogen is given that is 950 kilo calorie per mole, H naught for helium is 0.0102 centimetre cube per gram atmosphere, ES for helium 2300 kilo calorie per mole, H naught for argon 0.0878 centimetre cube, ES for argon 500 kilo calorie per mole, H naught for CO2 0.384 centimetre cube per atom and ES for CO2 is equal to 800 kilo calorie per mole.

For He
 $H = 0.0102 \text{ (cm}^3/\text{g atom)}$
 $H = 0.0619 \text{ cm}^3/\text{g atom}$
 Ans

④ CO₂
 $H = 0.348 \text{ (cm}^3/\text{g atom)}$
 $H = 0.417 \text{ cm}^3/\text{g atom}$
 Ans

③ A
 $H = 0.0878 \text{ (cm}^3/\text{g atom)}$
 $H = 0.118 \text{ cm}^3/\text{g atom}$
 Ans

So, for nitrogen, H is equal to 0.0351 centimetre cube plus atom 950 kilo calorie per mole, 1.987 into 10 to the power minus 3 kilo calorie per mole Kelvin, 461.16 Kelvin. Now, this H is equal to 0.043 centimetre cube per gram atom. This is the answer to the first segment. For helium, H is equal to 0.0102 centimetre cube per gram, 2300, 1.987 into 10 to the power minus 3 kilo calorie, 461.16 Kelvin. So, if we calculate then it comes out to be H is equal to 0.0619 centimetre cube per gram atom. So, this is our answer. Now, if we take for A, then H is equal to 0.0878 into 500 over 1.987 into 461.16. All other things are in the usual units. So, H is comes out to be 0.118 centimetre cube per gram atom. This is our answer. Now, if we talk about the carbon dioxide, so, this is H is equal to 0.348 centimetre cube per atom into 800 kilo calorie per mole, 1.987 into 10 to the power minus 3 kilo calorie per mole Kelvin into 461.16 Kelvin. So, if we calculate 0.417 centimetre cube per gram atom.

References

- Fundamental of Heat and Mass Transfer, Incropera and Dewitt, 5th Edn., John Wiley & Sons.
- Basmadjian D., "Mass Transfer and Separation Processes: Principles and Applications", 2007, CRC Press
- Treybal R.E., "Mass Transfer Operation", 3rd Ed., 1980, McGraw Hill.
- McCabe W.L., Smith J.C. and Harriott P., "Unit Operations of Chemical Engineering", 6th Ed., 2001, McGraw Hill
- Foust A. S., Wenzel L. A., Clump C. W., Maus L. and Andersen L.B., "Principles of Unit Operations", 2nd Ed., 2008, Wiley-India.
- Brown G. G. and Associates, "Unit Operations", 1995, CBS Publishers.
- Wankat P. C., "Separation Process Engineering", 2nd Ed., 2006, Prentice Hall.
- R. Taylor and R. Krishna, Multicomponent Mass Transfer, John Wiley & Sons Inc. Edition 1st, 1993
- J. A. Wesselingh and R. Krishna, Mass Transfer in Multicomponent Mixtures, Delft Academic Press. Edition 1st, 2000.

So, this is our answer to this particular segment. Dear friends, in this particular segment, we discussed different aspects of mass transfer operation and for your convenience, we have enlisted different references and which are very useful for the future studies and if you wish, you can take the help of all these references. Thank you very much.