

Derivation of Joule-Thomson Co-efficient

H is a state function of the system, for a gaseous system it may be represented as

$$H = f(P, T)$$

$$dH = \left(\frac{\partial H}{\partial P}\right)_T dP + \left(\frac{\partial H}{\partial T}\right)_P dT$$

when, enthalpy is constant i.e., $dH = 0$

$$\left(\frac{\partial H}{\partial P}\right)_T dP = -\left(\frac{\partial H}{\partial T}\right)_P dT$$

Dividing by dP at constant H, We get

$$\left(\frac{\partial H}{\partial P}\right)_T = -\left(\frac{\partial H}{\partial T}\right)_P \left(\frac{\partial T}{\partial P}\right)_H = C_P \mu_{J.T.} \dots \dots \dots (1)$$

$$C_P \mu_{J.T.} = -\left(\frac{\partial H}{\partial P}\right)_T$$

$$\mu_{J.T.} = -\frac{1}{C_P} \left(\frac{\partial H}{\partial P}\right)_T \dots \dots \dots (2)$$

We Know,

$$H = U + PV$$

$$dH = dU + PdV + VdP = TdS + VdP$$

Dividing by dP at constant T

$$\left(\frac{\partial H}{\partial P}\right)_T = T \left(\frac{\partial S}{\partial P}\right)_T + V \dots \dots \dots (3)$$

From Maxwell's relation we get

$$\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P$$

Putting the Maxwell's relation on equation (3) we get,

$$\left(\frac{\partial H}{\partial P}\right)_T = -T \left(\frac{\partial S}{\partial P}\right)_T + V \dots \dots \dots (4)$$

Equation (4) is called 2nd thermodynamic equation of state. Hence from equation (2) & (4) we get,

$$\mu_{J.T.} = -\frac{1}{C_p} \left[V - T \left(\frac{\partial V}{\partial T} \right)_P \right]$$

$$\mu_{J.T.} = \frac{1}{C_p} \left[T \left(\frac{\partial V}{\partial T} \right)_P - V \right] \dots \dots \dots (5)$$

Equation (5) is the general thermodynamic expression for the Joule –Thomson co-efficient of the gas.

For one mole of an ideal gas,

$$PV = RT$$

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

$$\left(\frac{\partial V}{\partial T} \right)_P = \frac{R}{P}$$

$$\mu_{J.T.} = \frac{1}{C_p} \left[T \left(\frac{\partial V}{\partial T} \right)_P - V \right] = \frac{1}{C_p} \left[\frac{RT}{P} - V \right] = \frac{1}{C_p} [V - V] = 0$$

Thus for an ideal gas, Joule –Thomson co-efficient is zero, i.e., an ideal gas does not exhibit the Joule-Thomson effect.

For one mole of Vander wall’s gas

$$\left(P + \frac{a}{V^2} \right) (V - b) = RT$$

$$PV - Pb + \frac{a}{V} - \frac{ab}{V^2} = RT$$

$$PV = RT + Pb - \frac{a}{V} + \frac{ab}{V^2}$$

$$V = \frac{RT}{P} + b - \frac{a}{PV} + \frac{ab}{PV^2} \dots \dots \dots (6)$$

The term a/PV & ab/PV², we are dividing a small quantity by a large quantity. So replacement of V by RT/P in these two terms does not introduce much error to the result. Thus V appearing in the correction terms a/PV & ab/PV² may be replaced by RT/P & equation (6) modifies to

$$V = \frac{RT}{P} + b - \frac{a}{RT} + \frac{abP}{R^2T^2} \dots \dots \dots (7)$$

Differentiating this equation with respect to T at constant P

$$\left(\frac{\partial V}{\partial T}\right)_P = \frac{R}{P} + \frac{a}{RT^2} - \frac{2abP}{R^2T^3} \dots \dots \dots (8)$$

From equation (7) we find that

$$\frac{R}{P} = \frac{V-b}{T} + \frac{a}{RT^2} - \frac{abP}{R^2T^3} \dots \dots \dots (9)$$

Substituting this on equation (8) we get,

$$\left(\frac{\partial V}{\partial T}\right)_P = \frac{V-b}{T} + \frac{a}{RT^2} - \frac{abP}{R^2T^3} + \frac{a}{RT^2} - \frac{2abP}{R^2T^3}$$

$$\left(\frac{\partial V}{\partial T}\right)_P = \frac{V-b}{T} + \frac{2a}{RT^2} - \frac{3abP}{R^2T^3} \dots \dots \dots (10)$$

Hence from Equation (5) and (10) we get,

$$\mu_{J.T.} = \frac{1}{C_p} \left[T \left\{ \frac{V-b}{T} + \frac{2a}{RT^2} - \frac{3abP}{R^2T^3} \right\} - V \right] = \frac{1}{C_p} \left[V - b + \frac{2a}{RT} - \frac{3abP}{R^2T^2} - V \right]$$

$$\mu_{J.T.} = \frac{1}{C_p} \left[\frac{2a}{RT} - \frac{3abP}{R^2T^2} - b \right] \dots \dots \dots (11)$$

At low pressure and high temperature $\frac{3abP}{R^2T^2}$ term is very small and in that case

$$\left(\frac{\partial T}{\partial P}\right)_H = \mu_{J.T.} = \frac{1}{C_p} \left[\frac{2a}{RT} - b \right] \dots \dots \dots (12)$$

The sign of $\mu_{J.T.}$ depends on the quantity within the square bracket of equation (12) and whether a gas suffers a fall or increase in temperature depends on the sign of $\mu_{J.T.}$. Thus when $\frac{2a}{RT} > b$, then $\mu_{J.T.}$ is +ve and dT is -Ve (since dP is always -Ve) and the gas suffers a fall in temperature. Conversely when $\frac{2a}{RT} < b$ then $\mu_{J.T.}$ is -ve and dT is +Ve (since dP is always -Ve), hence there is a rise of temperature. At high temperature $\frac{2a}{RT} < b$, hence $\mu_{J.T.}$ is -ve and at low temperature $\frac{2a}{RT} > b$, hence $\mu_{J.T.}$ is +ve

But for H₂ and He, "*a*" is very small and $\frac{2a}{RT} < b$, even at room temperature and therefore show the heating effect at room temperature in the Joule-Thomson expansion although the other gases show the cooling effect at room temperature.

For every gas there is a temperature where $\frac{2a}{RT} = b$ i.e., $\mu_{J.T.} = \text{zero}$, when neither heating nor cooling of the gas would occur due to passing through fine orifice. This is called the inversion temperature, *T_i* of the gas. Putting, $\mu_{J.T.} = \text{zero}$, at *T_i*, we get from equation (12).

$$\left[\frac{2a}{RT_i} - b \right] = 0$$

$$T_i = \frac{2a}{Rb} \dots \dots \dots (13)$$

Under the conditions when the term $\frac{3abP}{R^2T^2}$ is negligibly small the inversion temperature *T_i* of a gas according to equation (11) should be,

$$\left[\frac{2a}{RT_i} - \frac{3abP}{R^2T_i^2} - b \right] = 0$$

$$\left[T_i^2 - \frac{2a}{Rb} T_i + \frac{3aP}{R^2} \right] = 0 \dots \dots \dots (14)$$

Equation (14) being a quadratic equation in *T_i*, should yield two values of *T_i*, one minimum and other maximum., i.e., two inversion temperature is possible. This has been verified by experiment.

It is clear from the above discussion that in order to cool a gas by the Joule- Thomson expansion, the gas must first through a porous plug from a higher to lower pressure. As the temperature of the experiment decreases the extent of cooling increases.

Optical fiber

Plastic optical fibers (POFs) are a low-cost solution for low-speed, short-distance applications in digital car networks, industrial networks, and home networks and appliances. The plastic optical

fiber is made out of a plastic such as acrylic (PMMA) as the core material and fluorinated or perfluorinated polymers as the cladding materials. This research addresses the development of low-cost polymer optical fibers and waveguides with integrated gain and optical switching functionalities. Research team Jorge Morgado Luís Alcácer Rui Henriques Ana Charas Ana Luisa Mendonça Optical fibers are used to transmit light and, embedded in it, information. The working key principle is the total internal reflection at the interface between the core and the cladding (having a lower refractive index), which confines the propagating light beam within the core. Losses, due to scattering and absorption, limit the distance at which light can be transmitted. Silica is the material of choice for long distance transmission, being nearly transparent in the infra-red. So the selected wavelengths for data transmission are 850, 1310 and 1550 nm. Furthermore, the use of erbium as a dopant allows signal amplification when transmitting at 1.5 μm wavelength, which has led to a drastic improvement of this technology. However silica optical fibers are expensive, brittle and, having cores with diameters around 50 μm , make the connections difficult to perform. Plastic/polymeric optical fibers (POFs) are competing with silica fibers for short distance transmission (Local Area Networks, automotive, sensors) as they are flexible and, having larger cores, easier to connect. Polymethylmethacrylate, PMMA, is one of the most used core materials. However, losses are higher than in silica, limiting the application to shorter distances. Recent studies show that the use of fluorinated polymers as core materials significantly reduces losses. The aim of the project is to explore conjugated luminescent polymers, which show stimulated emission, as amplifiers of POFs, thereby played a role similar to that of erbium in the silica fibers. Furthermore, the gain of these conjugated polymers can be switched off, with a laser beam, in time scales around 1ps. This effect is being explored in ultrafast optical switches. STREP Contract number

026365 This photo shows four doped organic optical fibers, The active materials are fluorene oligomers of different lengths: a trimer (3), a pentamer (5), a heptamer (7), and a long chain (polymer) Following the first observation (Phys. Rev. Lett. 94 (2005) 117402) that dilution of a conjugated

Which polymer is used as Optical Fiber?

Ans: Polymethylmethacrylate, PMMA

Why Optical fiber conduct light and electrical energy?

Ans: Such type of Optical fiber shows total reflection of light and electrical energy.

What is the application of Optical Fiber?

Ans: Plastic optical fibers (POFs) are a low-cost solution for low-speed, short-distance applications in digital car networks, industrial networks, and home networks and appliances. The plastic optical fiber is made out of a plastic such as acrylic (PMMA) as the core material and fluorinated or perfluorinated polymers as the cladding materials.

However, losses are higher than in silica, limiting the application to shorter distances. Recent studies show that the use of fluorinated polymers as core materials significantly reduces losses. The aim of the project is to explore conjugated luminescent polymers, which show stimulated emission, as amplifiers of POFs, thereby played a role similar to that of erbium in the silica fibers. Furthermore, the gain of these conjugated polymers can be switched off, with a laser beam, in time scales around 1ps.

1. Explain the abnormally high conductance value of H^+ and OH^- ions.

Ans. Abnormally high conductance value of H^+ and OH^- ion is explained by Grothus types of conduction. We know that adjacent water molecules are bonded by H-bond.

When one H^+ is discharged the remaining half converts the hydrogen bond with its neighbor to an ordinary bond and rotates through 180° . On the other hand one OH^- ion is discharged at the other end of the chain. Thus discharge process becomes quick and conductance process becomes high. Relatively low values of OH^- ion is due to its larger size and more steps required to be converted to O_2 .

2. Velocity of Li^+ is smallest among alkali metals ion in aqueous solution; but in ORGANO aqueous solution it is highest-Why?

Ans. Li^+ is smallest in size among alkali metals ion. So it may be expected that its velocity should be high. But in aqueous solution velocity follows the order $Li^+ < Na^+ < K^+$ etc. This is due to hydration. Water is polar solvent. In aqueous solution every ion attracts the end of the water molecules whose charge is opposite to it. Thus every ion associated with a sheath of water layer. During movement the ion carries the associated water molecules with it. As a result the velocity decreases. The extent of hydration depends upon the charge density. All the alkali metals ions are uni-positive. Due to smaller size and high charge density Li^+ ion is highly associated by water molecules and velocity is lowest.

In organo-aqueous medium the dielectric constant of the medium and polar character is considerably lowered. So, hydration becomes less and hence due to smaller size and high charge density Li^+ ion velocity is highest.

3. Will transport number of Cl^- in HCl and in NaCl be same?

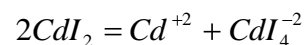
Ans. From the expression of transport number we know that it is also depend upon the counter ion.

$$t_{Cl^-} \text{ (in HCl)} = \frac{V_{Cl^-}}{V_{H^+} + V_{Cl^-}} \quad \text{and} \quad t_{Cl^-} \text{ (in NaCl)} = \frac{V_{Cl^-}}{V_{Na^+} + V_{Cl^-}}$$

As, $V_{Na^+} < V_{H^+}$, So, t_{Cl^-} (in HCl) and t_{Cl^-} (in NaCl) are not same so transport number will be different.

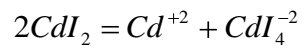
4. In concentrated CdI_2 solution the transport number of Cd^{+2} is – ve (negative) why?

Ans.



If we measure the transport number of Cd^{+2} and I^- in dilute solution we get normal values. As concentration is raised $t_{Cd^{+2}}$ begin to decrease and at sufficiently high concentration it becomes negative.

Negative transport of Cd^{+2} indicates that Cd^{+2} ion instead of being migrated out of anode is coming to the anode. This can only happen if Cd^{+2} enter into complex anion formation. Actually in concentrated solution the following equation becomes important.



Thus , Cd enters into anode as complex anion That is why we get - ve (negative) transport number