Chemistry (Honours)

10th lecture

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Derivation of the Joule-Thomson Coefficient

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It is difficult to think physically about what the Joule-Thomson coefficient μ_{JT} represents. Also modern determinations of μ_{JT} do not use the original method used by Joule-Thomson but instead measure a different ~~re~~ related quantity. Thus it is useful to derive relationship between μ_{JT} and other more convenient quantity.

The first step in obtaining these results is to note that Joule-Thomson coefficient involves the three variables T, P and H. A useful result is immediately obtained by applying the cyclic rule. In terms of these three variables may be written as:

$$\left(\frac{\partial T}{\partial P}\right)_H \left(\frac{\partial H}{\partial T}\right)_P \left(\frac{\partial P}{\partial H}\right)_T = -1$$

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Each of the three Partial derivates in this expression has a specic meaning. The first is μ_{JT}, the second is the constant Pressure heat capacity, C_p defined by

$$C_p = \left(\frac{\partial H}{\partial T}\right)_P$$

and the third is the inverse of the isothermal Joule-Thomson coefficient μ_T defined by

$$\mu_T = \left(\frac{\partial H}{\partial P}\right)_T$$

This last quantity is more easily measured than μ_{JT}. Thus the expression from the cyclic rules becomes.

$$\mu_{JT} = -\frac{\mu_T}{C_p}$$

This equation can be used to obtain Joule-Thomson Coefficient from the more easily measured isothermal Joule-Thomson Coefficient. It is used in the following to obtain a mathematical expression for the Joule-Thomson coefficient in terms of the volumetric Properties of a fluid.

To proceed further the

Starting point is the fundamental equation of thermodynamics in terms of enthalpy.

$$dH = TdS + VdP$$

Now dividing through by dP while holding temperature constant yields

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

The partial derivative on the left is the isothermal Joule-Thomson coefficient μ_T and one on the right can be expressed in terms of the coefficient of thermal expansion by a Maxwell relation. The relation is

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

where α is the cubic coefficient of thermal expansion. Replacing these two partial derivatives yields

$$\mu_T = -TV\alpha + V$$

This expression can now replace μ_T in the earlier equation for μ_{JT} obtain

$$\mu_{JT} = \left(\frac{\partial T}{\partial P}\right)_H = \frac{V}{C_P}(\alpha T - 1)$$

This provides an expression for the

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Joule-Thomson coefficient in terms of the commonly available properties heat capacity, molar volume and thermal expansion ~~coeff~~ coefficient. It shows that the Joule-Thomson inversion temperature at which μ_{JT} is zero, occurs when the co-efficient of thermal expansion is equal to the inverse of the temperature. Since this is true at all temperatures for ideal gases, the Joule-Thomson coefficient of an ideal gas is zero at all temperatures.

End

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