Chemistry Hons

9th Lecture

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Joule-Thomson Coefficient (Physical mechanism)

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There are two factors that can change the temperature of a fluid during an adiabatic expansion

a) A change in internal energy or
(b) the conversion between potential and kinetic energy

The internal energy is the sum of thermal kinetic and potential energy. If work is done on or by the fluid as it expands then the total internal energy changes. This is what happens in a Joule-Thomson expansion and can produce larger heating or cooling than observed in a free expansion.

In a Joule-Thomson expansion the enthalpy remains constant. The enthalpy H is defined as

$$H = U + PV$$

where U – Internal energy
P – Pressure
V – volume.

In Joule-Thomson expansion the change in PV represents the work done by the fluid. If PV increases with H constant then U must decrease as a result of the fluid doing work on its surroundings. This produce a decrease in temperature and results in a positive Joule-Thomson coefficient. ~~Conv~~ Conversely a decrease in PV means that work is done on fluid and the internal energy increases. If the increase in kinetic energy exceeds the increase in potential energy, there will be an increase in the temperature of the fluid and the Joule-Thomson coefficient will be negative.

For an ideal gas, PV does not change during a Joule-Thomson expansion. As a result there is no change in internal energy. Since there is no change in thermal potential energy there can be no change in temp. In real gas PV does change.

The ratio of of the value of PV to that expected for in ideal gas at the same temperature is called the compressibility factor Z.

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All real gases have an inversion point at which the value of μ_{JT} changes sign. The temperature of this point, the Joule-Thomson inversion temp depends on the gas before expansion.

If the gas temp. is	then μ_{JT} is	Since ∂P is	thus ∂T must be	So the gas
Below the inversion temp	Positive	Always negative	negative	cools
Above the inversion temp.	Negative	Always negative	negative	warms

For an ideal gas, μ_{JT} is always equal to zero. Ideal gas neither warm nor cool upon being expanded at constant enthalpy.

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Thus at low temp, Z and PV will increase as the gas expands, resulting in a positive Joule-Thomson co-efficient. At high temperature Z and PV decrease as the gas expands. If the decrease is large enough, the Joule-Thomson coefficient will be negative.

For liquids and for supercritical fluids under high pressure, PV increases as pressure increases. This is due to molecules being forced together so that volume can barely decrease due to higher pressure. Under such condition Joule-Thomson coefficient is negative.

The rate of change of temperature T with respect to pressure P in a Joule-Thomson process (where enthalpy H constant) is the Joulee-Thomson coefficient μ_{JT}. This coefficient can be expressed in terms of the gas's volume V.

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

C_P – Heat capacity at constant Pressure

α – Co-efficient of thermal expansion