

Chemical Thermodynamics 04

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Calculations of –

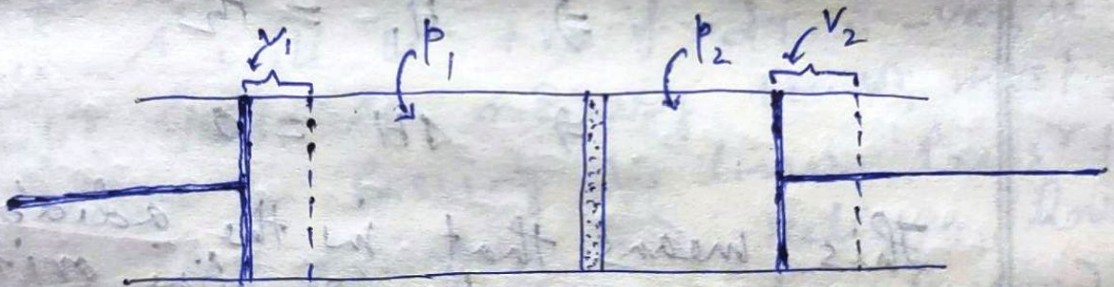
- i) Free expansion of ideal gas & van der Waals gases under isothermal conditions
- ii) Free expansion of ideal gas & van der Waals gases under adiabatic conditions
- iii) Law of equipartition of energy
- iv) Degrees of freedom & molecular basis of heat capacities.

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✓ Joule-Thomson's Experiment :-

* Joule-Thomson's Effect / Joule-Thomson's Coefficient / Adiabatic Expansions are Isoenthalpic:
 In Joule's experiment, the free expansion of a gas into a vacuum revealed that the temp. drop of the system was negligible and would be zero if the gas were ideal.

But Joule and Thomson's subsequent exp. on the passage of a gas from a higher Pressⁿ to a lower Pressⁿ through fine orifices of a porous plug revealed a drop in tempⁿ in many cases.



Suppose, the volⁿ V_1 of a gas under a const. Pressⁿ P_1 is allowed to pass through a porous barrier from the region on the left to the region on the right where the const. Pressⁿ is P_2 . The volⁿ of the gas becomes V_2 . The process is carried out with the slow motion of the two frictionless pistons at the two ends. The whole system is thermally insulated, $q = 0$.

The work done by the piston on the left
 $= P_1 V_1$

The work obtained from the system
on the right $= P_2 V_2$

From the 1st law, $\Delta U = -W$
 $= P_1 V_1 - P_2 V_2$

$$\Rightarrow U_2 - U_1 = P_1 V_1 - P_2 V_2$$

$$\Rightarrow U_1 + P_1 V_1 = U_2 + P_2 V_2$$

$$\Rightarrow H_1 = H_2$$

$$\Rightarrow \Delta H = 0$$

This means that in the adiabatic expansion of a gas through fine orifices the heat content remains unaltered. That is, such adiabatic expansion is also isoenthalpic. Nevertheless there is a drop of temp^r generally of the outgoing gas \rightarrow such variation of temp^r is called Joule-Thomson Effect.

The rate of change in temp^r with Press^r when enthalpy remains const. is called Joule-Thomson coefficient.

$$\mu = \left(\frac{\partial T}{\partial P} \right)_H \rightarrow (1)$$

* Joule Thomson's Cooling & Warming & Inversion temperature :-

If such flow through fine orifices, usually the gas runs into lower press^r. i.e. dP is -ve. Hence μ will be +ve if dT is -ve, i.e. if temp^r falls. At ordinary temp^r, most gases cool down in passing to lower press^r through porous plug. Hydrogen & Helium, however at room temp^r become heated instead of cooling, i.e. μ is -ve. We can explain this in the following way. We know,

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

If an isenthalpic change (like above); $dH=0$

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

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

$$\Rightarrow \beta = -\frac{1}{C_p} \left(\frac{\partial H}{\partial P} \right)_T \quad \text{--- (2)}$$

$$\Rightarrow \beta = -\frac{1}{C_p} \left(\frac{\partial U}{\partial P} \right)_T - \frac{1}{C_p} \left(\frac{\partial(PV)}{\partial P} \right)_T \quad \text{--- (3)}$$

In the case of an ideal gas, both the terms on the RHS separately vanish,

$$\text{for, } \left[\frac{\partial U}{\partial P} \right]_T = 0 \quad \Rightarrow \quad \left[\frac{\partial(PV)}{\partial P} \right]_T = 0 \quad \therefore \beta = 0$$

In the case of a real gas it is different, eqn

$$(3) \Rightarrow \beta = -\frac{1}{C_p} \left(\frac{\partial U}{\partial V} \right)_T \left(\frac{\partial V}{\partial P} \right)_T - \frac{1}{C_p} \left[\frac{\partial(PV)}{\partial P} \right]_T$$

In this eqn, $\left(\frac{\partial U}{\partial V} \right)_T$ of the gas is usually +ve while $\left(\frac{\partial V}{\partial P} \right)_T$ for any gas is always -ve. As a result, the first term is always +ve.

The magnitude of the second term $\left[\frac{\partial(PV)}{\partial P} \right]_T$ may be -ve or may be +ve. At low temp and low press, $\left[\frac{\partial(PV)}{\partial P} \right]_T$ is -ve, under such

conditions both the terms in the eqn being +ve, \Rightarrow thus β has a +ve value, that means, there would be a cooling of the gas.

But at higher pressⁿ $\left[\frac{\partial(PV)}{\partial P} \right]$ becomes +ve so that second term becomes -ve \rightarrow if its value exceeds that 1st term, μ becomes -ve. And at higher temp^r all gases have $\left[\frac{\partial(PV)}{\partial P} \right]_T$ is +ve, so μ is generally -ve that means, there would be a heating (i.e. warming) instead of cooling of the gas.

Again, for every gases there is a temp^r where $\mu = 0$, when the gas is neither warming nor cooling due to passage through the fine orifices would occur. This temp^r is called the inversion temperature, (T_i) of the gas.

* Mathematical Expression of μ (J-T coefficient)

Since, $H = f(T, P)$, we have

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

Deriving by $dp \rightarrow 0$ at constant H , i.e. $dH=0$

$$0 = \left(\frac{\partial H}{\partial T}\right)_P \left(\frac{\partial T}{\partial P}\right)_H + \left(\frac{\partial H}{\partial P}\right)_T$$

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

$$\Rightarrow \beta = - \frac{1}{C_p} \left(\frac{\partial H}{\partial P}\right)_T$$

$$\Rightarrow \beta = - \frac{1}{C_p} \left[-T \left(\frac{\partial V}{\partial T}\right)_P + V \right]$$

$$\Rightarrow \beta = \frac{T}{C_p} \left(\frac{\partial V}{\partial T}\right)_P - \frac{V}{C_p}$$

$$\Rightarrow \beta = \frac{1}{C_p} \left[T \left(\frac{\partial V}{\partial T}\right)_P - V \right] \quad \longrightarrow (1)$$

$$\Rightarrow \beta = \frac{V}{C_p} \left[\frac{T}{V} \left(\frac{\partial V}{\partial T}\right)_P - 1 \right] \quad \longrightarrow (2)$$

Equⁿ (1) or (2) are the expression for J-T Co-efficient.
 Note: The sign of J-T Coefficient is determined by the sign of the numerator in the above expression because C_p is +ve in all the cases.

For an ideal gas,

$$\left(\frac{\partial V}{\partial T}\right)_P = \frac{nR}{P} \quad ; \quad PV = nRT$$

\Rightarrow Equⁿ (1) or (2) now takes the form,

$$\text{Equⁿ (1)} \Rightarrow \beta = \frac{1}{C_p} \left[T \cdot \frac{nR}{P} - V \right] \quad \therefore \beta = 0$$

$$\begin{aligned} \therefore dH &= dU + PdV + VdP \\ &= Tds + vdp \end{aligned}$$

we may have,

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

ie, J-T coefficient for an ideal gas is zero \Rightarrow thus the tempⁿ of such a gas will not suffer any change in the J-T Experiment.

But for Real gases, the numerator (as well as the J-T coefficient) may be +ve, -ve or zero depending upon the tempⁿ & Pressⁿ of the gas.

⊗ J-T Coefficient and Vander Waals Equⁿ of State:

The J-T Coefficient expression is given by,

$$\mu = \frac{1}{C_p} \left[T \left(\frac{dv}{dT} \right)_p - v \right]$$

Equⁿ of Vander Waals gas:
 $(p + \frac{a}{v^2})(v-b) = RT$

$$\Rightarrow \mu = \frac{1}{C_p} \left[(v-b) + \frac{2a}{RT} - \frac{3abp}{R^2 T^2} - v \right]$$

$\left(\frac{dv}{dT} \right)_p = \frac{v-b}{T} + \frac{2a}{RT^2} - \frac{3abp}{RT^3}$

$$\Rightarrow \mu = \frac{1}{C_p} \left[\frac{2a}{RT} - \frac{3abp}{R^2 T^2} - b \right]$$

$$\Rightarrow \mu = \frac{1}{C_p} \left[\frac{2a}{RT} - b \right]$$

When, Tempⁿ of the gas is not too low and the pressⁿ is not too high, the term $\frac{3abp}{R^2 T^2}$ may be neglected.

The knowledge of C_p and the Vander Waals constants 'a' and 'b', it is possible to evaluate the μ at a given tempⁿ.

Case I: At high temp^r —

$$\text{Eqn (1)} \Rightarrow \beta = \frac{1}{C_p} \left[\frac{2a}{RT} - b \right] \text{ reflects}$$

$$\frac{2a}{RT} < b \therefore \beta \text{ is } -ve.$$

i.e. J-T warming is occur.

Case II: At low temp^r —

$$\frac{2a}{RT} > b \therefore \beta \text{ is } +ve$$

i.e. J-T cooling is occur.

Case III: For H_2 (hydrogen), where "a" is small, \therefore even for ordinary temp^r $\frac{2a}{RT} < b$, and there will occur a heating (warming) in J-T expansion.

It must be remembered that in the adiabatic expansion of a gas, there is always a cooling effect due to decrease in internal energy in the form of work. In J-T effect, cooling will occur only when β is +ve.

Case IV : At the inversion temp^r, T_i ,

$$\beta = 0$$

$$\text{ie, } \frac{1}{C_p} \left[\frac{2a}{RT_i} - b \right] = 0$$

$$\Rightarrow \frac{2a}{RT_i} - b = 0$$

$$\Rightarrow T_i = \frac{2a}{Rb}$$

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✓ * Liquefaction of gases :-

For liquefaction, it is essential that the gas should be cooled below its critical temp^r. Even then high Press^r & low temp^r are required to liquefy most of the gases. Of course, the lower the temp^r the lower would be the required Press^r. In ordinary cases, refrigeration with ammonia, methyl chloride or dry ice - ether etc, is sufficient for liquefaction of many gases. But often very low temp^r are needed to liquefy common gases such as O_2 , N_2 , He, H_2 etc. In such cases, J-T cooling effect is taken advantage of.

The principle may briefly be illustrated with the Linde process for the liquefaction of air

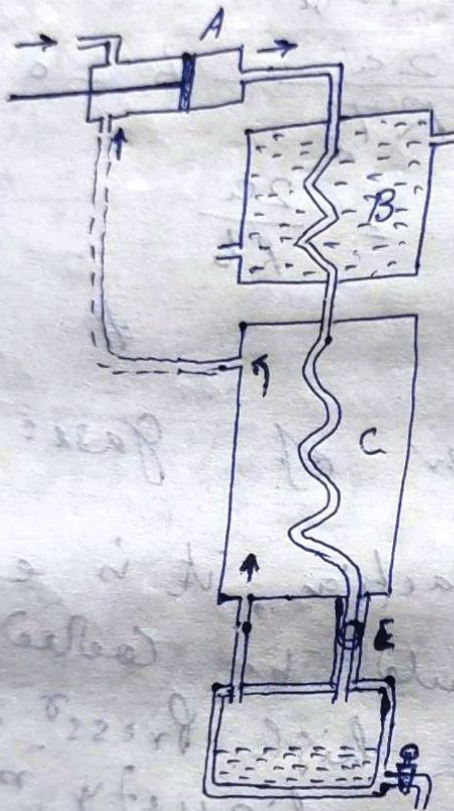


fig. 1

dry air first compressed to a high Press. say 100 atm. in A (fig. 1) and it is then passed through a coil surrounded by a refrigerant B, say evaporating ammonia or sulphur dioxide so that the heat of compression is removed. The relatively cool gas then passes through the coil C and finally it expands through a throttle E from a Press. of 100 atm. to nearly 1 atm.

This J-T expansion immediately lowers the temp^r considerably. This expanded gas is used to cool the incoming gas in chamber C \rightarrow recirculated to the high press^r line. The lower the temp^r of the incoming gas at E the lower will be the J-T cooling. Repetition of the cycle ultimately lowers the temp^r to such an extent that on passing the valve E, the gas is transformed into the liquid.

* Work done on Adiabatic Process :-

* Relation between P , V & T in adiabatic process :-

An adiabatic change, by definition is one which does not allow any transfer of heat i.e. $q = 0$, it follows from the first law,

$$\Delta U = -W$$

$$\Rightarrow dU = -dW$$

$$\because q = \Delta U + W$$

If only mechanical work of expansion or