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GE2T (Thermal physics and Statistical Mechanics) , Topic :- Joule- Thomson Effect

❖ **Introduction :**

We are at the point where we can make our first analysis of an actual experiment. The experiment will be explained first. Then thermodynamics will be used to show that the experiment is *isoenthalpic*. With this result, we can then explain the main result of the experiment in terms of the properties of the gases involved.

❖ **The Joule- Thomson Experiment :**

The apparatus itself is quite simple. Imagine a tube with a porous plate separating it into two parts. The porous plate will allow a gas to go through it, but only slowly. It acts as a *throttle*. On each side of the plate there is a piston that fits the tube tightly. Each piston can (in principle) be pushed up against the porous plate. The tube itself is insulated so that no heat can enter or leave the tube.

The initial volume of gas on side 1 is V_1. The pressure is p_1 and the temperature T_1.

The final volume on the right side (side 2) is, V_2 the pressure is p_2 and the temperature T_2.

❖ **Initial Analysis :**

The process starts with volume $V_1 = V_1$ and volume $V_2 = 0$. Its ends with volume $V_1 = 0$ and volume $V_2 = V_2$.

The total work done done is $\quad w = p_1 V_1 - p_2 V_2$ ………….(1)

Since the process is adiabatic, the total change in U is just the work, or

$$\nabla w = U_2 - U_1 = p_1 V_1 - p_2 V_2 \quad …………(2)$$
$$\Rightarrow U_2 + p_2 V_2 = U_1 + p_1 V_1 \quad ……………..(3)$$

So that :

$$\boxed{H_1 = H_2}$$ …….. (4) and the process is **isoenthalpic**.

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❖ **The Joule- Thomson Coefficient :**

What is measured experimentally is

$$\mu_{JT} = \lim_{\Delta p \to 0} \frac{T_2 - T_1}{p_2 - p_1} \quad \text{........(5)}$$

Which becomes, taking into account that the process is isoenthalpic :

$$\mu_{JT} = \left(\frac{\partial T}{\partial p}\right)_H \quad \text{.........(6)}$$

All that we've done so far is reduced the experiment to mathematics. The experimental result is that μ_{JT} is sometimes positive and sometimes negative. In fact it is found that there is a certain temperature called the **inversion temperature** such that if the initial, temperature T_1 is *above* the inversion temperature the final temperature is *higher* than the initial temperature. If the initial temperature is *below* the inversion temperature, the final temperature is *lower* than the initial temperature. The inversion temperature is found, experimentally, to depend on the pressure.

To do this we can start with the total differential of H assuming that T and p are the independent variables:

$$\partial H = \left(\frac{\partial H}{\partial T}\right)_p \partial T + \left(\frac{\partial H}{\partial p}\right)_T \partial p \quad \text{.........(7)}$$

Now our process is isoenthalpic, so *dH=0* . This gives

$$0 = \left(\frac{\partial H}{\partial T}\right)_p \partial T + \left(\frac{\partial H}{\partial p}\right)_T \partial p \quad \text{.......(8)}$$

Now We divide through by ∂p at constant H to get :

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

$$\left(\frac{\partial T}{\partial p}\right)_H = -\frac{\left(\frac{\partial H}{\partial p}\right)_T}{\left(\frac{\partial H}{\partial T}\right)_p} \quad \text{.........(9)}$$

This result simplifies a bit right away. We know that $\left(\frac{\partial H}{\partial T}\right)_p$ is the heat capacity C_p , so :

$$\left(\frac{\partial T}{\partial p}\right)_H = -\frac{\left(\frac{\partial H}{\partial p}\right)_T}{C_p} \quad \text{.......(10)}$$

But we can't make it any simpler. We need to express $\left(\frac{\partial H}{\partial p}\right)_T$ in terms that can be measured. Indeed, this can be done, but it requires one slight bit of magic. A result that will be proven later

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$$\left(\frac{\partial H}{\partial p}\right)_T = V - T\left(\frac{\partial V}{\partial T}\right)_p \quad \text{........(11)}$$

Which , when used in equ.(10) gives :

$$\boxed{\mu_{JT} = \left(\frac{\partial T}{\partial p}\right)_H = \frac{T\left(\frac{\partial V}{\partial T}\right)_p - V}{C_p}} \quad \text{..............(12)}$$

A equation in which all of the quantities are measureable.

❖ **The Joule- Thomson Coefficient for Model Gases :**

If we knew the equation of state for a gas, we could *calculate* the Joule-Thomson coefficient. For instance, for an ideal gas $\left(\frac{\partial V}{\partial T}\right)_p = \frac{V}{T}$, so

$$\mu_{JT} = 0 \text{ ideal gas ....(13)}$$

Ideal gas are boring.

But they hav e told us something. There is *no* Joule-Thomson effect for an ideal gas at all. And how do ideal gases differ from real gases? They hav e no interactions at all. No attractiions and no repulsions. But that's the only way in which they differ. So we conclude that *the Joule-Thomson effect depends on the interactions between gas molecules.*

A gas obeying van der Waals equation will prove more interesting. Since we can't solve van der Waals equation for *V* explicitly we have to use an approximation. This can be written

$$Z = 1 + \frac{1}{RT}\left(b - \frac{a}{RT}\right)p + \cdots \quad \text{.....(14)}$$

which is the first two terms of the *virial equation* approximation for a van der Waals gas. We want to take this expression, solve it for $\bar{V}$, and then differentiate it to get $\left(\frac{\partial V}{\partial T}\right)_p$. With this available we can plug into eq. (12) calculate μ_{JT} .

Now since $Z = p\bar{V}/RT$, we can solve eq.(14) for V to get :

$$\bar{V} = \frac{RT}{p} + \left(b - \frac{a}{RT}\right) + \cdots \quad \text{.......(15)}$$

What we want is $(\frac{\partial V}{\partial T})_p$. From eq.(15) we get :

$$(\frac{\partial V}{\partial T})_p = \frac{R}{p} + \frac{a}{RT^2} + \cdots \qquad \ldots..(16)$$

Now this has to be multiplied by T. We get

$$T(\frac{\partial V}{\partial T})_p = \frac{RT}{p} + \frac{a}{RT} + \cdots \qquad \ldots(17)$$

And now subtracting $\bar{V}$ as given in eq.(15) we get:

$$T(\frac{\partial V}{\partial T})_p - \bar{V} = -\left(b - \frac{2a}{RT}\right) + \cdots \qquad \ldots..(18)$$

And so, finally the Joule- Thomson coefficient for a gas obeying van der Waals equation is :

$$\mu_{JT} = \frac{\frac{2a}{RT} - b}{C_p} + \cdots \qquad \ldots\ldots\ldots(19)$$

Let's see what happens to the Joule-Thomson coefficient when the temperature gets very low. That is, what is the limit when T goes to 0? Well, as T goes to 0, all terms with T in the denominator get very large. So the term involving $2a/RT$ gets much larger than b. And the b term can be neglected at very low temperatures.

$$\mu_{JT} = \frac{2a}{RTC_p} + \cdots \qquad \text{(very low temperature)} \qquad \ldots(20)$$

which is clearly *positive* since every term in it is positive. This agrees with experiment. A positive Joule-Thomson coefficient means *cooling*. But also note that the resulting expression only contains the van der Waals a. All of the terms involving b have gone away at low temperature.

We can also look at what happens when T gets very large. This result is quite simple since all terms containing a T in the denominator go to zero. The result is:

$$\mu_{JT} = -\frac{b}{C_p} \text{ (very high temperature) } \ldots..(21)$$

and that's very interesting. First, it agrees with experiment since it is *negative*, meaning *heating*. Second, notice that all of the terms involving van der Waals a have now vanished, leaving only b.

Lastly, it should be pointed out that there is one way in which eq. (19) *does not* agree with experiment. Eq. (19) predicts an *inversion temperature* of:

$$T_{inversion} = \frac{2a}{bR}$$ (van der Waals gas)

which is gotten by setting μ_{JT} equal to zero in eq. (19). The problem is that this inversion temperature is not a function of the pressure. Experimentally the inversion temperature is a function of the pressure. If we'd carried one more term in eq. (15) we would have had a (much more messy) result that is a function of pressure.

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