

## 10.3: The Joule-Thomson Experiment

The experiment is also known as the Joule-Kelvin experiment. William Thomson was created Lord Kelvin. The experiment is also known as the porous plug experiment.

In the Joule-Thomson experiment a constant flow of gas was maintained along a tube which was divided into two compartments separated by a porous plug, such that the pressure and molar volume on the upstream side were  $P_1$ ,  $V_1$ , and the pressure and molar volume on the downstream side were  $P_2$ ,  $V_2$ . Under such circumstances the **net** work done **on** a mole of gas in passing from one compartment to the other is  $P_1V_1 - P_2V_2$ . (Imagine, for example, that a piston pushes a mole of gas towards the plug from the upstream side, through a distance  $x_1$ ; if  $A$  is the crosssectional area of the tube, the work done **on** the gas is  $P_1Ax_1 = P_1V_1$ . Imagine also that the gas on the downstream side pushes a piston away from the plug through a distance  $x_2$ . The work done by the gas is  $P_2Ax_2 = P_2V_2$ . Therefore the net external work done **on** the gas is  $P_1V_1 - P_2V_2$ .) If no heat is supplied to or lost from the system, the increase in internal energy of this gas is just equal to this work done on it:

$$U_2 - U_1 = P_1V_1 - P_2V_2,$$

or

$$U_1 + P_1V_1 = U_2 + P_2V_2. \quad (10.3.1)$$

That is, there is no change in enthalpy. Therefore, we want to find  $\left(\frac{\partial T}{\partial P}\right)_H$ , which is the *Joule-Thomson coefficient*, for which I shall be using the symbol  $\mu$ .

In the experiment we are discussing, we are interested in how temperature varies with pressure in an experiment in which the enthalpy is constant. We shall therefore choose  $H$  as our state function and  $P$  and  $T$  as our independent state variables. That is we shall write  $H = H(P, T)$ , so that

$$\left(\frac{\partial T}{\partial P}\right)_H \left(\frac{\partial H}{\partial T}\right)_P \left(\frac{\partial P}{\partial H}\right)_T = -1. \quad (10.3.2)$$

The second of these partial derivatives is  $C_P$ , and therefore

$$\left(\frac{\partial T}{\partial P}\right)_H = -\frac{1}{C_P} \left(\frac{\partial H}{\partial P}\right)_T. \quad (10.3.3)$$

Now

$$dH = TdS + VdP. \quad (10.3.4)$$

That is,

$$dS = \frac{1}{T}[dH - VdP] = \frac{1}{T} \left[ \left(\frac{\partial H}{\partial P}\right)_T dP + \left(\frac{\partial H}{\partial T}\right)_P dT - VdP \right]. \quad (10.3.5)$$

$$dS = \frac{1}{T} \left[ \left(\frac{\partial H}{\partial P}\right)_T - V \right] dP + \frac{1}{T} \left(\frac{\partial H}{\partial T}\right)_P dT. \quad (10.3.6)$$

But we also have

$$dS = \left(\frac{\partial S}{\partial P}\right)_T dP + \left(\frac{\partial S}{\partial T}\right)_P dT. \quad (10.3.7)$$

Therefore

$$\left(\frac{\partial S}{\partial P}\right)_T = \frac{1}{T} \left[ \left(\frac{\partial H}{\partial P}\right)_T - V \right] \quad (10.3.8)$$

and

$$\left(\frac{\partial S}{\partial T}\right)_P = \frac{1}{T} \left(\frac{\partial H}{\partial T}\right)_P. \quad (10.3.9)$$

The mixed second derivatives are

$$\frac{\partial^2 S}{\partial T \partial P} = -\frac{1}{T^2} \left[ \left( \frac{\partial H}{\partial P} \right)_T - V \right] + \frac{1}{T} \left[ \frac{\partial^2 H}{\partial T \partial P} - \left( \frac{\partial V}{\partial T} \right)_P \right] \quad (10.3.10)$$

and

$$\frac{\partial^2 S}{\partial P \partial T} = \frac{1}{T} \frac{\partial^2 H}{\partial P \partial T}. \quad (10.3.11)$$

But entropy is a function of state and  $dS$  is an exact differential, so the mixed second derivatives are equal. Whence, after simplification:

$$\left( \frac{\partial H}{\partial P} \right)_T = V - T \left( \frac{\partial V}{\partial T} \right)_P. \quad (10.3.12)$$

Hence, returning to equation 10.3.3, we obtain, for the Joule-Thomson coefficient,

$$\mu = \left( \frac{\partial T}{\partial P} \right)_H = \frac{1}{C_P} \left[ T \left( \frac{\partial V}{\partial T} \right)_P - V \right]. \quad (10.3.13)$$

*Trivial Exercise:* Show that, for an ideal gas, the Joule-Thomson coefficient is zero, and also that, for an ideal gas,

$$\left( \frac{\partial H}{\partial P} \right)_T = 0. \quad (10.3.14)$$

This is analogous to equation 8.1.4 for an ideal gas, namely  $\left( \frac{\partial U}{\partial V} \right)_T = 0$ .

*Exercise.* Show that, for a van der Waals gas, the Joule-Thomson coefficient is

$$\left( \frac{\partial T}{\partial P} \right)_H = -\frac{V}{C_P} \cdot \frac{(RTV^2b - 2a(V-b)^2)}{RTV^3 - 2a(V-b)^2}. \quad (10.3.15)$$

(Verify the dimensions of this expression.) Hint: It is difficult to calculate  $(\partial V/\partial T)_P$  directly, because it is difficult to express  $V$  explicitly as a function of  $P$  and  $T$ . It is not actually impossible to do it algebraically, because van der Waals' equation is a cubic equation in  $V$ , and a cubic equation does have an algebraic solution. It is easier, however, to calculate  $(\partial V/\partial T)_P$  from  $\left( \frac{\partial V}{\partial T} \right)_P = -\left( \frac{\partial P}{\partial T} \right)_V / \left( \frac{\partial P}{\partial V} \right)_T$ , or from  $\left( \frac{\partial V}{\partial T} \right)_P = 1 / \left( \frac{\partial T}{\partial V} \right)_P$ .

Note also that the Joule-Thomson coefficient may be negative or positive; i.e., it may result in cooling or heating. It will result in heating if you start above a certain temperature called the *inversion temperature*, and cooling if you start below the inversion temperature. The Joule-Thomson effect is used in the *Linde method* for cooling and ultimately liquefying gases. For most gases, the inversion temperature is higher than room temperature, so that cooling starts immediately. But for hydrogen, the inversion temperature is about  $-80^\circ\text{C}$ , and hydrogen must be cooled below this temperature before the Joule-Thomson effect can be used to cool it further and to liquefy it. You can see from equation 10.3.14 that the inversion temperature for a van der Waals gas is equal to  $\frac{2a(V-b)^2}{RV^2b} \approx \frac{2a}{Rb}$ . Here  $V$  is the molar volume.

### Summary:

Joule coefficient

$$\eta = \left( \frac{\partial T}{\partial V} \right)_U = \frac{1}{C_V} \left[ P - T \left( \frac{\partial P}{\partial T} \right)_V \right] \quad (10.3.16)$$

Joule-Thomson coefficient

$$\mu = \left( \frac{\partial T}{\partial P} \right)_H = \frac{1}{C_P} \left[ T \left( \frac{\partial V}{\partial T} \right)_P - V \right]. \quad (10.3.17)$$

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