

12.6: The Joule and Joule-Thomson Coefficients

In Chapter 10, we studied the Joule and Joule-Thomson experiments and we calculated the Joule and Joule-Thomson coefficients. Now that we are familiar with the Helmholtz and Gibbs functions, and, in particular, with two Maxwell relations that can be derived from them, we can obtain alternative derivations for these two coefficients. These may be easier than the derivations we gave in Chapter 10. I am indebted to Dr Greg Trayling for the derivation of the Joule coefficient; the derivation of the Joule-Thomson coefficient follows a parallel argument.

Let us start with the *Joule coefficient*. Here we are interested in how the temperature changes with volume in an experiment in which the internal energy is constant. That is, we want to derive the Joule coefficient, $\eta = (\partial T / \partial V)_U$.

Now entropy is a function of state – i.e. of the intensive state variables P , V and T . (V = molar volume.) But the intensive state variables for a particular substance are related by an equation of state, so we need express the entropy as a function of only two of P , V or T , and, since we are seeking a relation between V and T , let us choose to express S as a function of V and T , so that

$$dS = \left(\frac{\partial S}{\partial V} \right)_T dV + \left(\frac{\partial S}{\partial T} \right)_V dT. \quad (12.6.1)$$

Let us look at these three terms in turn.

First, dS . In the Joule experiment, the internal energy of the gas is constant, so that

$$TdS - PdV = 0. \quad (12.6.2)$$

That is,

$$dS = \frac{PdV}{T}. \quad (12.6.3)$$

For the first term on the right hand side of equation 12.7.1, we make use of the Maxwell relation, equation 12.6.15, which we derived from the Helmholtz function:

$$\left(\frac{\partial S}{\partial V} \right)_T = \left(\frac{\partial P}{\partial T} \right)_V. \quad (12.6.4)$$

For the second term on the right hand side we obtain

$$\left(\frac{\partial S}{\partial T} \right)_V = \left(\frac{\partial S}{\partial U} \right)_V \left(\frac{\partial U}{\partial T} \right)_V = \left(\frac{\partial U}{\partial T} \right)_V / \left(\frac{\partial U}{\partial S} \right)_V = \frac{C_v}{T}. \quad (12.6.5)$$

Thus, equation 12.7.1 becomes

$$\frac{PdV}{T} = \left(\frac{\partial P}{\partial T} \right)_V dV + \frac{C_v dT}{T}. \quad (12.6.6)$$

Multiply through by T , and divide by dV , taking the infinitesimal limit as $dV \rightarrow 0$, recalling that we are dealing with an experiment in which the internal energy is constant, and we arrive at

$$P = T \left(\frac{\partial P}{\partial T} \right)_V + C_v \left(\frac{\partial T}{\partial V} \right)_U, \quad (12.6.7)$$

from which we immediately obtain

$$\left(\frac{\partial T}{\partial V} \right)_U = \frac{1}{C_v} \left[P - T \left(\frac{\partial P}{\partial T} \right)_V \right], \quad (12.6.8)$$

quod erat demonstrandum.

Let us now consider the *Joule-Thomson coefficient*. Here we are interested in how the temperature changes with pressure in an experiment in which the enthalpy is constant. That is, we want to derive the Joule-Thomson coefficient, $\mu = (\partial T / \partial P)_H$.

Now entropy is a function of state – i.e. of the intensive state variables P , V and T . (V = molar volume.) But the intensive state variables for a particular substance are related by an equation of state, so we need express the entropy as a function of only two of

P , V or T , and, since we are seeking a relation between P and T , let us choose to express S as a function of P and T , so that

$$dS = \left(\frac{\partial S}{\partial P} \right)_T dP + \left(\frac{\partial S}{\partial T} \right)_P dT. \quad (12.6.9)$$

Let us look at these three terms in turn.

First, dS . In the Joule-Thomson experiment, the enthalpy of the gas is constant, so that

$$TdS + VdP = 0. \quad (12.6.10)$$

That is,

$$dS = -\frac{VdP}{T}. \quad (12.6.11)$$

For the first term on the right hand side of equation 12.7.9, we make use of the Maxwell relation, equation 12.6.16, which we derived from the Gibbs function:

$$\left(\frac{\partial S}{\partial P} \right)_T = -\left(\frac{\partial V}{\partial T} \right)_P. \quad (12.6.12)$$

For the second term on the right hand side we obtain

$$\left(\frac{\partial S}{\partial T} \right)_P = \left(\frac{\partial S}{\partial H} \right)_P \left(\frac{\partial H}{\partial T} \right)_P = \left(\frac{\partial H}{\partial T} \right)_P / \left(\frac{\partial H}{\partial S} \right)_P = \frac{C_P}{T}. \quad (12.6.13)$$

Thus, equation 12.7.9 becomes

$$-\frac{VdP}{T} = -\left(\frac{\partial V}{\partial T} \right)_P dP + \frac{C_P dT}{T}. \quad (12.6.14)$$

Multiply through by T , and divide by dP , taking the infinitesimal limit as $dP \rightarrow 0$, recalling that we are dealing with an experiment in which the enthalpy is constant, and we arrive at

$$-V = -T \left(\frac{\partial V}{\partial T} \right)_P + C_P \left(\frac{\partial T}{\partial P} \right)_H, \quad (12.6.15)$$

from which we immediately obtain

$$\left(\frac{\partial T}{\partial P} \right)_H = \frac{1}{C_P} \left[T \left(\frac{\partial V}{\partial T} \right)_P - V \right], \quad (12.6.16)$$

quod erat demonstrandum.

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