DS 9:
The Thermodynamics of Irreversible Processes

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1 Free expansion

Free (or "Joule") expansion occurs when a thermally isolated system expands into a vacuum. In this case, no heat is transferred to the system, and no work is done by the system. This is an *irreversible* process, but it can still be treated quite nicely through thermodynamics. Let us ask the following question: would a gas undergoing free expansion *cool down* or *heat up*?

(a) Start by arguing that in this case, the internal energy is a constant, i.e.

$$\mathrm{d}U(T,V) = 0. \tag{1}$$

(b) Show that this implies that

$$\left(\frac{\partial T}{\partial V}\right)_U = -\frac{(\partial U/\partial V)_T}{(\partial U/\partial T)_V}. \tag{2}$$

(c) The denominator of the above equation should be familiar. In order to find the numerator, we will need to do some more work. Show that

$$\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial S}{\partial V}\right)_T - P = T\left(\frac{\partial P}{\partial T}\right)_V - P, \tag{3}$$

where to get the last term you need to use a Maxwell relation.

(d) Putting it all together, show that

$$\left(\frac{\partial T}{\partial V}\right)_U = -\frac{1}{C_V}\left[T\left(\frac{\partial P}{\partial T}\right)_V - P\right]. \tag{4}$$

(e) We now have everything we need to find out how the temperature of a system changes under a free-expansion. Since the internal energy is a constant along such a process, we can just integrate the equation above to find the change in temperature ΔT, i.e.

$$\Delta T = -\int_{V_1}^{V_2} \mathrm{d}V\,\frac{1}{C_V}\left[T\left(\frac{\partial P}{\partial T}\right)_V - P\right]. \tag{5}$$

What is ΔT for an ideal gas? Could you have arrived at this answer in a much simpler way?

(f) Now, compute ΔT for a van der Waals gas, whose equation of state is given by

$$\left(P + a\frac{N^2}{V^2}\right)(V - Nb) = NRT. \tag{6}$$

2 The Joule-Thompson process

The Joule-Thompson process is a steady-state process in which a gas is passed through a porous plug (or "valve") from a region of high pressure P_1 to a region of lower pressure P_2, while being thermally isolated. Such a process can be used to heat or cool gasses.

The work done on the gas is given by

$$W = -\int_{V_1}^{0} P\mathrm{d}V - \int_{0}^{V_2} P\mathrm{d}V. \tag{7}$$

Since the pressure on either side is constant, this just means

$$W = P_1V_1 - P_2V_2. \tag{8}$$

(a) Show that this is a process that takes place at constant *enthalpy*, i.e. at constant $H = U + PV$. Thus, while our system passes through intermediate non-equilibrium states for which enthalpy is not defined, we can nevertheless say that the initial and final enthalpies are equal. **Hint:** Argue that the change in internal energy $\Delta U = U_2 - U_1$ is compensated by the work.

(b) Using the fact that the enthalpy is constant for such a process, show that

$$\mathrm{d}T = -\frac{\left(\partial H/\partial P\right)_T}{\left(\partial H/\partial T\right)_P}\mathrm{d}P. \tag{9}$$

(c) Show that the denominator is just C_P. Show that the numerator can be written as

$$\left(\frac{\partial H}{\partial P}\right)_T = T\left(\frac{\partial S}{\partial P}\right)_T + V = -T\left(\frac{\partial V}{\partial T}\right)_P + V, \tag{10}$$

where in the last step a Maxwell relation has been used. Use this to show that

$$\left(\frac{\partial T}{\partial P}\right)_H = \frac{V}{C_P}(T\alpha - 1), \tag{11}$$

where α is the coefficient of thermal expansion.

(d) Now, integrate the above expression to show that the temperature changes in constant enthalpy process as

$$\Delta T = T_2 - T_1 = \int_{P_1}^{P_2} \mathrm{d}P\, \frac{V}{C_P}(T\alpha - 1). \tag{12}$$

(e) Show that for an ideal gas, $\alpha = 1/T$ and so $\Delta T = 0$.

(f) Next, consider the case of a van der Waals gas. For simplicity, in the case of low densities, assume that the coefficient α for a van der Waals gas is just

$$\alpha = \frac{k_B(1 - b\rho)}{k_BT - 2a\rho(1 - b\rho)^2}. \tag{13}$$

Use the fact that $\rho \ll 1$ to show that

$$\alpha \approx \frac{1}{T}\left(1 - \rho\left(b - \frac{2a}{k_BT}\right)\right). \tag{14}$$

(g) Show that

$$T\alpha - 1 = \rho\left(\frac{2a}{k_B T} - b\right), \tag{15}$$

and find ΔT in a Joule-Thompson process for such a gas.

(h) An interesting result here is theat there is an *inversion temperature* $T_{\mathrm{inv}} = 2a/b$ for low-density gases. What happens when $T > T_{\mathrm{inv}}$ and what happens when $T < T_{\mathrm{inv}}$?