An important practical question is what happens when a gas is expanded into vacuum or a very low pressure (against “zero external pressure”). We saw already that $W=0$. And in a fundamental sense, it helps us to further illustrate the (usefulness of the) concept of **enthalpy**. Does the $T$ decrease, as is typical when it is expanded adiabatically? Should it, if no work is done? (Remember that the adiabatic expansion curve on the P-v diagram is *steeper* than that of isothermal expansion!)

Initial experiments (done by Joule in the 19th century) showed that, when the gas can be considered ideal, heat is neither evolved nor absorbed. Thus both heat and work are zero, which means that the internal energy remains constant:

$$\left(\frac{\partial U}{\partial V}\right)_T = 0$$

In fact, this condition is a complementary definition of an ideal gas, because Joule and Thomson -- two of the leading 'fathers' of thermodynamics, the latter immortalized as Lord Kelvin -- subsequently showed that this is not true in general (for non-ideal or real gases). In fact, the ability to predict the so-called Joule-Thomson inversion temperature (see relevant figures in the textbook) is often used as a litmus test for an equation of state. So the concept and the quantification of the **Joule-Thomson coefficient** is an essential topic in an introductory thermo course:

$$\left(\frac{\partial T}{\partial P}\right)_H \equiv \mu$$

It turns out that the assumption $Q=0$ is more reasonable than the assumption $W=0$, because of the need to overcome the attractive (or repulsive!) forces between molecules. In other words, no ‘external’ work is done (by compressing the surroundings), but some ‘internal’ work is done... justifying the convenience of defining an ‘internal’ pressure.

Therefore,

$$\Delta U = U_2 - U_1 = W$$

Joule and Thomson devised an apparatus (see relevant figure in the textbook) capable of measuring whether there is a difference in the product $PV$ on both sides of a porous plug that separates the two systems. **Note that the upstream work is** $W_1 = -P_1(0-V_1)$, whereas the downstream work is $W_2 = -P_2(V_2-0)$. In other words,

$$W = W_1 + W_2 = P_1 V_1 - P_2 V_2 = U_2 - U_1$$

and therefore

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

or

$$H_1 = H_2$$

Therefore, the enthalpy of the gas (and not its energy) is constant in the Joule-Thomson expansion. In terms of measurable properties, $T$ and $P$ being the most convenient independent variables in this case,

$$dh = \left(\frac{\partial h}{\partial T}\right)_P dT + \left(\frac{\partial h}{\partial P}\right)_T dP$$
and, as shown elsewhere,
\[ dh = C_p \, dT + \left[ v - T \left( \frac{\partial v}{\partial T} \right)_p \right] \, dP \]

Note the analogy with the expression for energy,
\[ du = C_v \, dT + \left[ T \left( \frac{\partial P}{\partial T} \right)_v - P \right] \, dv \]

where the dv multiplier represents the 'internal' pressure \( \pi_T \).

Note also that we can apply the cyclic rule to obtain an expression for \( \mu \):
\[ \left( \frac{\partial x}{\partial y} \right)_z = - \left( \frac{\partial x}{\partial z} \right)_y \left( \frac{\partial z}{\partial y} \right)_x \]

\[ \Rightarrow \left( \frac{\partial T}{\partial P} \right)_H = - \left( \frac{\partial T}{\partial H} \right)_P \left( \frac{\partial H}{\partial P} \right)_T = - \frac{1}{C_p} \left[ V - T \left( \frac{\partial V}{\partial T} \right)_P \right] = \frac{V}{C_p} (\alpha \, T - 1) \]

(The need to make a distinction between intensive and extensive properties should be obvious from the statement of the problem.)

From the above analysis it can be shown that
\[ dH = C_p \, dT - \mu \, C_p \, dP \]

If the system obeys the VDW EOS, from which one can determine \( \partial V/\partial T \), it can be shown that
\[ \mu = \frac{1}{C_{p,m}} \left( \frac{2a}{RT} - b - \frac{3ab}{R^2 T^2} \right) P \approx \frac{1}{C_{p,m}} \left( \frac{2a}{RT} - b \right) \]

This equation illustrates the fact that the JT coefficient can be positive (cooling) or negative (heating). The transition is called the inversion temperature, and for the VDW EOS it can be shown (see elsewhere on the class web site) that it takes the following form:
\[ T_i = \frac{1}{bR} \left( a \pm \sqrt{a^2 - 3ab^2 P} \right) \]

On the \( T \) vs \( P \) graph, \( T_i \) is the point on the \( H=\text{const} \) (isenthalpy) curve at which the slope changes. (It is instructive to construct such a graph based on detailed and accurate experimental documentation or a very successful EOS.)

For examples of the use of \( \mu \) in refrigeration (e.g., throttling of cooling devices such as shaving cream containers or liquefaction of gases), see relevant figure in the textbook. For a molecular interpretation of the JT effect, see the relevant section in the textbook, especially the last two sentences! (Upon expansion -- \( \Delta V > 0, \Delta P < 0 \) -- molecules become more separated and, since no heat is supplied, \( \Delta T < 0 \), the gas becomes cooler if attractive forces are dominant.)

Let's now see how good is the VDW EOS in reproducing the inversion temperatures shown in the relevant textbook table.
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