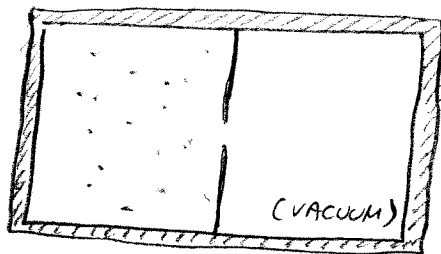


THE JOULE EFFECT IN A REAL GAS

Free expansion in an ideal gas. This case was treated earlier, and claimed that no change in temperature would result. The expansion is into a vacuum.



$$dQ=0, dW=0 \Rightarrow \boxed{dE=0} \Rightarrow dT=0 \text{ since } E=E(T).$$

This applies only to an ideal gas, for which $E=E(T)$. Notice that $dE=0$ will apply for any substance, although inference on T may vary according to the dependence of E on other parameters.

This process is clearly irreversible, as the direction of this process cannot be changed spontaneously. The process is also not a succession of equilibrium states, since it cannot be performed quasi-statically allowing the system to attain intermediate states of equilibrium. This is why:

~~$$\Delta S = \int \frac{dQ}{T}$$~~

cannot be used, as it only applies to infinitesimal reversible (=quasi-static) processes.

One can still calculate the entropy change as the entropy difference between the initial and final equilibrium states. For this purpose, one can envisage any reversible process that performs the change:

$$(P_1, V_1) \longrightarrow (P_2, V_2)$$

For example, an isothermal reversible change can be used for the purpose of calculating ΔS :

$$\Rightarrow \Delta S = \frac{1}{T} \int dQ = \frac{1}{T} \int \cancel{dE} - dW = \frac{1}{T} \int P dV$$

For an ideal gas, $PV = \nu RT$

$$\Rightarrow \Delta S = \nu R \int \frac{dV}{V} = \nu R \ln \left(\frac{V_2}{V_1} \right) > 0$$

which shows that the process is indeed irreversible.

Free expansion in a real gas. In this case, assume $E = E(T, V)$.
 The condition of $dE = 0$ can be written as:

$$\left. \frac{\partial E}{\partial T} \right|_V dT + \left. \frac{\partial E}{\partial V} \right|_T dV = 0$$

From this, define the coefficient $\alpha_J = \left. \frac{\partial T}{\partial V} \right|_E$ and write

$$\alpha_J = \frac{\partial T}{\partial V} = - \frac{\left. \frac{\partial E}{\partial V} \right|_T}{\left. \frac{\partial E}{\partial T} \right|_V} \quad (4)$$

This expression can be simplified by noting that $C_V = \left. \frac{\partial E}{\partial T} \right|_V$. Also the numerator can be expanded by considering the first law:

$$dQ = dE + p dV = \left. \frac{\partial E}{\partial T} \right|_V dT + \left. \frac{\partial E}{\partial V} \right|_T dV + p dV$$

$$\Rightarrow dQ = C_V dT + \left[p + \left. \frac{\partial E}{\partial V} \right|_T \right] dV$$

Need the fundamental thermodynamical relation for a fluid:

$$dE = T dS - p dV \quad \Rightarrow \quad dS = \frac{1}{T} \left(\left. \frac{\partial E}{\partial T} \right|_V dT + \left. \frac{\partial E}{\partial V} \right|_T dV \right) + p dV$$

$$\Rightarrow dS = \frac{1}{T} \left. \frac{\partial E}{\partial T} \right|_V dT + \frac{1}{T} \left[p + \left. \frac{\partial E}{\partial V} \right|_T \right] dV$$

Since S is a function of state, the cross-derivatives are equal

$$\left\{ \begin{array}{l} \left. \frac{\partial S}{\partial T} \right|_V = \frac{1}{T} \left. \frac{\partial E}{\partial T} \right|_V \\ \left. \frac{\partial S}{\partial V} \right|_T = \frac{1}{T} \left[p + \left. \frac{\partial E}{\partial V} \right|_T \right] \end{array} \right. \Rightarrow \frac{\partial}{\partial V} \left(\frac{1}{T} \left. \frac{\partial E}{\partial T} \right|_V \right) = \frac{\partial}{\partial T} \left(\frac{1}{T} \left[p + \left. \frac{\partial E}{\partial V} \right|_T \right] \right)$$

It is also true that $\frac{\partial^2 E}{\partial T \partial V} = \frac{\partial^2 E}{\partial V \partial T}$, therefore the previous equation becomes

$$\frac{1}{T} \frac{\partial^2 E}{\partial T \partial V} = - \frac{1}{T^2} \left[p + \left. \frac{\partial E}{\partial V} \right|_T \right] + \frac{1}{T} \left[\frac{\partial^2 E}{\partial V \partial T} + \left. \frac{\partial p}{\partial T} \right|_V \right]$$

$$\Rightarrow T \left. \frac{\partial p}{\partial T} \right|_V - p = \left. \frac{\partial E}{\partial V} \right|_T \quad (5)$$

Use (5) into (4)

$$\Rightarrow \alpha_J = - \frac{1}{C_V} \left[T \left. \frac{\partial p}{\partial T} \right|_V - p \right] \quad (6)$$

As it was already evident from equation (4), $\alpha_J = 0$ for an ideal gas.

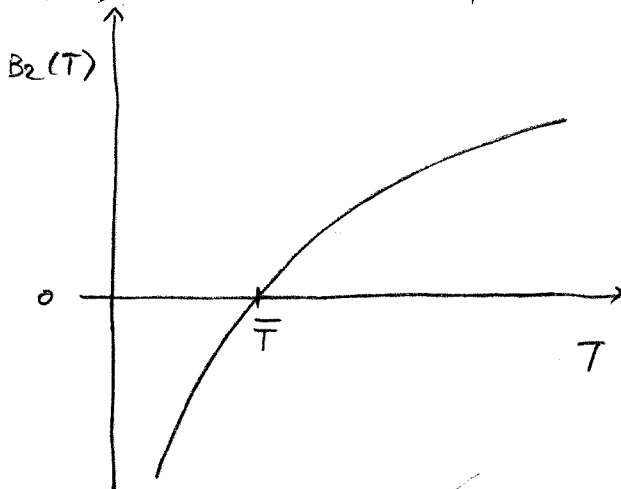
A generalization of the equation of state of an ideal gas can be written as

$$PV = \nu RT \left[1 + \frac{B_2}{V} + \frac{B_3}{V^2} + \dots \right] \quad (7)$$

in which B_i is called the i -th virial coefficient, and it is $B_i = B_i(T)$. These terms can be measured experimentally, and the general behavior can be predicted based on simple considerations.

{ Large separation between molecules : slight attractive force between them.
 { Small separation : strong repulsive force

At low temperature, the kinetic energy is small and the slight attractive force is important, and this causes a slight reduction in pressure (e.g., on the walls of the container). At high temperature, the opposite is true: kinetic energy is significant, molecules are more frequently in contact, and the short-range forces (repulsive) cause an increase in pressure with respect to the ideal case.



$$\Rightarrow dJ \approx -\frac{1}{C_V} \left[T \cdot \frac{\partial R}{\partial V} \left(1 + \frac{B_2}{V} \right) + T \cdot \frac{\partial R}{\partial V} T \cdot \left[\frac{\partial B_2}{\partial T} \cdot \frac{1}{V} \right] + \right. \\ \left. - \frac{\nu RT}{V} \left[1 + \frac{B_2}{V} \right] \right)$$

$$\Rightarrow dJ \approx -\frac{1}{C_V} \cdot \frac{\nu R T^2}{V^2} \cdot \frac{\partial B_2}{\partial T}$$

Notice the case of Argon at STP, with $B_2 \approx -22 \text{ cm}^3/\text{mol}$. In this case, $dJ < 0$ showing that the free expansion is actually accompanied by a slight decrease in temperature.

Ex: Estimate the temperature change for 1 mole of Ar which undergoes free expansion to double its volume at STP.