

## S2.A. Cooling and Liquefaction of Gases

In general, the interaction between two neutral molecules consists of a hard (impenetrable) inner core and a short-range attractive outer region. If a gas of such molecules is allowed to expand, it must do work against the attractive forces so that its temperature will decrease. This rather small effect is called **free expansion cooling**. It can be turned into a cyclic process by throttling the gas repeatedly through a porous plug or constriction. In fact, liquefaction of gases is often done this way in laboratories.

### S2.A.1. The Joule Effect: Free Expansion Cooling

In a **Joule effect** experiment, a gas, initially in a small chamber of volume  $V_i$  and pressure  $P_i$ , is released into a much larger, evacuated, chamber. When the gas finally settles down, its pressure is  $P_f$  throughout the combined chamber of volume  $V_f$ . The walls of the chambers are immobile and insulated so that the process causes no work, heat, or matter transferred to the environment, i.e.,

$$\Delta Q = 0 \quad \Delta W = 0 \quad \Delta n = 0 \quad (2.188a)$$

The 1st law then gives

$$\Delta U = \Delta Q - \Delta W = 0 \quad (2.188b)$$

Choosing  $(T, V, n)$  as the independent variables, we have

$$(dU)_n = \left(\frac{\partial U}{\partial T}\right)_{V,n} dT + \left(\frac{\partial U}{\partial V}\right)_{T,n} dV \quad (2.188)$$

Combining (2.188b) & (2.188) gives

$$\begin{aligned} dT &= -\frac{\left(\frac{\partial U}{\partial V}\right)_{T,n}}{\left(\frac{\partial U}{\partial T}\right)_{V,n}} dV \\ &= \left(\frac{\partial T}{\partial V}\right)_{U,n} dV \quad [ (2.6) \text{ used. } ] \end{aligned} \quad (2.189)$$

The temperature change due to the expansion is therefore

$$\Delta T = \int_{V_i}^{V_f} \left(\frac{\partial T}{\partial V}\right)_{U,n} dV \quad (2.189a)$$

where  $\left(\frac{\partial T}{\partial V}\right)_{U,n}$  is called the **Joule coefficient**.

Using (2.8), we have

$$\begin{aligned} \left(\frac{\partial U}{\partial V}\right)_{T,n} &= \left(\frac{\partial U}{\partial V}\right)_{S,n} + \left(\frac{\partial U}{\partial S}\right)_{V,n} \left(\frac{\partial S}{\partial V}\right)_{T,n} \\ &= -P + T \left(\frac{\partial S}{\partial V}\right)_{T,n} \quad [ (2.68-9) \text{ used. } ] \\ &= -P + T \left(\frac{\partial P}{\partial T}\right)_{V,n} \quad [ (2.100) \text{ used. } ] \end{aligned} \quad (2.190)$$

Also, from (2.135), we have

$$\left(\frac{\partial U}{\partial T}\right)_{V,n} = C_{V,n} \quad (2.190a)$$

so that (2.189) gives

$$\left(\frac{\partial T}{\partial V}\right)_{U,n} = -\frac{1}{C_{V,n}} \left[ -P + T \left(\frac{\partial P}{\partial T}\right)_{V,n} \right] \quad (2.190b)$$

For an ideal gas,

$$PV = nRT$$

so that

$$\left(\frac{\partial P}{\partial T}\right)_{V,n} = \frac{nR}{V} = \frac{P}{T}$$

and (2.190b) gives

$$\left(\frac{\partial T}{\partial V}\right)_{U,n} = 0 \quad \text{for an ideal gas.} \quad (2.190c)$$

Therefore, there is no temperature change in the free expansion of an ideal gas.

Now, the temperature of a system is just a measure of its average kinetic energy. Since the internal energy of an ideal gas is purely kinetic, its Joule effect, which conserves the internal energy, is therefore null.

For a van der Waals gas [ see (2.12) of §2.C.3 ],

$$\left(P + \frac{an^2}{V^2}\right)(V - nb) = nRT \quad [a, b > 0] \quad (2.190d)$$

so that

$$\left(\frac{\partial P}{\partial T}\right)_{V,n} = \frac{nR}{V - nb} = \frac{1}{T} \left(P + \frac{an^2}{V^2}\right) \quad (2.190e)$$

and (2.190b) gives

$$\left(\frac{\partial T}{\partial V}\right)_{U,n} = -\frac{1}{C_{V,n}} \frac{an^2}{V^2} \quad (2.194)$$

$< 0$  [ (2.180) used. ]

Hence, there is a temperature drop in the free expansion of a van der Waals gas.

Using (2.146), we have

$$\left(\frac{\partial C_{V,n}}{\partial V}\right)_{T,n} = T \left(\frac{\partial^2 P}{\partial T^2}\right)_{V,n} = 0 \quad [ (2.190a) \text{ used. } ] \quad (2.192)$$

so that

$$C_{V,n} = C_{V,n}(T, n) \quad (2.193)$$

Putting (2.194) into (2.189a) thus gives

$$\begin{aligned} \Delta T &= -\frac{an^2}{C_{V,n}} \int_{V_i}^{V_f} \frac{1}{V^2} dV \\ &= \frac{an^2}{C_{V,n}} \left( \frac{1}{V_f} - \frac{1}{V_i} \right) \end{aligned} \quad (2.195)$$

$$= -\frac{an^2}{C_{V,n} V_i V_f} \Delta V \quad [ \Delta V = V_f - V_i ] \quad (2.195a)$$

The fraction temperature change is defined as

$$\frac{\Delta T}{T_i} = \frac{a n^2}{C_{V,n} T_i} \left( \frac{1}{V_f} - \frac{1}{V_i} \right) \quad (2.196)$$

The maximum  $\Delta T$  is obtained by setting  $V_f = \infty$ , giving

$$(\Delta T)_{\max} = -\frac{a n^2}{C_{V,n} V_i} \quad (2.195b)$$

Now, according to the equipartition theorem,

$$C_{V,n} \approx \frac{1}{2} f n R$$

where  $f$  is the number of quadratic terms in the single-particle Hamiltonian of the system, and

$$R \approx 8.314 \text{ J/mol} \cdot \text{K}$$

From Table 2.1 of Reichl's text, we have, for non-inert gases,

$$a \approx 10^{-1} \text{ Pa} \cdot \text{m}^6 / \text{mol}^2 = 10^{-1} \text{ N} \cdot \text{m}^4 / \text{mol}^2 = 10^{-1} \text{ J} \cdot \text{m}^3 / \text{mol}^2$$

so that (2.195b) becomes

$$(\Delta T)_{\max} = -\frac{2a}{f R V_i} \approx -\frac{10^{-2}}{v_i} \quad v_i = \frac{V_i}{n} = \text{molar volume}$$

At standard conditions ( $T = 300 \text{ K}$ ,  $P = 1 \text{ atm}$ ), we have

$$v \approx 22.4 \text{ l} \approx 10^{-2} \text{ m}^3$$

$$\rightarrow (\Delta T)_{\max} \approx -1 \text{ K}$$

The Joule effect is thus rather weak.

This finite Joule effect can be attributed to the attractive interaction between neutral molecules in a van der Waals gas. As the gas expands, this attraction weakens so that the average potential energy of the gas is raised. Since the total energy is preserved, the average kinetic energy, and hence the temperature, must become lower.

## S2.A.2. The Joule-Kelvin Effect: Throttling

Since Lord Kelvin was born William Thomson, the effect is also known as the **Joule-Thomson effect**.

In an idealized Joule-Kelvin effect (or throttling) experiment, an insulated chamber with a fixed porous partition in the center is fitted with a frictionless insulated piston at each end [ see Fig.2.13 ].

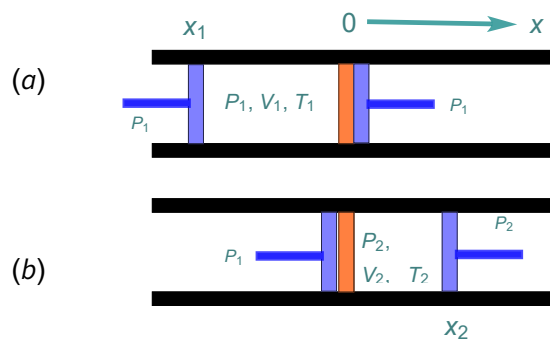


Fig.2.13.

Initially, as shown in Fig.2.13(a), the gas with equilibrium parameters  $(P_1, V_1, T_1)$  is entirely on the left hand side of the porous (red) partition. Next, we reduce suddenly the pressure on the right hand side so that  $P_2 < P_1$ . The gas is thus forced into the right hand side of the porous partition. As it emerges from the holes on the partition, it undergoes sudden expansion and is in a chaotic state due to the turbulence. After equilibrium is reestablished, its parameters become  $(P_2, V_2, T_2)$ .

Note that the porous partition divides the gas into separate streams that undergo their own sudden expansion. However, this is not an essential feature of the effect since we can replace the porous partition by one with a single hole. The true difference between the Joule and Joule-Kelvin effects is that  $\Delta T$  depends on  $\Delta V$  for the former, but on  $\Delta P$  for the latter. Furthermore, the latter is readily turned into a cyclic process by alternating the sign of  $\Delta P$  repeatedly.

Let  $A$  be the cross section of the chamber and  $x_j$  the position of the piston as measured from the porous partition. The work done by the pistons is

$$\begin{aligned}\Delta W_{\text{pis}} &= \sum_{j=1,2} \mathbf{f}_j \cdot \Delta \mathbf{x}_j \\ &= P_1 A (0 - x_1) - P_2 A (x_2 - 0) \quad [x_1 < 0 \ \& \ x_2 > 0] \\ &= P_1 V_1 - P_2 V_2\end{aligned}$$

The work done by the gas is therefore

$$\begin{aligned}\Delta W &= -\Delta W_{\text{pis}} \\ &= P_2 V_2 - P_1 V_1\end{aligned} \quad (2.197)$$

This round-about way to find  $\Delta W$  is necessary because  $P$  in the recipe  $\Delta W = \int P dV$  is not defined for a non-equilibrium process.

Since the system is insulated,  $\Delta Q = 0$ , and the 1st law gives

$$U_2 - U_1 = \Delta U = -\Delta W = P_1 V_1 - P_2 V_2 \quad [(2.197) \text{ used.}] \quad (2.198)$$

$$\rightarrow H_1 = U_1 + P_1 V_1 = U_2 + P_2 V_2 = H_2 \quad (2.199)$$

$$\therefore \Delta H = H_2 - H_1 = 0 \quad (2.199a)$$

so that the (irreversible) throttling process preserves enthalpy.

From (2.84) of §2.F.2, we have

$$\begin{aligned}(dH)_n &= T dS + V dP \\ &= 0 \quad [(2.199a) \text{ used.}] \end{aligned} \quad (2.200)$$

Choosing  $(T, P)$  as independent variables, we have

$$(dS)_n = \left( \frac{\partial S}{\partial T} \right)_{P,n} dT + \left( \frac{\partial S}{\partial P} \right)_{T,n} dP \quad (2.201)$$

so that (2.200) becomes

$$\begin{aligned}(dH)_n &= T \left( \frac{\partial S}{\partial T} \right)_{P,n} dT + \left[ T \left( \frac{\partial S}{\partial P} \right)_{T,n} + V \right] dP \\ &= C_{P,n} dT + \left[ -T \left( \frac{\partial V}{\partial T} \right)_{P,n} + V \right] dP \quad [(2.144) \ \& \ (2.112) \text{ used.}] \\ &= 0\end{aligned} \quad (2.202)$$

$$= \left( \frac{\partial H}{\partial T} \right)_{P,n} dT + \left( \frac{\partial H}{\partial P} \right)_{T,n} dP \quad [H = H(T, P, n)] \quad (2.202a)$$

$$\rightarrow \frac{dT}{dP} = - \frac{\left( \frac{\partial H}{\partial P} \right)_{T,n}}{\left( \frac{\partial H}{\partial T} \right)_{P,n}} = \frac{1}{C_{P,n}} \left[ T \left( \frac{\partial V}{\partial T} \right)_{P,n} - V \right] \quad (2.204a)$$

$$= \left( \frac{\partial T}{\partial P} \right)_{H,n} \quad [ (2.5-6) \text{ of } \S 2.B \text{ used. } ]$$

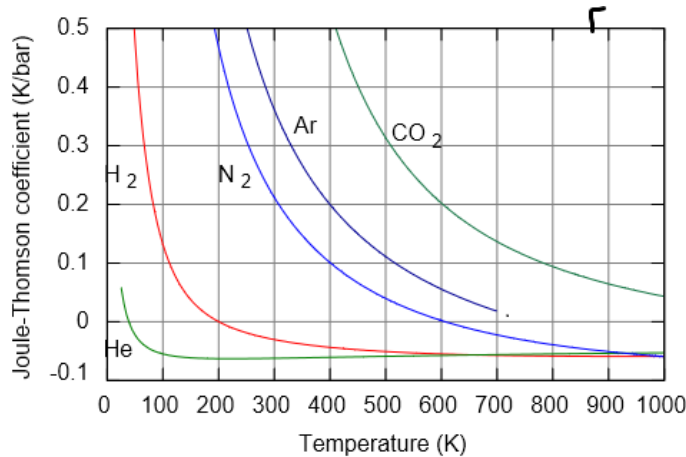
$$\equiv \mu_{JK} = \text{Joule-Kelvin coefficient.} \quad (2.204)$$

$$\therefore \Delta T = \int \mu_{JK} dP \quad (2.204b)$$

Since the gas experiences a pressure drop in the throttling process, we have  $dP < 0$  and

$$\begin{aligned} \Delta T < 0 \quad (\text{gas cools}) & \quad \text{if } \mu_{JK} > 0 \\ \Delta T > 0 \quad (\text{gas heats up}) & \quad \text{if } \mu_{JK} < 0 \end{aligned} \quad (2.204c)$$

Temperature dependence of  $\mu_{JK}$  at  $P = 1$  atm is plotted for some common gases in the figure below. Note that  $H_2$  heats up upon expansion for  $T \gtrsim 200$  K so that its leakage from storage at room temperature easily causes explosion.



Units of pressure: 1 bar =  $10^5$  Pa = 0.987 atm.

For an ideal gas, we have

$$PV = nRT$$

$$\rightarrow \left( \frac{\partial V}{\partial T} \right)_{P,n} = \frac{nR}{P} = \frac{V}{T}$$

$$\therefore \mu_{JK} = 0 \quad [ (2.204a) \text{ used. } ]$$

(2.204b) then gives

$$\Delta T = 0 \quad \text{for an ideal gas.}$$

For a van der Waals gas,  $\left( \frac{\partial (2.190d)}{\partial T} \right)_{P,n}$  gives

$$\left[ -\frac{2an^2}{V^3}(V-nb) + \left( P + \frac{an^2}{V^2} \right) \right] \left( \frac{\partial V}{\partial T} \right)_{P,n} = nR$$

$$\rightarrow \left[ -\frac{2an^2}{V^3}(V-nb) + \frac{nRT}{V-nb} \right] \left( \frac{\partial V}{\partial T} \right)_{P,n} = nR \quad [(2.190d) \text{ used.}]$$

$$\therefore \left( \frac{\partial V}{\partial T} \right)_{P,n} = \frac{nRV^3(V-nb)}{-2an^2(V-nb)^2 + nRTV^3}$$

(2.204a) then gives

$$\begin{aligned} \mu_{JK} &= \frac{1}{C_{P,n}} \left[ \frac{nRTV^3(V-nb)}{-2an^2(V-nb)^2 + nRTV^3} - V \right] \\ &= \frac{1}{C_{P,n}} \left[ \frac{-n^2RTV^3b + 2an^2(V-nb)^2V}{-2an^2(V-nb)^2 + nRTV^3} \right] \\ &= \frac{1}{nC_{P,n}} \left[ \frac{-n^5RTv^3b + 2an^5(v-b)^2v}{-2an^4(v-b)^2 + n^4RTv^3} \right] \quad \left[ v = \frac{V}{n}, c_{P,n} = \frac{C_{P,n}}{n} \right] \\ &= \frac{1}{C_{P,n}} \left[ \frac{-RTv^3b + 2a(v-b)^2v}{-2a(v-b)^2 + RTv^3} \right] \\ &= \frac{1}{C_{P,n}} \left( \frac{\frac{2a}{RT} \left( \frac{v-b}{v} \right)^2 - b}{1 - \frac{2a}{RTv} \left( \frac{v-b}{v} \right)^2} \right) \end{aligned} \quad (2.205a)$$

Plugging in the ideal gas value  $C_{P,n} = \frac{5}{2}nR$ , we have

$$\mu_{JK} = \frac{1}{R} \left( \frac{\frac{2a}{RT} \left( \frac{v-b}{v} \right)^2 - b}{\frac{5}{2} - \frac{5a}{RTv} \left( \frac{v-b}{v} \right)^2} \right) \quad (2.205)$$

Consider now the molar van der Waals equation [ see (2.190d) ]

$$\left( P + \frac{a}{v^2} \right) (v-b) = RT$$

$$\rightarrow P = \frac{RT}{v-b} - \frac{a}{v^2} \quad (2.205b)$$

For low densities, (2.205b) approaches the molar ideal gas law

$$P = \frac{RT}{v}$$

which means

$$v \gg b \quad \& \quad RTv \gg a \quad (2.205c)$$

(2.205) then reduces to

$$\mu_{JK} \approx \frac{2}{5R} \left( \frac{2a}{RT} - b \right) \quad [\text{For low densities.}] \quad (2.206)$$

$$\begin{cases} > 0 & \text{for } T < T_{inv} \\ < 0 & \text{for } T > T_{inv} \end{cases} \quad (2.206a)$$

where

$$T_{\text{inv}} = \frac{2a}{bR} = \text{inversion temperature.} \quad (2.206b)$$

(2.204c) then gives

$$\Delta T < 0 \text{ (gas cools down)} \quad \text{if} \quad T < T_{\text{inv}}$$

$$\Delta T > 0 \text{ (gas heats up)} \quad \text{if} \quad T > T_{\text{inv}} \quad (2.206c)$$

A more general expression for  $T_{\text{inv}}$  is given by setting  $\mu_{JK} = 0$  in (2.204) so that

$$T_{\text{inv}} = \frac{V}{\left(\frac{\partial V}{\partial T}\right)_{P,n}} \quad (2.207)$$

For the van der Waals gas, setting  $\mu_{JK} = 0$  in (2.205) gives

$$T_{\text{inv}} = \frac{2a}{Rb} \left(\frac{v-b}{v}\right)^2 \quad (2.208)$$

which reduces to (2.206b) for  $v \gg b$ , as expected.

Solving for  $v$  from (2.208), we have

$$\frac{v-b}{v} = \sqrt{\frac{bRT_{\text{inv}}}{2a}}$$

$$\rightarrow v = \frac{b}{1 - \sqrt{\frac{bRT_{\text{inv}}}{2a}}} \quad v-b = \frac{b \sqrt{\frac{bRT_{\text{inv}}}{2a}}}{1 - \sqrt{\frac{bRT_{\text{inv}}}{2a}}}$$

Putting this into the molar vdW equation (2.205b), we get

$$P = \frac{RT_{\text{inv}}}{b} \left( \sqrt{\frac{2a}{bRT_{\text{inv}}}} - 1 \right) - \frac{a}{b^2} \left( 1 - \sqrt{\frac{bRT_{\text{inv}}}{2a}} \right)^2$$

$$= \frac{1}{b} \sqrt{\frac{2aRT_{\text{inv}}}{b}} - \frac{RT_{\text{inv}}}{b} - \frac{a}{b^2} \left( 1 - 2\sqrt{\frac{bRT_{\text{inv}}}{2a}} + \frac{bRT_{\text{inv}}}{2a} \right)$$

$$= \frac{2}{b} \sqrt{\frac{2aRT_{\text{inv}}}{b}} - \frac{3RT_{\text{inv}}}{2b} - \frac{a}{b^2} \quad (2.209)$$

$$\rightarrow \frac{dP}{dT_{\text{inv}}} = \frac{1}{b} \sqrt{\frac{2aR}{bT_{\text{inv}}}} - \frac{3R}{2b}$$

$$\frac{d^2P}{dT_{\text{inv}}^2} = -\frac{1}{2b} \sqrt{\frac{2aR}{bT_{\text{inv}}^3}} < 0$$

Therefore,  $P$  has at maximum at

$$T_{\text{inv}} = \frac{2aR}{b} \left( \frac{2}{3R} \right)^2 = \frac{8a}{9bR} \quad (2.209a)$$

with value

$$P_{\max} = \frac{2}{b} \sqrt{\frac{2aR}{b} \cdot \frac{8a}{9bR} - \frac{3R}{2b} \cdot \frac{8a}{9bR} - \frac{a}{b^2}} = \frac{a}{3b^2} \quad (2.209b)$$

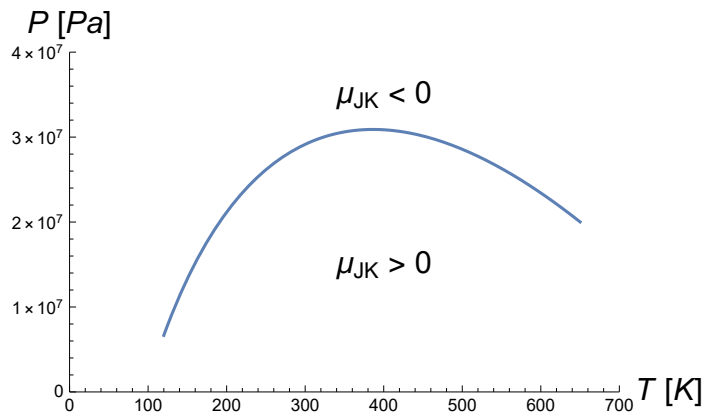
For a  $N_2$  gas, Table 2.1 of §2.C.3 gives [ caution: units of  $b$  in Reichl's table should be  $L/mol$ . ]

$$a \approx 0.141 \text{ Pa m}^6/\text{mol} \quad b \approx 0.039 \times 10^{-3} \text{ m}^3/\text{mol}$$

so that

$$P_{\max} \approx 3.07 \times 10^7 \text{ Pa}$$

The plot of (2.209) for a  $N_2$  gas is shown in the figure below [ see Reichl's Fig.2.14 for a comparison with experimental data].



If we ignore the small pressure dependence of  $\mu_{JK}$ , (2.204b) becomes

$$\Delta T \approx \mu_{JK} \Delta P$$

Thus, there is an approximately constant temperature drop under a given pressure drop, if the gas remains in the  $\mu_{JK} > 0$  region. The cooling process can therefore be turned into a cycle that forces the gas to go through a pressure drop, and hence a temperature drop, repeatedly. This is called the **Hampson-Linde cycle** and can be used to liquefy atmospheric gases.

## Code

```
par = {R → 8.314, a → 0.141, b → 0.039 × 10-3};
P =  $\frac{2}{b} \sqrt{\frac{2aRT}{b} - \frac{3RT}{2b} - \frac{a}{b^2}}$ ;
Plot[P /. par, {T, 120, 650}, PlotRange → {{0, 700}, {0, 4 × 107}},
  AxesLabel → {"T [K]", "P [Pa]"},
  Epilog → {Text["μJK > 0", {400, 1.5 × 107}],
    Text["μJK < 0", {400, 3.5 × 107}]}
```