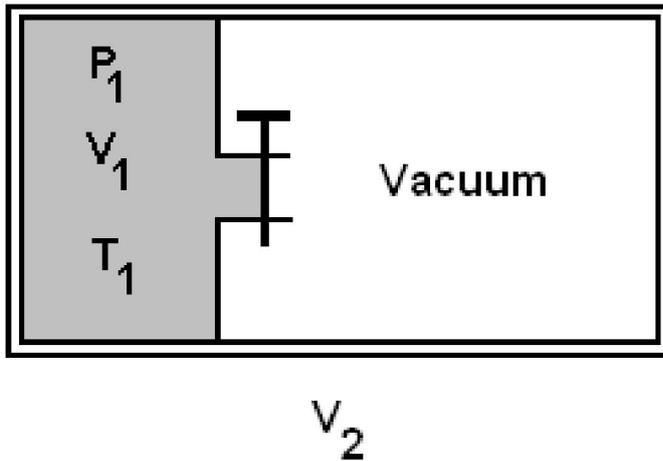


## Y. Typical examples of irreversible processes

### Y.1 The Joule free expansion of a gas

Imagine a gas confined in a partition (of volume  $V_1$ ) of an adiabatically insulated container of total volume  $V_2$  (Figure 1). The other part of the container is initially evacuated. Let  $T_1$  be the initial temperature of the gas. The following natural question arises: what happens to the gas if it is



**Figure 1:** Schematic of the free expansion apparatus.

allowed to expand suddenly into the whole volume of the container by opening the tap? Intuitively, one can readily say that this phenomenon is irreversible, since no spontaneous re-confinement of the gas back into the original partition can be imagined. The irreversible character of this expansion will be proven in the following by means of the overall framework of the Laws of Thermodynamics. This phenomenon was first studied in an attempt to obtain the caloric equation of state for a perfect gas. The most consistent report was made first by James Prescott Joule in a paper published in 1845 [1].

In analyzing the phenomenon one may readily observe that the work done by the gas during the expansion is nil, since there is no opposition from the evacuated compartment of the container. Therefore, the work channel is closed for the expanding gas, by the very experimental arrangement. Moreover, the caloric channel is also closed due to the assumed adiabatic enclosure of the system. Needless to say that the chemical channel is also blocked as no amount of gas is allowed to leak neither outside the container nor inside it. The First Law of Thermodynamics then states that *the internal energy of the system is constant during the process*.

To check the reversibility of the process, assume an infinitesimal version of it, in which the gas expands from the volume  $V$  to  $V + dV$ . As there should be a reversible process connecting the initial and final states of this process, one may write the fundamental equation of Thermodynamics:

$$T dS = dU + P dV - \mu dv. \quad (1)$$

As the internal energy and the mass of the gas should be the same in both states,  $dU = 0$  and  $dv = 0$ , so that Eq. (1) becomes:

$$dS = \frac{P}{T} dV . \quad (2)$$

Therefore, as the process is necessarily an expansion and thus  $dV > 0$ , and since  $P$  and  $T$  are strictly positive quantities, one may conclude that  $dS > 0$  in the infinitesimal process. On the other hand, the system being insulated, one has  $\delta Q = 0$  during the free expansion. Therefore,  $dS > \delta Q/T$  and so, the process should be *irreversible*.

Moreover, an important question related to the free expansion of a gas is how its temperature changes in the final state. To answer this question consider again an infinitesimal free expansion, for which we again have  $dU = 0$ . Writing down the internal energy variation from the caloric equation of state, one readily obtains:

$$dU = \left( \frac{\partial U}{\partial T} \right)_{V,v} dT + \left( \frac{\partial U}{\partial V} \right)_{T,v} dV + \left( \frac{\partial U}{\partial v} \right)_{T,V} dv = 0 . \quad (3)$$

But, as  $dv = 0$ ,  $\left( \frac{\partial U}{\partial T} \right)_{V,v} = C_V$ ,  $\left( \frac{\partial U}{\partial V} \right)_{P,v} = T \left( \frac{\partial P}{\partial T} \right)_{V,v} - P = P(T \beta_V - 1)$ , Eq. (3) becomes:

$$dT = \frac{P}{C_V} (1 - T \beta_V) dV . \quad (4)$$

As  $P$ ,  $C_V$  and  $dV$  are strictly positive quantities, it turns out that the sign of  $dT$  is determined by the parenthesis of Eq. (4). For an ideal gas, one readily finds:

$$\beta_V = \frac{1}{P} \left( \frac{\partial P}{\partial T} \right)_{V,v} = \frac{1}{T} , \quad (5)$$

so that no temperature variation should be detected. This was actually obtained in the early experiments on free expansion of gases and led Joule to formulate the thermal equation of state for an ideal gas as a function of temperature only. However, subsequent experiments revealed that slight temperature variations can always be detected following the free expansion, so that the ideal gas model has a limited validity. As discussed in Chapter 8, a more realistic thermal equation of state for a gas would be given by the Van der Waals formula:

$$\left( P + a \frac{v^2}{V^2} \right) (V - v b) = v R T , \quad (6)$$

where  $a$  and  $b$  are the Van der Waals parameters of the specified gas. By taking the partial derivative with respect to the temperature in both sides of Eq. (6), one readily obtains:

$$\left(\frac{\partial P}{\partial T}\right)_{V,v} = \frac{1}{T} \left(P + a \frac{v^2}{V^2}\right), \quad (7)$$

so that

$$1 - T \beta_V = 1 - \frac{1}{P} \left(P + a \frac{v^2}{V^2}\right) = -a \frac{v^2}{P V^2}, \quad (8)$$

which is a *strictly negative* quantity. Therefore, according to Eq. (4), one may always expect that *real gases get cooled after a free expansion*. More exactly, an infinitesimal free expansion of a Van der Waals gas will produce the following temperature variation:

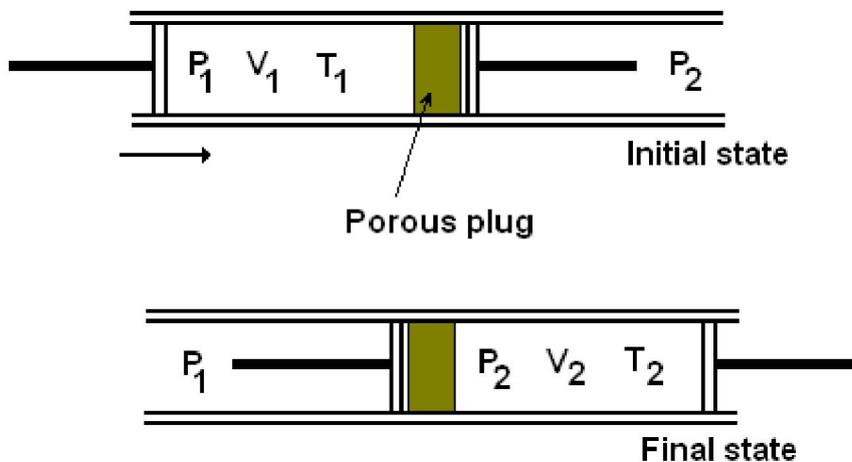
$$dT = -\frac{a}{C_V} \frac{v^2}{V^2} dV. \quad (9)$$

By partitioning a macroscopic free expansion (from the volume  $V_1$  to  $V_2$ ) into infinitesimal such processes, one may readily compute the corresponding temperature variation of a Van der Waals gas:

$$(\Delta T)_{free\ expansion} = -\frac{a v^2}{C_V} \frac{\Delta V}{V_1 V_2}. \quad (10)$$

## Y.2 The Joule-Thomson effect

Another example of irreversible process with gases is the Joule-Thomson effect. This phenomenon is not only interesting by itself, but has also very important practical implications. It is



**Figure 2:** Schematic of the Joule-Thomson apparatus.

named for James Prescott Joule and William Thomson, 1st Baron Kelvin who discovered the effect in 1852 [2, 3] following earlier work by Joule on free expansion of gases. The effect is applied in the Linde technique as a standard process in the petrochemical industry for example, where the cooling effect is used to

liquefy gases, and also in many cryogenic applications (e.g. for the production of liquid oxygen, nitrogen and argon).

The Joule-Thomson effect refers to the changes in the state of a gas that is expanding under pressure through a porous plug or a throttle. This kind of gas expansion is actually denoted as **throttling** in the literature. The phenomenon takes place in a thermally insulating cylinder (Figure 2), which the plug or throttle divides into two compartments. The gas being initially at the temperature  $T_1$  in a volume  $V_1$  is pushed with an adiabatic piston, under high constant pressure  $P_1$ , through the throttle and collected on the other side at a constant pressure  $P_2$ , which is controlled by another adiabatic piston. The final state of the gas is also characterized by the temperature  $T_2$  and the volume  $V_2$ . The amount of gas is supposed to remain unchanged. Thus, the gas throttling takes place with both the chemical and thermal channels closed. The First Law written for the process takes therefore the form:

$$\Delta U = W . \quad (11)$$

As both pressures are kept constant, the total work performed on the system will be:

$$W = -P_1(0 - V_1) - P_2(V_2 - 0) = P_1 V_1 - P_2 V_2 . \quad (12)$$

Therefore, as  $\Delta U = U_2 - U_1$ , Eq. (11) becomes:

$$U_1 + P_1 V_1 = U_2 + P_2 V_2 , \quad (13)$$

thus showing that the throttling takes place so that the enthalpy of the gas does not change (isenthalpic process):  $H_1 = H_2$ .

The throttling of a gas is an irreversible process. To prove this, let us consider an infinitesimal transformation of this kind, where all the state parameters (except of those which are kept constants) vary by infinitesimal amounts. Consider a reversible process linking the initial and final states. Still this reversible transformation keeps the enthalpy and the mass constants (since both quantities are state parameters). Therefore, by using the fundamental equation of Thermodynamics, one may write:

$$(dS)_{H,v} = \left( \frac{1}{T} dU + \frac{P}{T} dV - \frac{\mu}{T} dv \right)_{H,v} = \left( \frac{1}{T} dH - \frac{V}{T} dP - \frac{\mu}{T} dv \right)_{H,v} = -\frac{V}{T} dP . \quad (14)$$

As the gas's pressure decreases following the throttling,  $dP < 0$  and thus Eq. (14) shows that  $dS > 0$ . Moreover, as the throttling occurs under adiabatic enclosure, one may observe that  $\delta Q = 0$ . Therefore, one readily finds that during throttling:

$$dS > \frac{\delta Q}{T} \quad (15)$$

So that ***the process is irreversible***.

To account for the temperature variation during throttling, one may again resort on infinitesimal isenthalpic processes, for which:

$$dH = \left( \frac{\partial H}{\partial T} \right)_{P,v} dT + \left( \frac{\partial H}{\partial P} \right)_{T,v} dP + \left( \frac{\partial H}{\partial v} \right)_{T,P} dv = 0. \quad (16)$$

As the mass is constant, one readily obtains:

$$dT = - \left[ \left( \frac{\partial H}{\partial P} \right)_{T,v} / \left( \frac{\partial H}{\partial T} \right)_{P,v} \right] dP. \quad (17)$$

The enthalpy derivatives can be obtained explicitly as follows:

$$\begin{aligned} \left( \frac{\partial H}{\partial P} \right)_{T,v} &= \left( \frac{\partial H}{\partial V} \right)_{T,v} \left( \frac{\partial V}{\partial P} \right)_{T,v} = \left( \frac{\partial(U + PV)}{\partial V} \right)_{T,v} \left( \frac{\partial V}{\partial P} \right)_{T,v} = \\ &= \left[ \left( \frac{\partial U}{\partial V} \right)_{T,v} + P + V \left( \frac{\partial P}{\partial V} \right)_{T,v} \right] \left( \frac{\partial V}{\partial P} \right)_{T,v} = T \left( \frac{\partial P}{\partial T} \right)_{V,v} \left( \frac{\partial V}{\partial P} \right)_{T,v} + V \end{aligned} \quad (18)$$

More over, since  $\left( \frac{\partial T}{\partial V} \right)_{P,v} \left( \frac{\partial P}{\partial T} \right)_{V,v} \left( \frac{\partial V}{\partial P} \right)_{T,v} = -1$ , it follows that  $\left( \frac{\partial P}{\partial T} \right)_{V,v} \left( \frac{\partial V}{\partial P} \right)_{T,v} = - \left( \frac{\partial V}{\partial T} \right)_{P,v}$ , so that we finally get from Eq. (18):

$$\left( \frac{\partial H}{\partial P} \right)_{T,v} = -T \left( \frac{\partial V}{\partial T} \right)_{P,v} + V = V(1 - T \alpha_p). \quad (19)$$

Now, for the other derivative of the enthalpy in Eq. (17) we can most conveniently start from the definition of the constant-pressure molar heat capacity,  $C_p$ :

$$\begin{aligned} \nu C_p = (\delta Q)_p : dT &= (dU + PdV)_p : dT = \\ &= \left[ \left( \frac{\partial U}{\partial T} \right)_p dT + \left( \frac{\partial U}{\partial P} \right)_T dP + PdV \right]_p : dT = \\ &= \left[ \left( \frac{\partial U}{\partial T} \right)_p dT + P \left( \frac{\partial V}{\partial T} \right)_p dT + P \left( \frac{\partial V}{\partial P} \right)_T dP \right]_p : dT = \\ & \left[ \left( \frac{\partial U}{\partial T} \right)_p dT + P \left( \frac{\partial V}{\partial T} \right)_p dT \right]_p : dT = \left( \frac{\partial U}{\partial T} \right)_p + \left( \frac{\partial(PV)}{\partial T} \right)_p = \left( \frac{\partial H}{\partial T} \right)_p \end{aligned} \quad (20)$$

Thus, using Eqs. (17), (19) and (20), the temperature variation in an infinitesimal Joule-Thomson process reduces to:

$$dT = \frac{\nu}{C_p} (T \alpha_p - 1) dP, \quad (21)$$

where  $v$  is the molar volume of the gas. The coefficient of  $dP$  in Eq. (21) is called **Joule-Thomson coefficient**:

$$\mu_{JT} \equiv \frac{v}{C_p} (T \alpha_p - 1). \quad (22)$$

Owing to the fact that  $dP < 0$  in Eq. (21), the gas is cooled following the Joule-Thomson effect if the coefficient  $\mu_{JT}$  is positive. For an ideal gas, one readily finds that  $\alpha_p = 1/T$ , so that such a system cannot be cooled or heated through Joule-Thomson expansion ( $dT = 0$ ). On the contrary, real gases obeying the Van der Waals equation of state may either be cooled or heated through such a throttling process. For any given gas a temperature exists for which the Joule-Thomson coefficient vanishes. This value of  $T$  is called **inversion temperature**,  $T_{inv}$ . When  $T$  crosses the value of the inversion temperature the Joule-Thomson coefficient changes sign and the effect of throttling is reversed. It turns out that the  $\mu_{JT}$  is a **decreasing function of temperature**, so that if the  $T$  is below the inversion temperature then the gas is cooling when subject to Joule-Thomson throttling. The heating effect appears when  $T$  is above  $T_{inv}$ . To see how this works, let us consider again Eq. (6) to compute  $\alpha_p$ . For convenience, the derivative of the temperature with respect to the volume should be taken:

$$\left( \frac{\partial T}{\partial V} \right)_{P,v} = \frac{1}{vR} \left[ P + a \frac{v^2}{V^2} - 2a \frac{v^2}{V^3} (V - vb) \right] = \frac{1}{vR} \left[ \frac{vRT}{V - vb} - 2a \frac{v^2}{V^3} (V - vb) \right].$$

It proves more convenient to use the molar volume  $v$  to express the previous derivative:

$$\left( \frac{\partial T}{\partial V} \right)_{P,v} = \frac{1}{vR} \left[ \frac{1}{v} \frac{RT}{1 - \frac{b}{v}} - \frac{a}{v^2} + \frac{2ab}{v^3} \right] \cong \frac{1}{vR} \left[ \frac{RT}{v} \left( 1 + \frac{b}{v} \right) - \frac{2a}{v^2} + \frac{2ab}{v^3} \right] \quad (23)$$

where the approximation  $\frac{1}{1 - \frac{b}{v}} \cong 1 + \frac{b}{v}$  has been used. This is a valid assumption since for gases

$b \ll v$ . Using Eq. (23) in the definition of the expansivity  $\alpha_p$ , one readily finds:

$$\frac{1}{\alpha_p} = V \left( \frac{\partial T}{\partial V} \right)_{P,v} = \frac{v}{R} \left[ \frac{RT}{v} \left( 1 + \frac{b}{v} \right) - \frac{2a}{v^2} + \frac{2ab}{v^3} \right] = T \left[ 1 + \frac{b}{v} - \frac{2a}{vRT} \left( 1 - \frac{b}{v} \right) \right]. \quad (24)$$

Therefore, by replacing in Eq. (22), the Joule-Thomson coefficient takes the form:

$$\mu_{JT} = \frac{v}{C_p} \left[ \frac{1}{1 + \frac{b}{v} - \frac{2a}{vRT} \left( 1 - \frac{b}{v} \right)} - 1 \right] \cong \frac{v}{C_p} \left[ 1 - \frac{b}{v} + \frac{2a}{vRT} \left( 1 - \frac{b}{v} \right) - 1 \right],$$

since both  $b \ll v$  and  $a \ll vRT$ . It may be concluded that

$$\mu_{JT} \cong \frac{1}{C_p} \left[ \frac{2a}{RT} \left( 1 - \frac{b}{v} \right) - b \right]. \quad (25)$$

By further neglecting  $b/v$  with respect to 1 in Eq. (25) the following expression is obtained for the Joule-Thomson coefficient of a Van der Waals gas:

$$\mu_{JT} \cong \frac{1}{C_p} \left( \frac{2a}{RT} - b \right). \quad (26)$$

The corresponding inversion temperature becomes:

$$T_{inv} = \frac{2a}{Rb}. \quad (27)$$

It is now clear that for  $T < T_{inv}$  the Joule-Thomson coefficient is positive and the gas is cooling. Helium and hydrogen are two gases whose Joule-Thomson inversion temperatures at one atmosphere are very low (e.g., about  $-222$  °C for helium). Thus, helium and hydrogen will warm



**Figure 3:** PHYWE experimental setup for demonstrating the Joule-Thomson effect.

when expanded at constant enthalpy at typical room temperatures. For this reason, simple Linde cycle liquefiers cannot normally be used to liquefy *helium, hydrogen and neon*. On the other hand nitrogen has an inversion temperature of 621 K (348 °C) and oxygen has an inversion temperature of 764 K (491 °C): *the two most abundant gases in air can be cooled by the Joule-Thomson effect at typical room temperatures.*

Figure 3 shows a laboratory setup for demonstrating the Joule-Thomson effect. The cylinder where the throttling takes place is made of glass (a sufficiently adiabatic enclosure for the demonstrative purposes). The gas is injected from a pressurized canister through a long thermal conductive metal pipe which is coiled on the base cylinder. This component is intended for thermalizing the gas to the room temperature before throttling. The initial pressure of the gas is read on a manometer and the pressure after the throttling is the ambient atmospheric one. The temperature difference is measured by a couple of thermocouples immersed in the two compartments of the throttling vessel. Typical values for the Joule-Thomson coefficient are of the order of  $10^{-5}$  K/Pa at the room temperatures. From Eq. (26) it may be seen that  $\mu_{JT}$  decreases with the temperature, so the effect can be obtained more clearly at lower ambient temperatures.

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