

**Lecture TOPIC 10**

(Finn: 7.1, 7.2, 7.3, 7.4, 7.5, 7.6, 7.7, 7.8; )

**Synopsis:** Properties and processes, including applications of Maxwell relations part 2, mainly expansion processes (Joule and Joule-Kelvin).

**The Joule coefficient for a free expansion**

We reanalyse the irreversible free expansion inside a rigid adiabatic enclosure from topic 3. For the *surroundings*, rigid implies constant volume and adiabatic implies constant entropy, so the natural thermodynamic potential is  $U(S, V)$ . For the *system*, we are interested in changes in  $T$  as  $V$  is increased. To calculate the temperature change, we need to find an expression for  $\left(\frac{\partial T}{\partial V}\right)_U$  using path-independent state properties. This suggests working with  $T = T(V, U)$  and considering an equivalent reversible process between initial equilibrium state with coordinates  $(U_i, V_i, T_i)$  and the final state with coordinates  $(U_f, V_f, T_f)$ :

$$dT = \left(\frac{\partial T}{\partial V}\right)_U dV + \left(\frac{\partial T}{\partial U}\right)_V dU$$

Choosing  $U = \text{constant}$  along the reversible path gives the change in temperature,  $\Delta T$ ,

$$\Delta T = \int_{V_i}^{V_f} \left(\frac{\partial T}{\partial V}\right)_U dV = \int_{V_i}^{V_f} \mu_J dV$$

The cyclical rule allows  $U$  to be incorporated inside the partial derivative [anticipating that the derivative of  $U$  with respect to  $T$  can then be replaced with  $C_V$ ].

$$\mu_J = \left(\frac{\partial T}{\partial V}\right)_U = - \left(\frac{\partial T}{\partial U}\right)_V \left(\frac{\partial U}{\partial V}\right)_T = -\frac{1}{C_V} \times \left(\frac{\partial U}{\partial V}\right)_T$$

Using the central equation, the derivative of  $U$  with respect to  $V$  can be written:

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

leading to

$$\mu_J = \frac{1}{C_V} \left( P - T \left(\frac{\partial P}{\partial T}\right)_V \right)$$

where a Maxwell relation was used in deriving the final expression. Three examples:

- (1) **Ideal gas** :  $\mu_J = 0$  see Topic 3.
- (2) **van der Waals fluid** : For one mole  $(P + \frac{a}{v^2})(v - b) = RT$ .

$$\mu_J = \frac{1}{c_V} \left[ P - \frac{RT}{(v - b)} \right] = -\frac{a}{c_V v^2}$$

(3) **Virial expansion:** equation of state (per mole) of a real gas can be written as a power series in the small quantity  $1/v$  where the *virial coefficients*  $B_2, B_3, \dots$  are temperature dependent.

$$Pv = RT \left( 1 + B_2/v + B_3/v^2 + \dots \right) \implies \mu_J = P - (R/v) \left( 1 + B_2/v + B_3/v^2 + \dots \right)$$

Usually  $B_1 = 1$  giving ideal gas behaviour in the low density limit, and  $B_n$  have been measured for many gases in practice. To estimate of the temperature change  $\Delta T$  for a real gas starting at “standard temperature and pressure”, it is sufficient to know its Joule coefficient ( $\mu_J$ ) and the **increase**  $\Delta v$  in its volume per mole. Taking only the first two terms in the virial expansion series, ie disregarding (because they are assumed small) the terms in  $(\frac{1}{v})^n$  for  $n \geq 2$ :

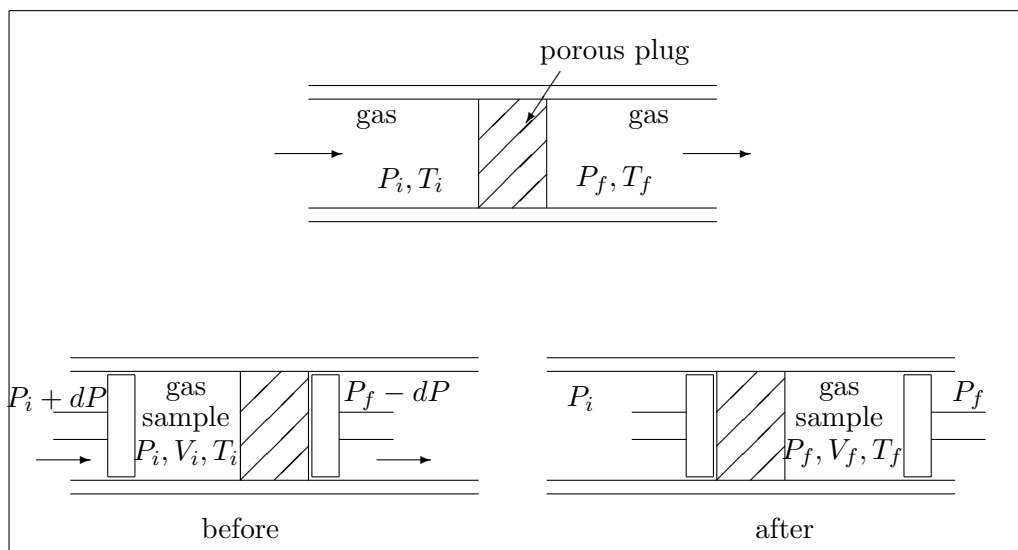
$$\mu_J = -\frac{1}{c_v} \times \frac{RT^2}{v^2} \times \frac{dB_2}{dT}$$

For argon,  $dB_2/dT = 0.25 \text{ cm}^3\text{mol}^{-1}\text{K}^{-1}$ . If a sample of 1 mole of argon at STP doubles its volume in a free expansion, then assuming  $\mu_J$  is constant,  $\Delta T \approx -0.6 \text{ K}$ .

### Continuous Flow Process: The Joule-Kelvin Expansion and Coefficient

In contrast with the Free (or Joule) Expansion, the Joule-Kelvin Expansion is a more practical expansion process, referred to as a throttling process. The gas is forced steadily through a porous plug (various designs possible) held in a cylinder with adiabatic walls, see upper sketch.

To analyse the process, consider (lower sketch) a sample of the gas initially in an equilibrium state with thermodynamic coordinates  $P_i, V_i$  and  $T_i$ . The gas behind it, pushing it forward, behaves like a piston which maintains the gas at its original equilibrium pressure ( $P_i$ ) as it is forced slowly but irreversibly through the plug. Beyond the plug, another imaginary piston maintains the expanded gas at the equilibrium pressure of the gas sample as it emerges to form its final equilibrium state ( $P_f, V_f, T_f$ ).



If we only want to calculate initial and final equilibrium state variables, we can ignore irreversibility. In steady flow, the plug remains in its initial state after all the gas sample has passed through it: The process is adiabatic ( $\Delta Q = 0$ ).

For the work done, it is easiest to consider the pistons: the first “piston” does work  $\int_{V_i}^0 P_i dV$  (the second is similar). So the first law gives

$$U_f - U_i = P_i(V_i - 0) - P_f(V_f - 0) = P_i V_i - P_f V_f.$$

In terms of enthalpy ( $H = U + PV$ ) this becomes  $H_i = H_f$ : the Joule-Kelvin process is traditionally called *isenthalpic*. So calculations of the change in state variables such as temperature with changing pressure are made using an equivalent, unspecified reversible isenthalpic process.

We can always write  $T$  as a function of any *two* other state variables. It is convenient to use the conserved quantity  $H$  and the applied quantity  $P$ , and write  $T = T(H, P)$ . Then

$$dT = \left( \frac{\partial T}{\partial P} \right)_H dP + \left( \frac{\partial T}{\partial H} \right)_P dH = \left( \frac{\partial T}{\partial P} \right)_H dP = \mu_{JK} dP$$

$\mu_{JK}$  is the Joule-Kelvin coefficient, a state variable whose value depends on the gas being used and the conditions. For a Joule-Kelvin expansion of a gas from  $P_i$  to  $P_f$ , the temperature change can be calculated from  $\Delta T = \int_{P_i}^{P_f} \mu_{JK} dP$ .

The Joule-Kelvin temperature change for an ideal gas is always zero, but the temperature change for real gases can be either positive or negative (or zero), depending on the sign of  $\mu_{JK}$ . If  $\Delta T$  is negative and large, the process can be used to liquefy gases. The sequence of equations used to describe the process is similar to that for the free expansion process, but with the enthalpy rather than internal energy held constant.

### The Joule-Kelvin coefficient for a throttling process

A process taking place in an isolated box is of little practical use. Real refrigeration requires cycling of the working fluid, i.e. flow. In a throttling process gas is forced through a nozzle or porous plug from a region of high pressure to one of low pressure. For free, adiabatic expansion the *surroundings*, have no entropy change and exert zero external pressure. Hence the relevant thermodynamic potential for the *system* is the enthalpy,  $H$ . We now follow a similar procedure to the previous section, this time looking at the expansion of a gas subject to a different constant potential, namely enthalpy  $H$ . The properties of a reversible isenthalpic process are used to calculate a temperature change when a gas expands irreversibly.

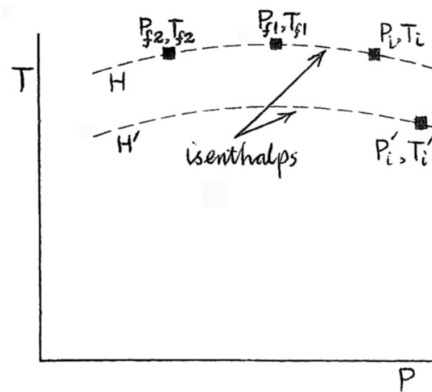
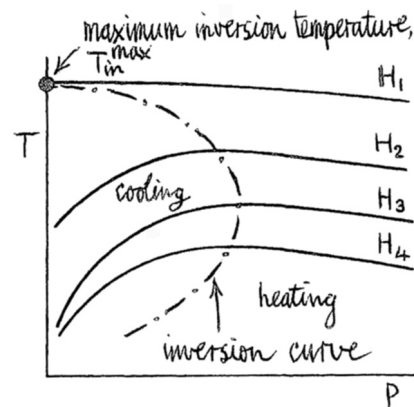
The initial state of the gas has thermodynamic coordinates  $(P_i, T_i)$ , and a number of possible final coordinates  $(P_{f1}, T_{f1})$ ,  $(P_{f2}, T_{f2})$ . The various  $P_{fn}$  are all  $< P_i$  because the gas expands. However, all the equilibrium states have the same value of enthalpy  $H = U + PV$ .

The most appropriate indicator diagram is a  $TP$  diagram. A line through a set of points  $(P_i, T_i)$ ,  $(P_{f1}, T_{f1})$ ,  $(P_{f2}, T_{f2})$ , etc. is an isenthalp, and different isenthalps are found for different starting coordinates  $(P_i, T_i)$ ,  $(P'_i, T'_i)$ ,  $(P''_i, T''_i)$  etc. A set of experimentally-determined isenthalps resemble the schematic sketch shown alongside.

The initial and final coordinates,  $(P_i, T_i)$ , and  $(P_f, T_f)$ , determine the size **and sign, positive or negative** of the temperature change  $\Delta T$ . The curve through the maxima of the isenthalps (second figure) is called the inversion curve. The temperature at the maximum on any isenthalp is called the inversion temperature for this particular value of enthalpy. As drawn, cooling occurs to the left of the inversion curve where  $(\partial T / \partial P)_H > 0$  and warming to the right where  $(\partial T / \partial P)_H < 0$ .

To calculate the change in temperature we need an expression for  $(\partial T / \partial P)_H$ . We get this from  $T = T(P, H)$  by considering an equivalent reversible process between equilibrium states with initial coordinates  $(H_i, P_i, T_i)$  and final coordinates  $(H_f, P_f, T_f)$ :

$$dT = \left( \frac{\partial T}{\partial P} \right)_H dP + \left( \frac{\partial T}{\partial H} \right)_P dH = \left( \frac{\partial T}{\partial P} \right)_H dP$$



The last equality follows from the constant enthalpy  $dH = 0$  process. The finite change in temperature is then

$$\Delta T = \int_{P_i}^{P_f} \left( \frac{\partial T}{\partial P} \right)_H dP = \int_{P_i}^{P_f} \mu_{JK} dP$$

The cyclical rule is then used to incorporate  $H$  inside the partial derivatives [anticipating making use of  $C_P = (\partial H / \partial T)_P$ ] and then using  $dH = TdS + VdP$  [by analogy with  $dU = TdS - PdV$  for a Free expansion] to re-express the pressure derivative of the enthalpy.

$$\mu_{JK} = \left( \frac{\partial T}{\partial P} \right)_H = - \left( \frac{\partial T}{\partial H} \right)_P \left( \frac{\partial H}{\partial P} \right)_T = - \frac{1}{C_P} \times \left( \frac{\partial H}{\partial P} \right)_T$$

From  $dH = TdS + VdP \Rightarrow \left( \frac{\partial H}{\partial P} \right)_T = T \left( \frac{\partial S}{\partial P} \right)_T + V$  we get

$$\mu_{JK} = \frac{1}{C_P} \left( T \left( \frac{\partial V}{\partial T} \right)_P - V \right)$$

using a Maxwell relation in the final step.

From the equation of state of the gas,  $\Delta T$  for a pressure drop  $\Delta P$  in a throttling process can be found, approximately, from  $\Delta T = \mu_{JK} \Delta P$ , assuming  $\mu_{JK}$  to be constant. As with free expansion, there is no change in temperature for an ideal gas. However, for a real gas the change of temperature may be negative **or positive** depending on conditions, and can be estimated from a virial expansion approximation of the equation of state or directly from the equation of state itself.

The Inversion temperature is obtained from the condition  $\mu_{JK} = 0$  and the maximum inversion temperature by then setting  $P = 0$ . The maximum inversion temperature,  $T_{in}^{max}$  varies enormously for different gases:  $T_{in}^{max}$  is higher for gases with strong interactions. Unfortunately, those strong interactions mean that the gas liquifies at higher T, so can't be used.

gas	$(T_{in}^{max})$	$T_{liq}$
argon	723 K	87 K
nitrogen	621 K	77 K
hydrogen	205 K	20 K
helium	51 K	4 K

### Reversible adiabatic expansion

A decrease in temperature can also be produced by a simple adiabatic expansion, and in general – for the same pressure drop – is larger than for a Joule-Kelvin expansion.

### Production of liquid helium and other gases

Typical refrigerators have an (idealised) cycle of

- 1) isenthalpic expansion.
- 2) isobaric warming of the working substance (extracting heat from the cool box).
- 3) compression pump (external work done).
- 4) isobaric cooling of the working substance (back to room temperature).

Commercially, the Joule-Kelvin expansion is used as the basis of gas liquefaction devices since it has fewer moving parts to be maintained than any purely adiabatic device could possibly have.

For He, pre-cooling is needed to get an initial temperature the maximum inversion temperature for He of 51K. Pre-cooling is typically done by controlled adiabatic expansions of helium in which there is cooling but no vapour-to-liquid phase transition. Once the temperature of the helium is low enough, the gas, at high pressure, goes through a throttling process where some of it liquefies and the rest – now at low pressure – is used to contribute to pre-cooling of the incoming gas, at high pressure, via a heat exchanger. Earlier helium liquefiers used other liquefied gases (nitrogen and hydrogen not without serious accidents) to produce the pre-cooling.