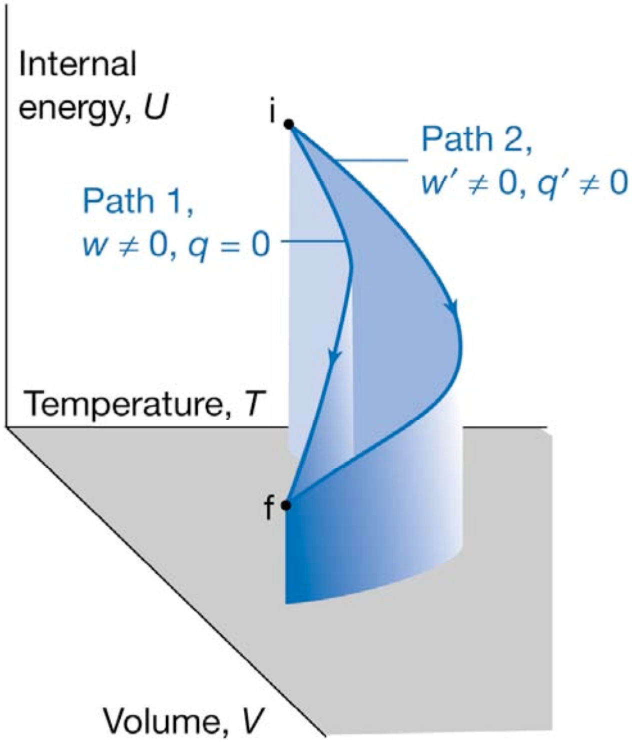
The First Law: the machinery

The power of thermodynamics – how to establish relations between different properties of a system. The procedure is based on the experimental fact that the internal energy and the enthalpy are state functions. We shall see that a property can be measured indirectly by measuring others and then combining their values. We shall also discuss the liquefaction of gases and establish the relation between C_p and C_V.

State functions and exact differentials

State and path functions



The initial state of the system is i and in this state the internal energy is U_i. Work is done by the system as it expands adiabatically to a state f (an internal energy U_f). The work done on the system as it changes along Path 1 from i to f is w. U – a property of the state; w – a property of the path. Consider another process, Path 2: the initial and final states are the same, but the expansion is not adiabatic. Because U is a state function, the internal energy of both the initial and the final states are the same as before, but an energy q' enters the system as heat and the work w' is not the same as w. The work and the heat are path functions.

Exact and inexact differentials

If a system is taken along a path, U changes from U_i to U_f and the overall change is the sum (integral) of all infinitesimal changes along the path:

$$\Delta U = \int_i^f dU$$

ΔU depends on the initial and final states but is independent of the path between them. We say in this case that dU – ‘exact differential’. An **exact differential** is an infinitesimal quantity that, when integrated, gives a result that is independent of the path between the initial and final states.

When a system is heated, the total energy transferred as heat is a sum of all individual contributions as each point of the path:

$$q = \int_{i,path}^f dq$$

We do not write Δq because q is not a state function and the energy supplied as heat cannot be expressed as $q_\mathrm{f} - q_\mathrm{i}$. Also, we must specify the path of integration because q depends on the path selected. We say that dq is an ‘inexact differential’. An **inexact differential** is an infinitesimal quantity that, when integrated, gives a result that depends on the path between the initial and final states. dw is also inexact differential because the work done on a system to change it from one state to another depends on the path taken; in general, the work is different if the change takes place adiabatically or non-adiabatically.

Example 1. Calculating work, heat, and internal energy.

Consider a perfect gas inside a cylinder fitted with a piston. The initial state is T, V_i and the final state is T, V_f. Path 1: free expansion against zero external pressure. Path 2: reversible isothermal expansion. Calculate w, q, and ΔU for each process.

Because the internal energy of a perfect gas arises only from the kinetic energy of its molecules, it is independent of V; for any isothermal change, $\Delta U = 0$. In general, $\Delta U = q + w$.

$\Delta U = 0$ for both paths $\Rightarrow q = -w$

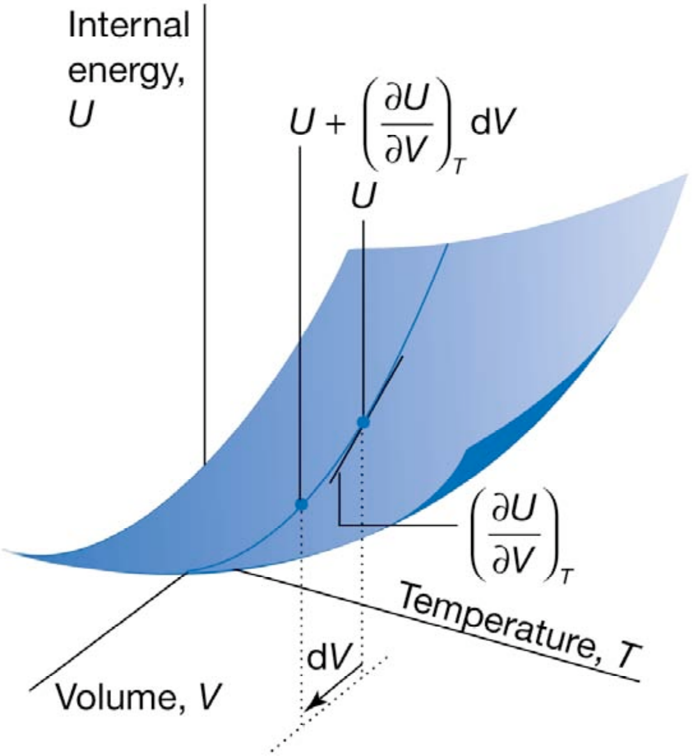
Path 1: the work of free expansion is zero: $w = 0$, $q = 0$.

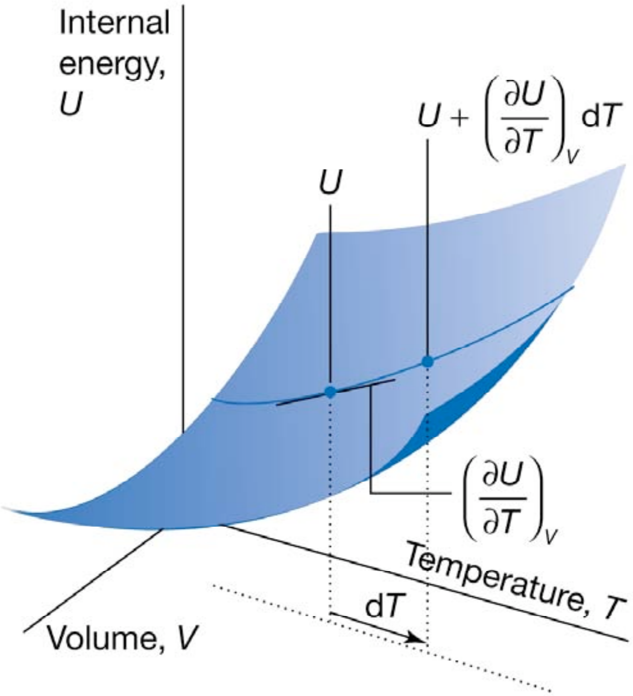
Path 2: $w = -nRT \ln(V_\mathrm{f}/V_\mathrm{i})$, $q = nRT \ln(V_\mathrm{f}/V_\mathrm{i})$.

Thermodynamic consequences

Changes in internal energy

We consider the consequences of dU being an exact differential – U is a function of volume and temperature. U could be regarded as a function of V, T, and p but, because there is an equation of state, it is possible to express p in terms of V and T, so p is not an independent variable).





When V changes to $V + \mathrm{d}V$ at constant T:

$$U' = U + \left(\frac{\partial U}{\partial V}\right)_T dV$$

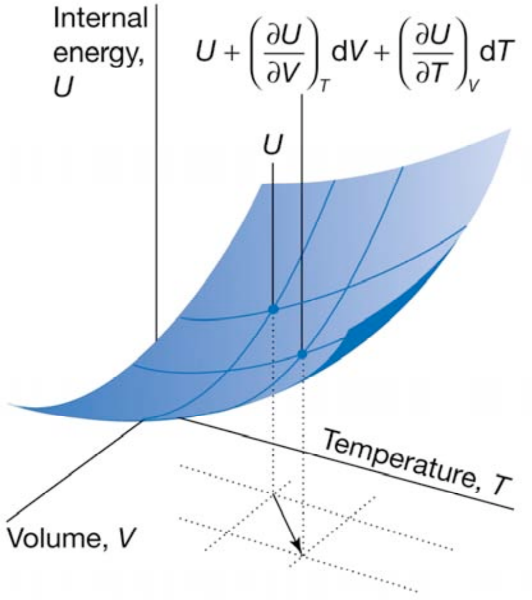
When T changes to $T + \mathrm{d}T$ at constant V:

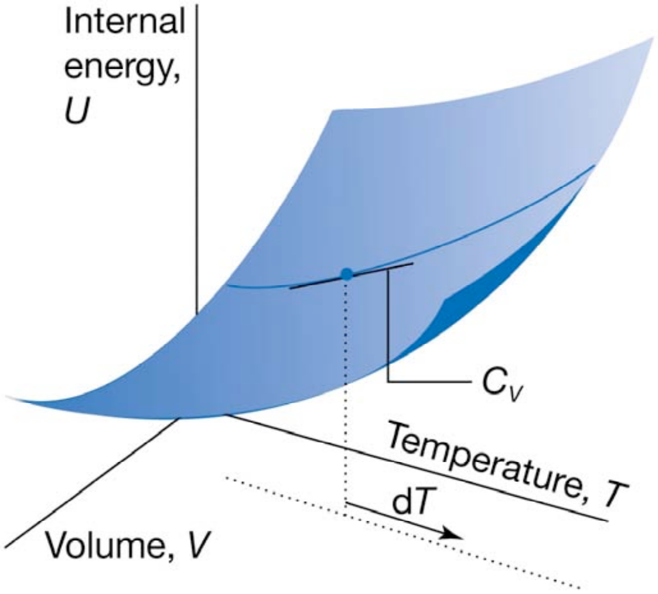
$$U' = U + \left(\frac{\partial U}{\partial T}\right)_V dT$$

When both V and T change:

$$U' = U + \left(\frac{\partial U}{\partial V}\right)_T dV + \left(\frac{\partial U}{\partial T}\right)_V dT$$

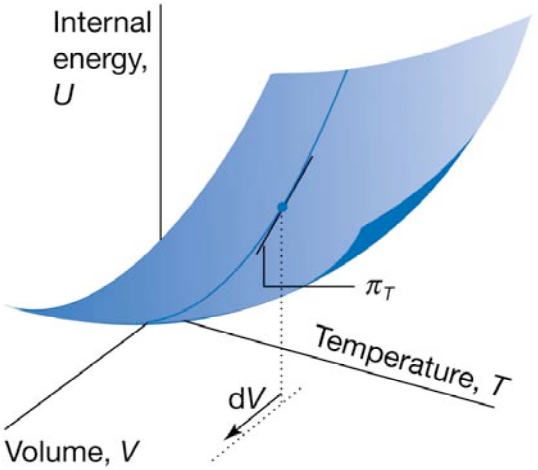
$$dU = \left(\frac{\partial U}{\partial V}\right)_T dV + \left(\frac{\partial U}{\partial T}\right)_V dT$$

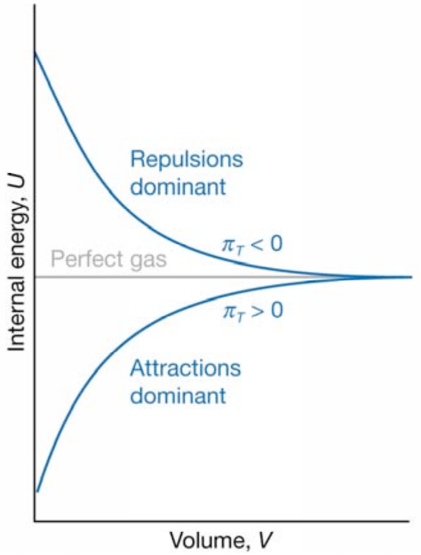




$$C_V = \left(\frac{\partial U}{\partial T}\right)_V \qquad dU = \left(\frac{\partial U}{\partial V}\right)_T dV + C_V dT$$

$\pi_T = \left(\frac{\partial U}{\partial V}\right)_T$ - **internal pressure**, a measure of the variation of the internal energy of a substance as its volume changes at constant temperature.





The internal pressure – a measure of the strength of the cohesive forces in the sample. If the internal energy increases as the volume expands isothermally, there are attractive forces between the particles, $\pi_T > 0$.

No interactions between molecules (a perfect gas), the internal energy is independent of their separation ⇒ $\pi_T = \left(\frac{\partial U}{\partial V}\right)_T = 0$. The statement $\pi_T = 0$ can be taken as the definition of a perfect gas; later we shall see that it implies the equation of state $pV = nRT$.

If repulsions are dominant, the internal energy decreases as the gas expands, $\pi_T < 0$.

$$dU = \pi_T dV + C_V dT$$

For ammonia, $\pi_{T,\mathrm{m}} = 840$ Pa at 300 K and 1.0 bar where $\pi_{T,m} = \left(\partial U_m / \partial V\right)_T$, and $C_{V,\mathrm{m}} = 27.32\ \mathrm{J\ K^{-1}\ mol^{-1}}$. The change in molar internal energy of ammonia when it is heated through 2 K and compressed through 100 $\mathrm{cm^3}$ is

$\Delta U_\mathrm{m} = (840\ \mathrm{J\ m^{-3}\ mol^{-1}})\times(-100\times10^{-6}\ \mathrm{m^3}) + (27.32\ \mathrm{J\ K^{-1}\ mol^{-1}})\times(2\ \mathrm{K}) = -0.084\ \mathrm{J\ mol^{-1}} + 55\ \mathrm{J\ mol^{-1}}$

The contribution from the heating term greatly dominates that of the compression term.

Changes in internal energy at constant pressure

At constant pressure, we can divide the expression for dU by dT: $\left(\frac{\partial U}{\partial T}\right)_p = \pi_T \left(\frac{\partial V}{\partial T}\right)_p + C_V$

$\left(\frac{\partial V}{\partial T}\right)_p$ - the slope of the plot of volume against temperature (at constant pressure). This property is normally tabulated as the **expansion coefficient**, α, of a substance: $\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p$.

A large value of α - the sample responds strongly to changes in temperature.

Example 2. Using the expansion coefficient of a gas.

Derive an expression for the expansion coefficient for a perfect gas.

We use the expression defining the expansion coefficient and express V in terms of T using the equation of state for the gas. p is treated as a constant:

$$pV = nRT \qquad \alpha = \frac{1}{V}\left(\frac{\partial(nRT/p)}{\partial T}\right) = \frac{nR}{pV} = \frac{1}{T}$$

The higher the temperature, the less responsive is its volume to a change in temperature.

Using the definition of α we can write

$$\left(\frac{\partial U}{\partial T}\right)_p = \alpha\pi_T V + C_V$$

This equation is entirely general for a closed system with constant composition. It expresses the dependence of the internal energy on the temperature at constant pressure in terms of C_V, which ca be measured in one experiment, in terms of α, which can be measured in another, and in terms of π_T. For a perfect gas, $\pi_T = 0$, so $\left(\frac{\partial U}{\partial T}\right)_p = C_V$

The constant-volume heat capacity of a perfect gas is equal to the slope of a plot of internal energy against temperature at constant pressure as well as (by definition) to the slope at constant volume.

The temperature dependence of the enthalpy
Changes in the enthalpy at constant volume

The variation of enthalpy with temperature – the constant pressure heat capacity, C_p. We shall therefore regard H as a function of p and T and find an expression for the variation of H with temperature at constant volume.

$$dH = \left(\frac{\partial H}{\partial p}\right)_T dp + \left(\frac{\partial H}{\partial T}\right)_p dT \qquad dH = \left(\frac{\partial H}{\partial p}\right)_T dp + C_p dT$$

Now, we divide the equation by dT and impose constant V:

$$\left(\frac{\partial H}{\partial T}\right)_V = \left(\frac{\partial H}{\partial p}\right)_T \left(\frac{\partial p}{\partial T}\right)_V + C_p$$

We then use the Euler chain relation to relate the third differential to the expansion coefficient $\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p$:

$$\left(\frac{\partial y}{\partial x}\right)_z \left(\frac{\partial x}{\partial z}\right)_y \left(\frac{\partial z}{\partial y}\right)_x = -1 \qquad \left(\frac{\partial p}{\partial T}\right)_V \left(\frac{\partial T}{\partial V}\right)_p \left(\frac{\partial V}{\partial p}\right)_T = -1$$

$$\left(\frac{\partial p}{\partial T}\right)_V = -\frac{1}{(\partial T/\partial V)_p (\partial V/\partial p)_T}$$

Next, we use the reciprocal identity: $\left(\frac{\partial y}{\partial x}\right)_z = \frac{1}{\left(\partial x/\partial y\right)_z}$

$$\left(\frac{\partial T}{\partial V}\right)_p = \frac{1}{\left(\partial V/\partial T\right)_p} \qquad \left(\frac{\partial p}{\partial T}\right)_V = -\frac{\left(\partial V/\partial T\right)_p}{\left(\partial V/\partial p\right)_T} = \frac{\alpha}{\kappa_T},$$

where κ_T, the **isothermal compressibility**, is defined as $\kappa_T = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_T$. Next step is to work with the $\left(\frac{\partial H}{\partial p}\right)_T$ term:

$$\left(\frac{\partial H}{\partial p}\right)_T = -\frac{1}{\left(\partial p/\partial T\right)_H\left(\partial T/\partial H\right)_p} = -\left(\frac{\partial T}{\partial p}\right)_H\left(\frac{\partial H}{\partial T}\right)_p = -\mu C_p$$

Here, μ, the **Joule-Thompson coefficient**, is defined as $\mu = \left(\frac{\partial T}{\partial p}\right)_H$

$$\left(\frac{\partial H}{\partial T}\right)_V = -\mu C_p\frac{\alpha}{\kappa_T} + C_p = \left(1 - \frac{\alpha\mu}{\kappa_T}\right)C_p \qquad \left(\frac{\partial H}{\partial T}\right)_V = \left(1 - \frac{\alpha\mu}{\kappa_T}\right)C_p$$

The last equation applies to any substance. All the quantities that appear in it can be measured in suitable experiments, so we know now how *H* varies with *T* when the volume of a sample is constant.

The isothermal compressibility

The negative sign in the definition of κ_T ensures that the compressibility is a positive quantity, because an increase of pressure brings about a reduction of volume. The isothermal compressibility is obtained from the slope of the plot of volume against pressure at constant temperature (an isotherm). For a perfect gas, $\kappa_T = -\frac{1}{V}\left(\frac{\partial(nRT/p)}{\partial p}\right)_T = -\frac{nRT}{V}\left(-\frac{1}{p^2}\right) = \frac{1}{p}$

The higher the pressure of the gas, the lower its compressibility.

Example 3. Using the isothermal compressibility.

The isothermal compressibility of water at 20°C and 1 atm is 4.96×10^{-5} atm^{-1}. What change of volume occurs when a sample of volume 50 cm^3 is subjected to an additional 1000 atm at constant T?

$$\kappa_T = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_T \qquad dV = \left(\frac{\partial V}{\partial p}\right)_T dp = -\kappa_T V dp \qquad \int_{V_i}^{V_f} dV = -\int_{p_i}^{p_f} \kappa_T V dp$$

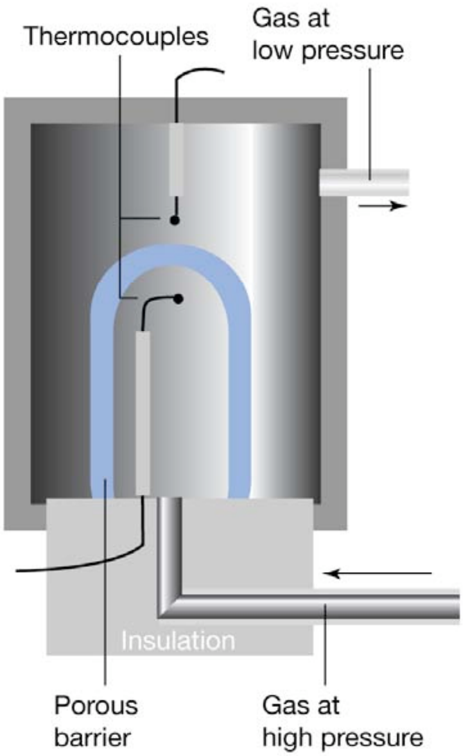
Assuming that κ_T and V are approximately constant over the range of pressures of interest,

$$\Delta V = -\kappa_T V \int_{p_i}^{p_f} dp = -\kappa_T V \Delta p \quad \Delta V = -(4.96\times10^{-5}\ \text{atm}^{-1})\times(50\ \text{cm}^3)\times(1000\ \text{atm}) = -2.5\ \text{cm}^3$$

Because the compression results in a decrease of volume of only 5%, the assumption of constant κ_T and V is acceptable as a first approximation. Very high pressures are needed to bring about significant changes of volume.

The Joule-Thompson effect

The analysis of the Joule-Thompson effect is central for understanding the liquefaction of gases.

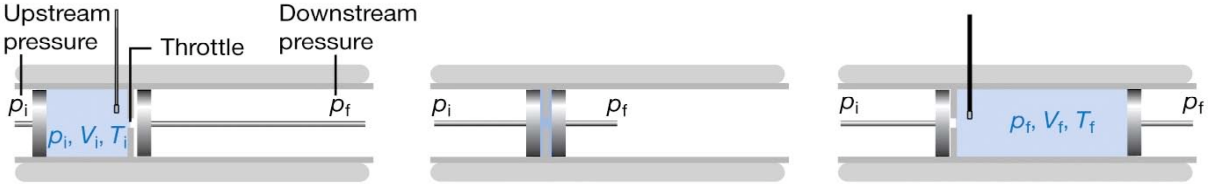


How to impose the constrain of constant enthalpy, so that the process is **isenthalpic**?

Joule and Thompson let a gas expand through a porous barrier from one constant pressure to another and monitored the difference of temperature that arose from the expansion. The whole apparatus was insulated, so that the process was adiabatic. They observed a lower temperature on the low pressure side, the difference in T was proportional to the pressure difference. This cooling by adiabatic expansion is called the **Joule-Thompson effect**.

Adiabatic process: $q = 0 \Rightarrow \Delta U = w$

Consider the work done as the gas passes through the barrier.



We focus on the passage of a fixed amount of gas from the high pressure side (p_i, V_i, T_i) to the low pressure side (p_f, V_f, T_f). The gas on the left is compressed isothermally by the upstream gas acting as a piston and the volume changes from V_i to 0: $w_1 = -p_i(0 - V_i) = p_iV_i$

The gas expands isothermally (at a different constant T) against the pressure p_f provided by the downstream gas acting as a piston to be driven out.

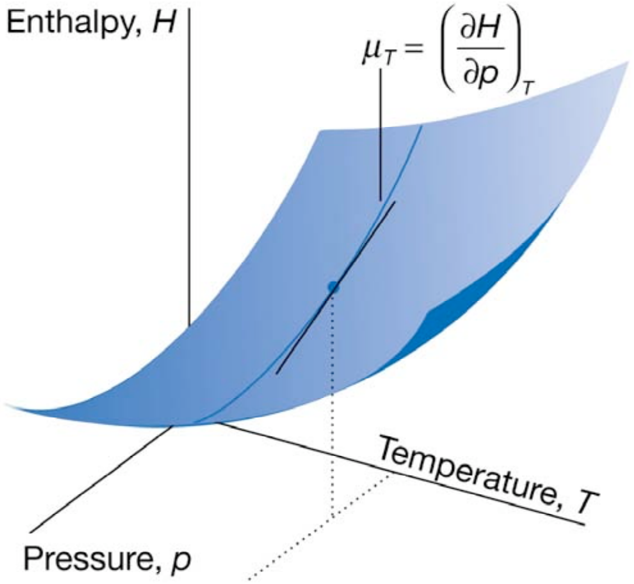
$$w_2 = -p_f(V_f - 0) = -p_f V_f$$

$$w = w_1 + w_2 = p_i V_i - p_f V_f \qquad U_f - U_i = w = p_i V_i - p_f V_f$$

$$U_f + p_f V_f = U_i + p_i V_i \qquad H_f = H_i$$

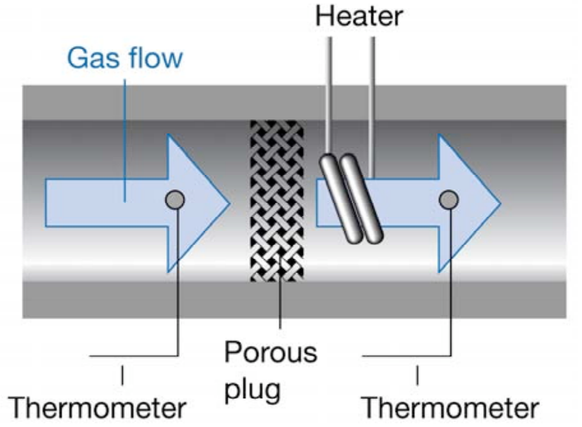
Thus, the expansion occurs without change of enthalpy.

The property measured in the experiment is the ratio of the temperature change to the change of pressure, $\Delta T/\Delta p$. With the constraint of constant enthalpy and taking the limit of small Δp, the quantity measured is $(\partial T/\partial p)_H$ - the Joule-Thompson coefficient μ. The physical interpretation of μ - the ratio of the change in temperature to the change in pressure when a gas expands under adiabatic conditions.

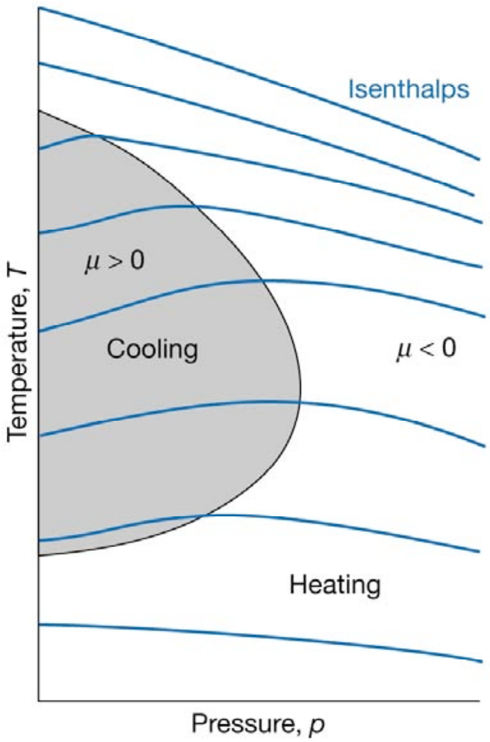


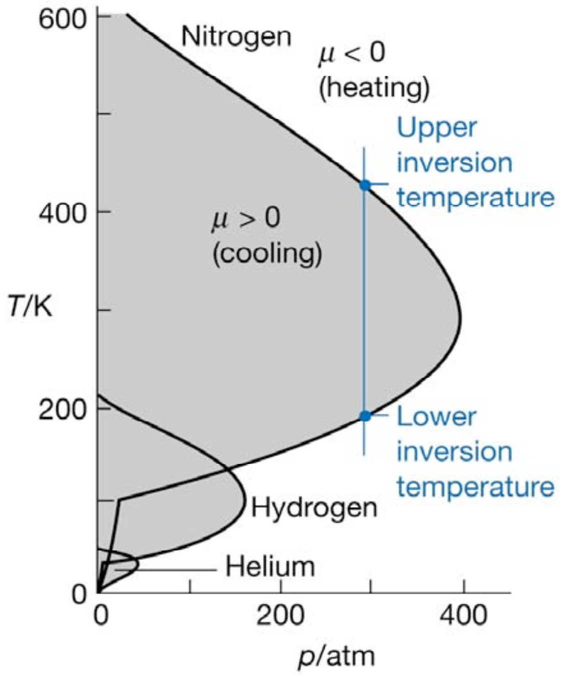
The modern method of measuring μ - measuring the **isothermal Joule-Thompson coefficient**, $\mu_T = \left(\frac{\partial H}{\partial p}\right)_T$, the slope of enthalpy against pressure at constant temperature. The two coefficients are related:

$$\mu_T = -C_p\, \mu$$

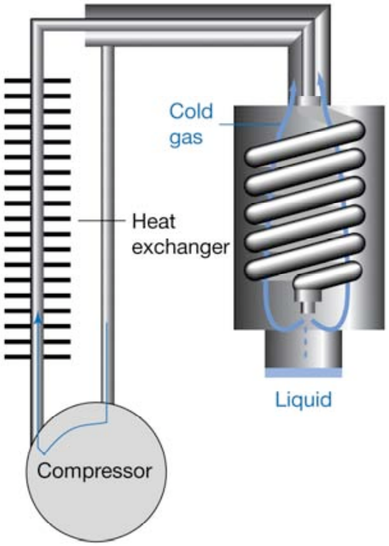


To measure μ_T, the gas is pumped continuously at a steady pressure through a heat exchanger (which brings it to the required T), and then through a porous plug inside a thermally isolated container. The steep pressure drop is measured, and the cooling effect is exactly offset by an electric heater. The energy provided by the heater is monitored. The heat can be identified with ΔH ($\Delta H = q_p$), Δp is known, so we can find μ_T as $\Delta H/\Delta p$ at $\Delta p \rightarrow 0$.





Real gases have non-zero Joule-Thompson coefficients. Depending on the identity of the gas, the pressure, the relative magnitudes of the attractive and repulsive intermolecular forces, and T, the sign of μ may be positive or negative. A positive sign means that dT is negative when dp is negative – the gas cools on expansion. Gases that show a heating effect ($\mu < 0$) at one temperature show a cooling effect ($\mu > 0$) when T is below their upper **inversion temperature**, T_I. Typically, a gas has two inversion temperatures, upper and lower.



The 'Linde refrigerator' uses Joule-Thompson expansion to liquefy gases. The gas at high pressure is allowed to expand through a throttle; it cools and is circulated past the incoming gas. The gas is cooled, and its subsequent expansion cools it still further. Then come a stage when the circulating gas becomes so cold that it condenses to a liquid.

For a perfect gas $\mu = 0$; T in a perfect gas is unchanged by Joule-Thompson expansion.

(Remember that simple adiabatic expansion does cool a perfect gas, because the gas does work). Clearly, intermolecular forces are involved in determining μ. The Joule-Thompson coefficient of a real gas does not necessarily approach zero as the pressure is reduced because μ depends on derivatives (recall dZ/dp).

The relation between C_V and C_p

C_p differs from C_V by the work needed to change the volume of the system. Two types of work: the work of driving back the atmosphere and the work of stretching the bonds of the material including any weak intermolecular interactions. Perfect gas – the second type makes no contribution. So, for the perfect gas:

$$C_p - C_V = \left(\frac{\partial H}{\partial T}\right)_p - \left(\frac{\partial U}{\partial T}\right)_V \qquad H = U + pV = U + nRT$$

$$C_p - C_V = \left(\frac{\partial U}{\partial T}\right)_p + nR - \left(\frac{\partial U}{\partial T}\right)_V = nR$$ $$\boldsymbol{C_{p,\mathrm{m}} - C_{V,\mathrm{m}} = R}$$

For a general case,

$$C_p - C_V = \left(\frac{\partial H}{\partial T}\right)_p - \left(\frac{\partial U}{\partial T}\right)_V = \left(\frac{\partial U}{\partial T}\right)_p + \left(\frac{\partial (pV)}{\partial T}\right)_p - \left(\frac{\partial U}{\partial T}\right)_V$$

We already know that $\left(\frac{\partial U}{\partial T}\right)_p - \left(\frac{\partial U}{\partial T}\right)_V = \alpha\pi_T V$. The factor αV gives the change in volume when the temperature is raised and $\pi_T = \left(\partial U/\partial V\right)_T$ converts this change in volume into a change in U.

$$\left(\frac{\partial (pV)}{\partial T}\right)_p = p\left(\frac{\partial V}{\partial T}\right)_p = \alpha pV \qquad C_p - C_V = \alpha\left(p + \pi_T\right)V$$

Using $\pi_T = T\left(\frac{\partial p}{\partial T}\right)_V - p$ (to be proven in Ch. 3), we obtain

$$C_p - C_V = \alpha TV\left(\partial p/\partial T\right)_V \qquad \left(\partial p/\partial T\right)_V = \alpha/\kappa_T \qquad C_p - C_V = \alpha^2 TV/\kappa_T$$