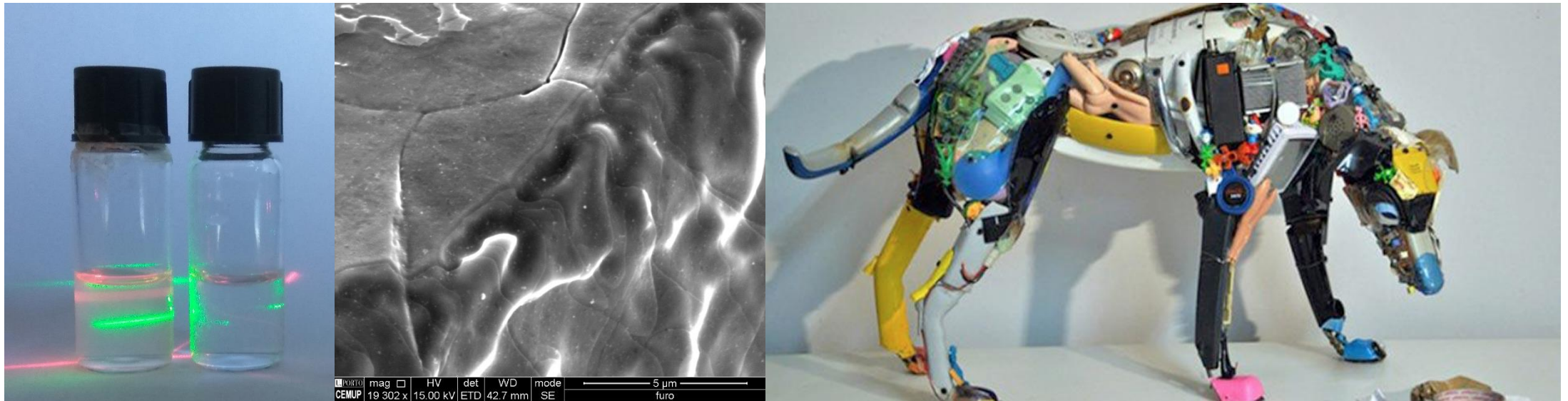


Physical Chemistry

... iremos explorar, refletir, aprender ?..

Area of chemistry concerned with the **application of the techniques and theories of physics** to the study of chemical systems.



$$U(V, T, n)$$

Changes in internal energy at constant pressure

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

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

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

$$\left(\frac{\partial U}{\partial T}\right)_p = C_V \quad \text{Perfect gas !}$$

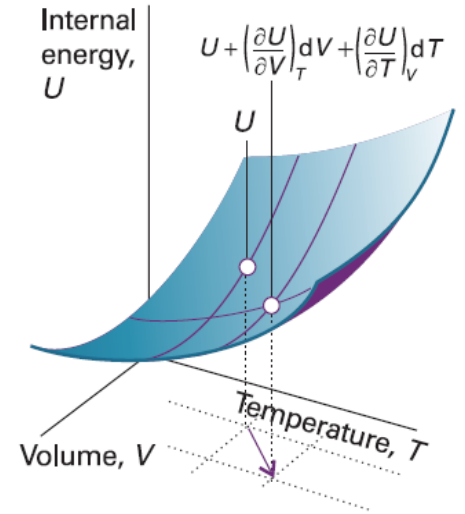
$\pi_T = 0$

Isobaric expansion coefficient,

$$\alpha = \frac{1}{V} \left(\frac{\partial V}{\partial T}\right)_p$$

isothermal compressibility coefficient

$$\kappa_T = -\frac{1}{V} \left(\frac{\partial V}{\partial p}\right)_T$$



Synoptic Table 2.8* Expansion coefficients (α) and isothermal compressibilities (κ_T) at 298 K

	$\alpha/(10^{-4} \text{ K}^{-1})$	$\kappa_T/(10^{-6} \text{ bar}^{-1})$
Benzene	12.4	90.9
Diamond	0.030	0.185
Lead	0.861	2.18
Water	2.1	49.0

* More values are given in the *Data section*.

$$U(V, T, n)$$

First Law of Thermodynamics

$$\left(\frac{\partial U}{\partial T}\right)_p = C_V \quad \text{Perfect gas !}$$

$\pi_T = 0$

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

$$H = U + pV = U + nRT$$

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

$$C_p - C_V = \frac{\alpha^2 TV}{\kappa_T}$$

α ... for liquids and solids

$$C_p \approx C_V$$

If ... κ_T is small .then,

α^2 / κ_T might be large

Expansion coefficient,

$$\alpha = \frac{1}{V} \left(\frac{\partial V}{\partial T}\right)_p$$

Compressibility coefficient

$$\kappa_T = -\frac{1}{V} \left(\frac{\partial V}{\partial p}\right)_T$$

$$U(V, T, n)$$

First Law of Thermodynamics

Changes in internal energy at constant pressure

Isobaric expansion coefficient,
e.q 2.43

$$\alpha = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_p$$

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Lead	0.861	2.18
Water	2.1	49.0

More values are given in the *Data section*.

Example 2.8 Calculating the expansion coefficient of a gas

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

Method The expansion coefficient is defined in eqn 2.43. To use this expression, substitute the expression for V in terms of T obtained from the equation of state for the gas. As implied by the subscript in eqn 2.43, the pressure, p , is treated as a constant.

Answer Because $pV = nRT$, we can write

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

The higher the temperature, the less responsive is the volume of a perfect gas to a change in temperature.

Self-test 2.9 Derive an expression for the isothermal compressibility of a perfect gas. [$\kappa_T = 1/p$]

$$U(V, T, n)$$

Type equation here. $k_T = (-1/V nRT) \cdot (-1/p^2)$

$$k_T = (-p) \cdot (-1/p^2) = 1/p$$

Changes in internal energy at constant pressure

Isobaric expansion coefficient,
e.q 2.43

$$\alpha = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_p$$

isothermal compressibility coefficient

$$\kappa_T = -\frac{1}{V} \left(\frac{\partial V}{\partial p} \right)_T$$

Self-test 2.9 Derive an expression for the isothermal compressibility of a perfect gas. $[\kappa_T = 1/p]$

$$\kappa_T = -\frac{1}{V} \left(\frac{\partial V}{\partial p} \right)_T$$

$$k_T = -\frac{1}{V} \left(\frac{\partial(nRT)}{\partial p} \right)_T = -\frac{1}{V} nRT \cdot \frac{-1}{p^2}$$

$$k_T = -p \cdot \frac{-1}{p^2} = \frac{1}{p}$$

Synoptic Table 2.8* Expansion coefficients (α) and isothermal compressibilities (κ_T) at 298 K

	$\alpha/(10^{-4} \text{ K}^{-1})$	$\kappa_T/(10^{-6} \text{ bar}^{-1})$
Benzene	12.4	90.9
Diamond	0.030	0.185
Lead	0.861	2.18
Water	2.1	49.0

* More values are given in the *Data section*.

$$H(p, T, n)$$

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

Joule–Thomson coefficient, μ

$$\mu = \left(\frac{\partial T}{\partial p} \right)_H \quad \text{For a perfect gas, } \mu = 0:$$

isothermal Joule–Thomson coefficient

$$\mu_T = \left(\frac{\partial H}{\partial p} \right)_T$$

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

First Law of Thermodynamics

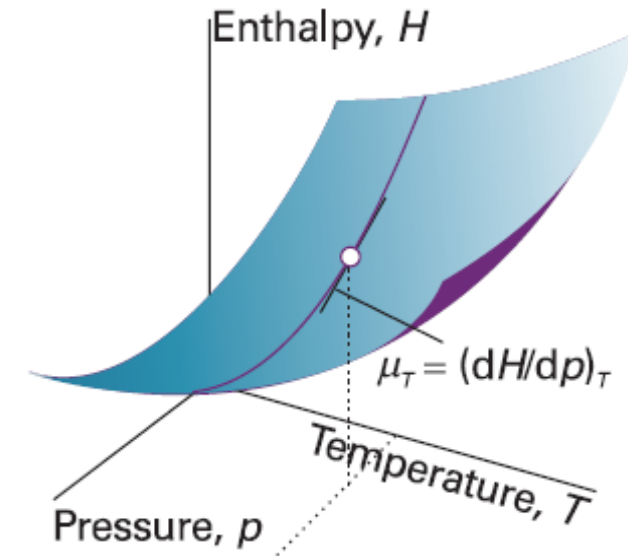


Fig. 2.29 The isothermal Joule–Thomson coefficient is the slope of the enthalpy with respect to changing pressure, the temperature being held constant.

$$H(p, T, n)$$

First Law of Thermodynamics

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

isothermal Joule–Thomson coefficient

$$\mu_T = \left(\frac{\partial H}{\partial p}\right)_T$$

For a perfect gas, $\mu = 0$:

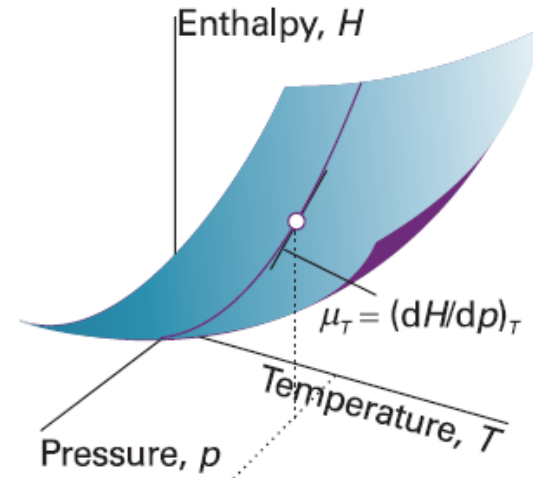


Fig. 2.29 The isothermal Joule–Thomson coefficient is the slope of the enthalpy with respect to changing pressure, the temperature being held constant.

Synoptic Table 2.9* Inversion temperatures (T_i), normal freezing (T_f) and boiling (T_b) points, and Joule–Thomson coefficient (μ) at 1 atm and 298 K

	T_i /K	T_f /K	T_b /K	μ /(K bar ⁻¹)
Ar	723	83.8	87.3	
CO ₂	1500		194.7	+1.10
He	40		4.2	-0.060
N ₂	621	63.3	77.4	+0.25

* More values are given in the *Data section*.

First Law of Thermodynamics

$$H(p, T, n)$$

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

Joule–Thomson coefficient, μ

$$\mu = \left(\frac{\partial T}{\partial p}\right)_H$$

positive sign .. cooling
Negative sign .. heating

Real gases have nonzero Joule–Thomson coefficients

isothermal Joule–Thomson coefficient

$$\mu_T = \left(\frac{\partial H}{\partial p}\right)_T$$

For a perfect gas, $\mu = 0$:

$\mu > 0$, is observed under conditions
 $\mu < 0$ when attractive interactions are dominant

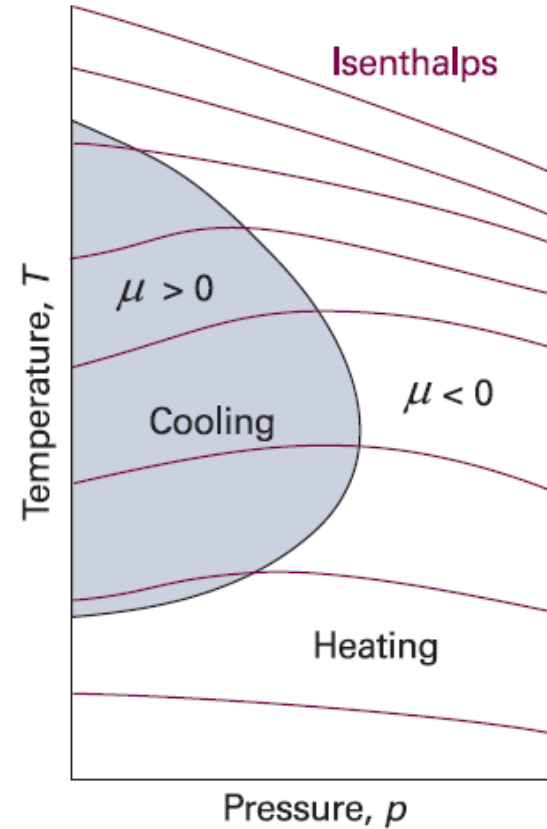


Fig. 2.31 The sign of the Joule–Thomson coefficient, μ , depends on the conditions.

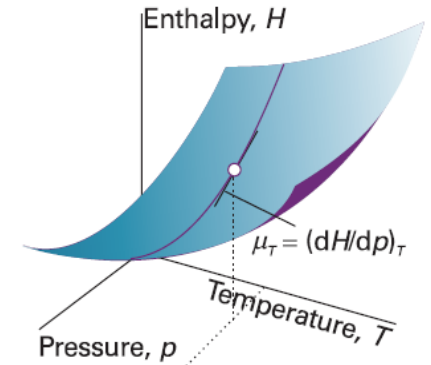


Fig. 2.29 The isothermal Joule–Thomson coefficient is the slope of the enthalpy with respect to changing pressure, the temperature being held constant.

$$H(p, T, n)$$

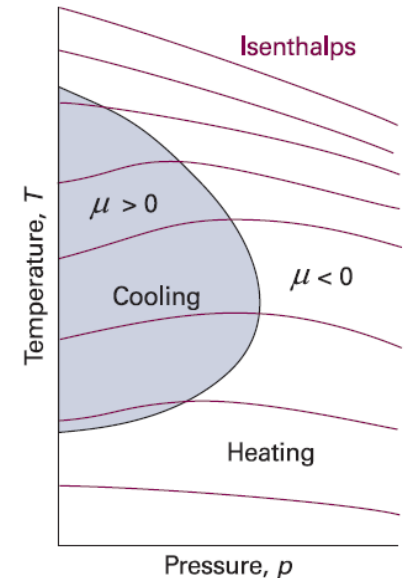
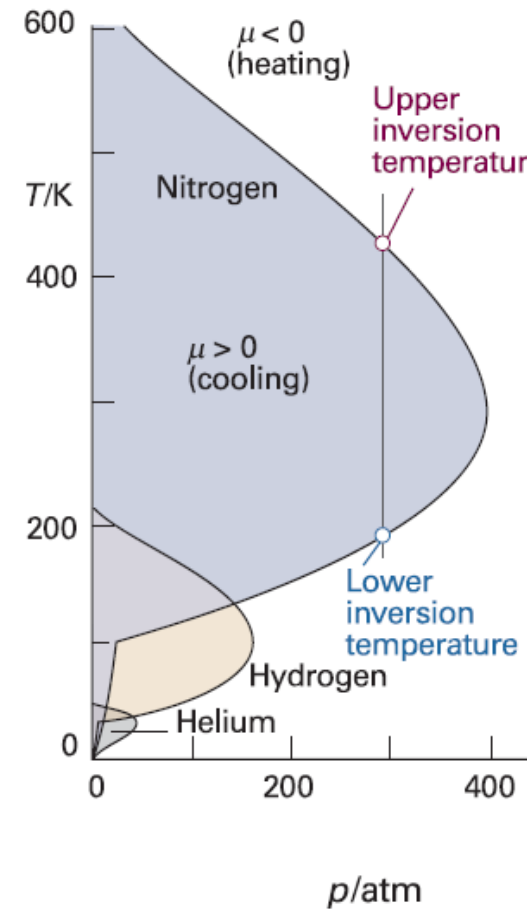
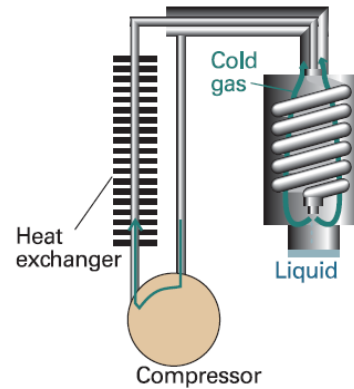
$$dH = \left(\frac{\partial H}{\partial p} \right)_T dp + \left(\frac{\partial H}{\partial T} \right)_p dT$$

isothermal Joule–Thomson coefficient

$$\mu_T = \left(\frac{\partial H}{\partial p} \right)_T$$

For a perfect gas, $\mu = 0$;

$\mu > 0$, is observed under conditions
 μ when attractive interactions are dominant



First Law of Thermodynamics

First Law of Thermodynamics

$$H(p, T, n)$$

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

isothermal Joule–Thomson coefficient

$$\mu_T = \left(\frac{\partial H}{\partial p}\right)_T$$

Joule–Thomson coefficient, μ

$$\mu = \left(\frac{\partial T}{\partial p}\right)_H$$

positive sign .. cooling
Negative sign .. heating

Real gases have nonzero Joule–Thomson coefficients

For a perfect gas, $\mu = 0$:

$\mu > 0$, is observed under conditions
 $\mu < 0$ when attractive interactions are dominant
 $Z < 1$

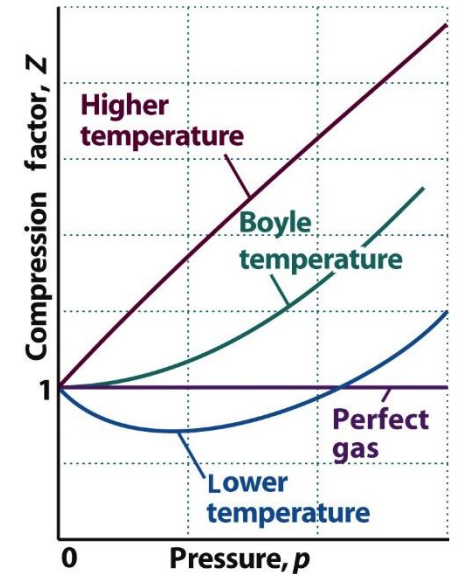
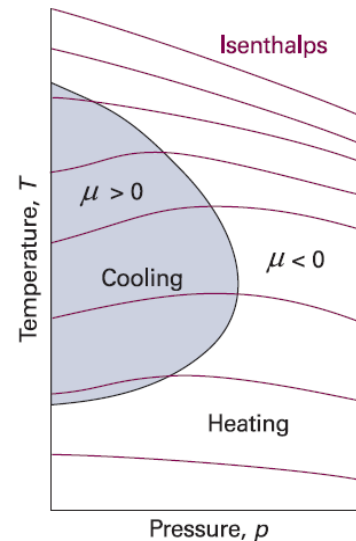


Figure 1-16
Atkins Physical Chemistry, Eighth Edition
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This sequence of molecular events explains the Joule–Thomson effect: the cooling of a real gas by adiabatic expansion. The cooling effect, which corresponds to $\mu > 0$, is observed under conditions when attractive interactions are dominant ($Z < 1$, eqn 1.17), because the molecules have to climb apart against the attractive force in order for them to travel more slowly. For molecules under conditions when repulsions are dominant ($Z > 1$), the Joule–Thomson effect results in the gas becoming warmer, or $\mu < 0$.