Lecture Contents

2. The First Law

Thermochemistry

State functions and exact differentials

2.7 Standard enthalpy changes

The enthalpy change for a process in the standard states

► **The standard state of a substance:** Its pure form at a specific temperature and 1 bar

   ex) The standard state of ethanol at 298 K : a pure liquid ethanol at 298 K and 1 bar
     The standard state of iron at 500 K : a pure solid iron at 500 K and 1 bar

► **Standard enthalpy change for a reaction:** The difference between the products in their standard states and the reactants in their standard states at the same specified temperature

   ex) The standard enthalpy of vaporization, ΔH^o_{vap}
     The enthalpy change per mole when a pure liquid at 1 bar vaporizes to gas at 1 bar

$$H_2O(l) \rightarrow H_2O(g) \qquad \Delta H^o_{vap}(373\ K) = +40.66\ kJ/mol$$

   - Conventional temperature for reporting thermodynamic data? 298.15K (25.00°C)

Contents

   (a) Enthalpies of physical change
   (b) Enthalpies of chemical change
   (c) Hess's law

2.7 Standard enthalpy changes

(a) Enthalpies of physical change

- **Standard enthalpy of transition, ΔH^o_{trs}**: the standard enthalpy change that accompanies change of physical state (see Table 2.3)
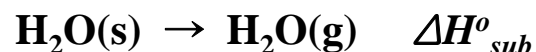
  ex) Standard enthalpy of vaporization, ΔH^o_{vap}
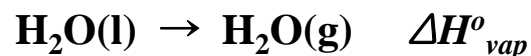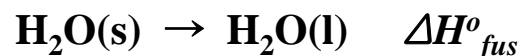
  Standard enthalpy of fusion, ΔH^o_{fus}

  $H_2O(l) \rightarrow H_2O(s)$ $\Delta H^o_{fus}(273\ K) = +6.01\ kJ/mol$

- **Enthalpy is a state function**
  (Independent of the path between the two states)

  (i) Directly from solid to vapor: sublimation

  $H_2O(s) \rightarrow H_2O(g)$ ΔH^o_{sub}

  (ii) In two steps : fusion + vaporization

  $H_2O(s) \rightarrow H_2O(l)$ ΔH^o_{fus}

  $H_2O(l) \rightarrow H_2O(g)$ ΔH^o_{vap}

  $H_2O(s) \rightarrow H_2O(g)$ $\Delta H^o_{sub} = \Delta H^o_{fus} + \Delta H^o_{vap}$

Synoptic Table 2.3* Standard enthalpies of fusion and vaporization at the transition temperature, $\Delta_{trs}H^{\ominus}/(kJ\ mol^{-1})$

	T_f/K	Fusion	T_b/K	Vaporization
Ar	83.81	1.188	87.29	6.506
C_6H_6	278.61	10.59	353.2	30.8
H_2O	273.15	6.008	373.15	40.656 (44.016 at 298 K)
He	3.5	0.021	4.22	0.084

- **The standard enthalpy changes of a forward process and its reverse differ only in sign**

  $\Delta H^o(A \rightarrow B) = - \Delta H^o(B \rightarrow A)$

2.7 Standard enthalpy changes

Different types of enthalpies in thermochemistry

Table 2.4 Enthalpies of transition

Transition	Process	Symbol*
Transition	Phase $\alpha \rightarrow$ phase β	$\Delta_{trs}H$
Fusion	$s \rightarrow l$	$\Delta_{fus}H$
Vaporization	$l \rightarrow g$	$\Delta_{vap}H$
Sublimation	$s \rightarrow g$	$\Delta_{sub}H$
Mixing	Pure $\rightarrow$ mixture	$\Delta_{mix}H$
Solution	Solute $\rightarrow$ solution	$\Delta_{sol}H$
Hydration	$X^{\pm}(g) \rightarrow X^{\pm}(aq)$	$\Delta_{hyd}H$
Atomization	Species$(s, l, g) \rightarrow$ atoms(g)	$\Delta_{at}H$
Ionization	$X(g) \rightarrow X^{+}(g) + e^{-}(g)$	$\Delta_{ion}H$
Electron gain	$X(g) + e^{-}(g) \rightarrow X^{-}(g)$	$\Delta_{eg}H$
Reaction	Reactants $\rightarrow$ products	$\Delta_{r}H$
Combustion	Compounds$(s, l, g) + O_2(g) \rightarrow CO_2(g), H_2O(l, g)$	$\Delta_{c}H$
Formation	Elements $\rightarrow$ compound	$\Delta_{f}H$
Activation	Reactants $\rightarrow$ activated complex	$\Delta^{\ddagger}H$

* IUPAC recommendations. In common usage, the transition subscript is often attached to ΔH, as in ΔH_{trs}.

2.7 Standard enthalpy changes

(b) Enthalpies of chemical change

- **Standard enthalpy of chemical reaction, ΔH^o :** the standard enthalpy change that accompanies chemical reactions

- **Two ways reporting the enthalpy change**

  (1) Thermochemical equation : a combination of a chemical equation and the corresponding change in standard enthalpy

  ex) $CH_4(g) + 2\ O_2(g) \rightarrow CO_2(g) + 2\ H_2O(l)$ $\Delta H^o = -890\ kJ$
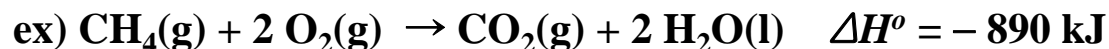
  pure, unmixed reactants in their standard states $\rightarrow$ pure, separated products in their standard states (298K, 1bar)

  (2) Standard reaction enthalpy : a combination of the chemical equation and the standard reaction enthalpy

  ex) $CH_4(g) + 2\ O_2(g) \rightarrow CO_2(g) + 2\ H_2O(l)$ $\Delta_r H^o = -890\ kJ/mol$
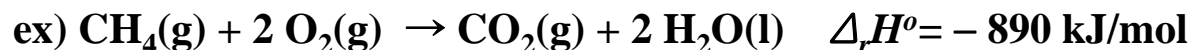
  For the reaction $2\ A + B \rightarrow 3\ C + D$

- **The standard reaction enthalpy**

  $\Delta_r H^o = \{3H^o_m\ (C) + H^o_m\ (D)\} - \{2H^o_m\ (A) + H^o_m\ (B)\}$

  where $H^o_m\ (J)$: the standard molar enthalpy of species J at the temperature of interest

  In general, $\Delta_r H^o\quad =\quad \sum_\nu H^o_m - \sum_\nu H^o_m$ ν : stoichiometric coefficients

  Products   Reactants

2.7 Standard enthalpy changes

- **Standard enthalpy of combustion, $\Delta_c H^o$**

The standard reaction enthalpy for the complete oxidation of a compound

(c) Hess's law

- The standard enthalpy of an overall reaction is the sum of the standard enthalpies of the individual reactions into which a reaction may be divided

- The individual steps need not be realized in practice (i.e., hypothetical reactions are possible) (The only requirement is that chemical equations should be balanced)

- The thermodynamic basis of the law : the path-independence of the value of $\Delta_r H^o$

- The information about a reaction of interest can be obtained from information on other reactions

2.8 Standard enthalpies of formation

The standard enthalpy of formation $\Delta_f H^o$ of a substance : the standard reaction enthalpy for the formation of the compound from its elements in their reference states

- Reference state of an element : the most stable state at the specified temperature and 1bar

ex) At 298 K, N_2 gas for nitrogen (N), a liquid mercury for mercury (Hg), graphite for carbon (C), white (metallic) form for tin (Sn)

Exception: white phosphorous for phosphorous (not the most stable but more reproducible)

- Expression of $\Delta_f H^o$: enthalpy change for the formation per mole of the compound

Contents

(a) The reaction enthalpy in terms of enthalpies of formation

(b) Enthalpies of formation and molecular modeling

2.8 Standard enthalpies of formation

(a) The reaction enthalpy in terms of enthalpies of formation

$$\Delta_r H^\circ = \sum_{\text{products}} v\Delta_f H^\circ - \sum_{\text{reactants}} v\Delta_f H^\circ$$

v = stoichiometric coefficients

(b) Enthalpy of formation and molecular modeling

- We can construct standard enthalpies of formation from a knowledge of the chemical constitution of the species

- Different standard enthalpies of formation even though they consist of the same thermochemical groups for conformers

- Computer-aided molecular modeling

- Mean bond enthalpies ΔH(A-B)

    A-B(g) → A(g) + B(g) ΔH(A-B)
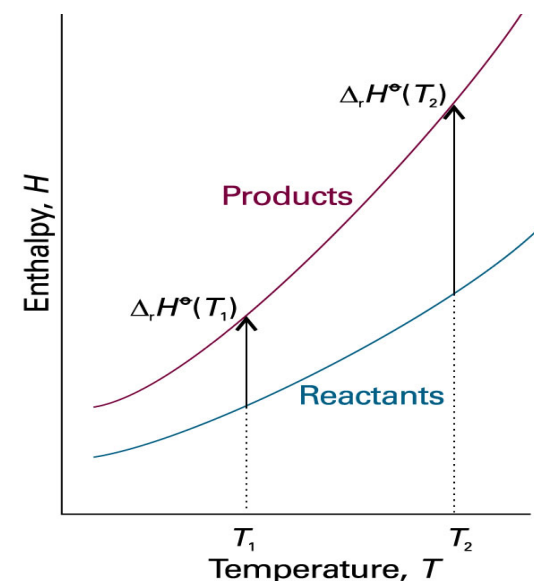
Fig. 2.19 An illustration of the content of Kirchhoff's law. When the temperature is increased, the enthalpy of the products and the reactants both increase, but may do so to different extents. In each case, the change in enthalpy depends on the heat capacities of the substances. The change in reaction enthalpy reflects the difference in the changes of the enthalpies.

2.9 The temperature dependence of reaction enthalpies

Enthalpy changes from $H(T_1)$: $T_1 \rightarrow T_2$

$$H(T_2) = H(T_1) + \int_{T_1}^{T_2} C_p dT$$

Standard reaction enthalpy changes from $\Delta_f H^o(T_1)$:

$$\Delta_r H^o(T_2) = \Delta_r H^o(T_1) + \int_{T_1}^{T_2} \Delta_r C_p^{\circ} dT$$

► **Kirchhoff's law: temperature dependence of reaction enthalpy**

Where $\Delta_r C_p^o$ is the difference of the molar heat capacities of products and reactants under standard conditions weighted by the stochiometric coefficients that appear in the chemical equation;

$$\Delta_r C_p^{\circ} = \sum_{\text{Products}} vC_{p,m}^o - \sum_{\text{Reactants}} vC_{p,m}^o$$

Normally, $\Delta_r C_p$ is assumed to be independent of the temperature.
Although the individual heat capacities may vary, their difference varies less significantly

2.10 Exact and inexact differentials

State function : a property dependent on the current state of the system and
independent of its previous history
ex) Internal energy, Enthalpy

Path function : a property related to the preparation of the state
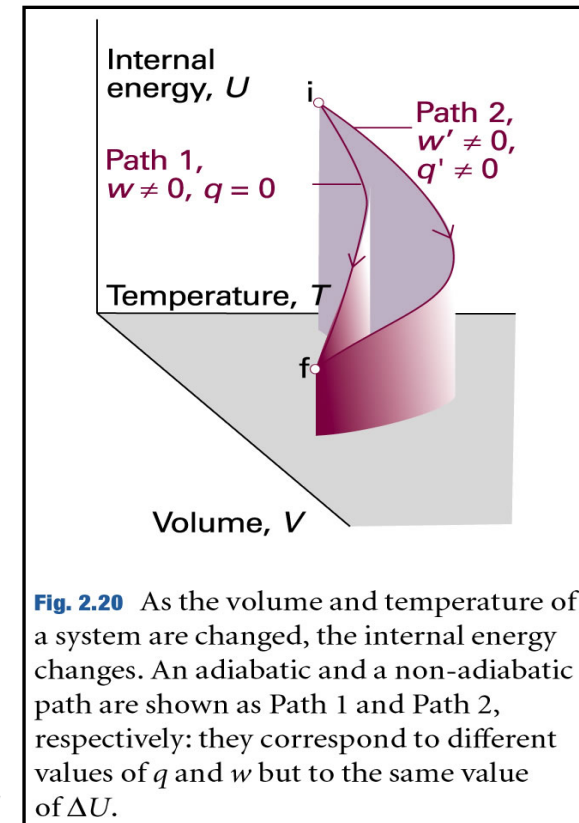ex) work, heat

Consider a system in Fig. 2.20

Path 1: adiabatic expansion from the initial state i
to final state f

$$w \neq 0, \ q = 0$$

Path 2:   nonadiabatic expansion from the initial state i
to final state f

$$w' \neq 0, \ q' \neq 0$$

$\Delta U = U_f - U_i = constant,$ since U_f and U_i are state functions

Fig. 2.20 As the volume and temperature of a system are changed, the internal energy changes. An adiabatic and a non-adiabatic path are shown as Path 1 and Path 2, respectively: they correspond to different values of q and w but to the same value of ΔU.

2.10 Exact and inexact differentials

Overall change if a system is heated from the initial state i to the final state f
The path independence of the integral : dU is an exact differential

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

In general, an exact differential is an infinitesimal quantity that, when integrated, gives a result independent of the path between i and f

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

- We do not write Δq because q is not a state function $q \neq q_f - q_i$
- q is path dependence : dq is an inexact differential.
  In general, an inexact differential is an infinitesimal quantity that, when integrated,
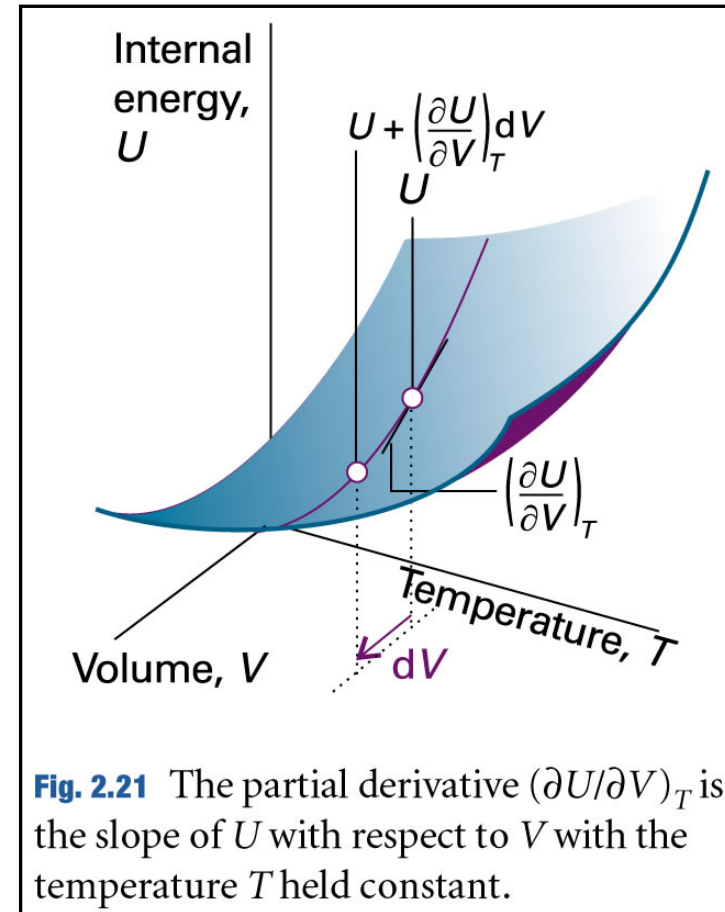 gives a result dependent on the path between i and f

2.11 Changes in internal energy

(a) General considerations

For a closed system of constant composition $U = U(V, T)$

When V changes to $V + dV$ at constant T, U changes to

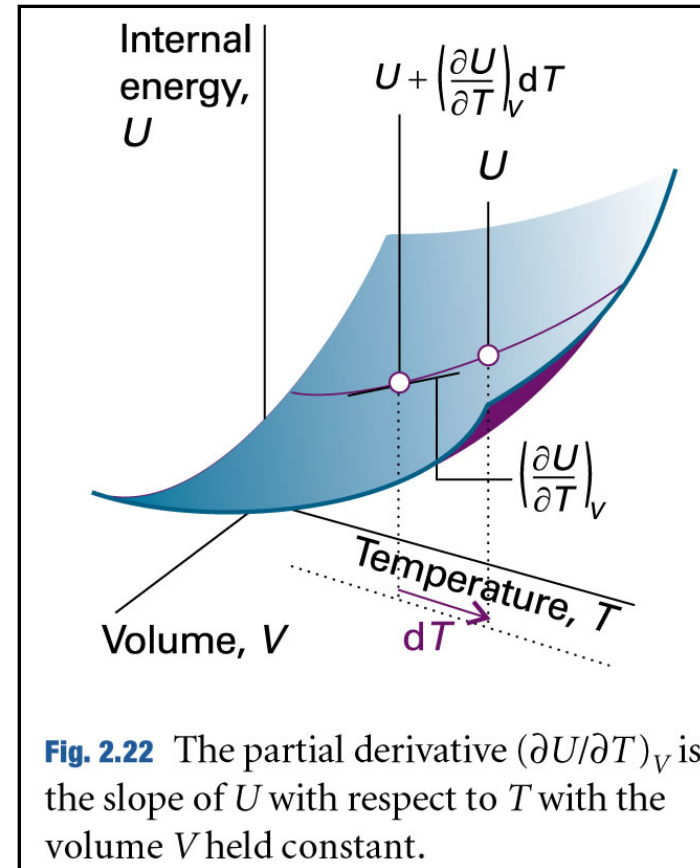$$U' = U + \left(\frac{\partial U}{\partial V}\right)_T dV$$

Fig. 2.21 The partial derivative $(\partial U/\partial V)_T$ is the slope of U with respect to V with the temperature T held constant.

2.11 Changes in internal energy

For a closed system of constant composition, $U = U(V, T)$

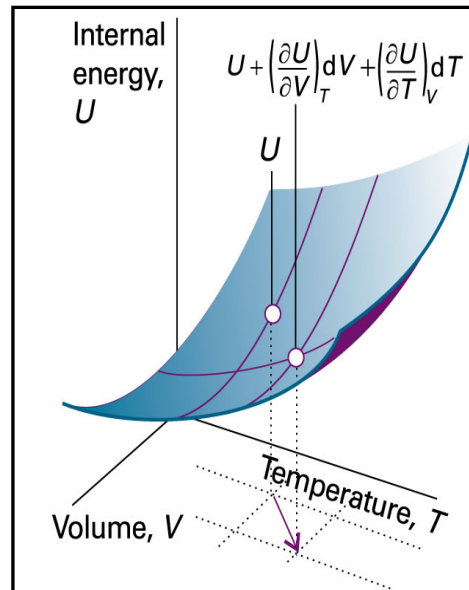**If** T **changes to** $T + dT$ **at constant** V, U **changes to**

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

Fig. 2.22 The partial derivative $(\partial U/\partial T)_V$ is the slope of U with respect to T with the volume V held constant.
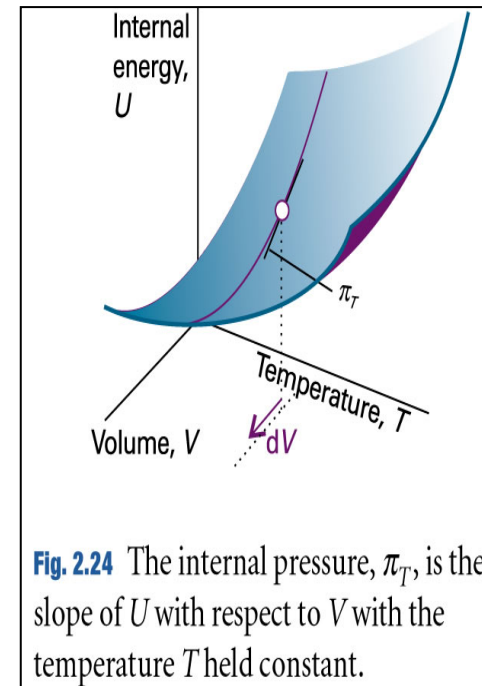
2.11 Changes in internal energy

Suppose that both *V* and *T* change infinitesimally,
***U* changes to (neglecting second-order infinitesimals)**

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

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

$$\pi_T = \left(\frac{\partial U}{\partial V}\right)_T \qquad \textbf{Internal Pressure}$$

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

Fig. 2.23 An overall change in *U*, which is denoted d*U*, arises when both *V* and *T* are allowed to change. If second-order infinitesimals are ignored, the overall change is the sum of changes for each variable separately.

Fig. 2.24 The internal pressure, π_T, is the slope of *U* with respect to *V* with the temperature *T* held constant.

2.11 Changes in internal energy

(b) The Joule experiment

James Joule tried to measure π_T by observing the change in T of a gas when it is allowed to expand into a vacuum
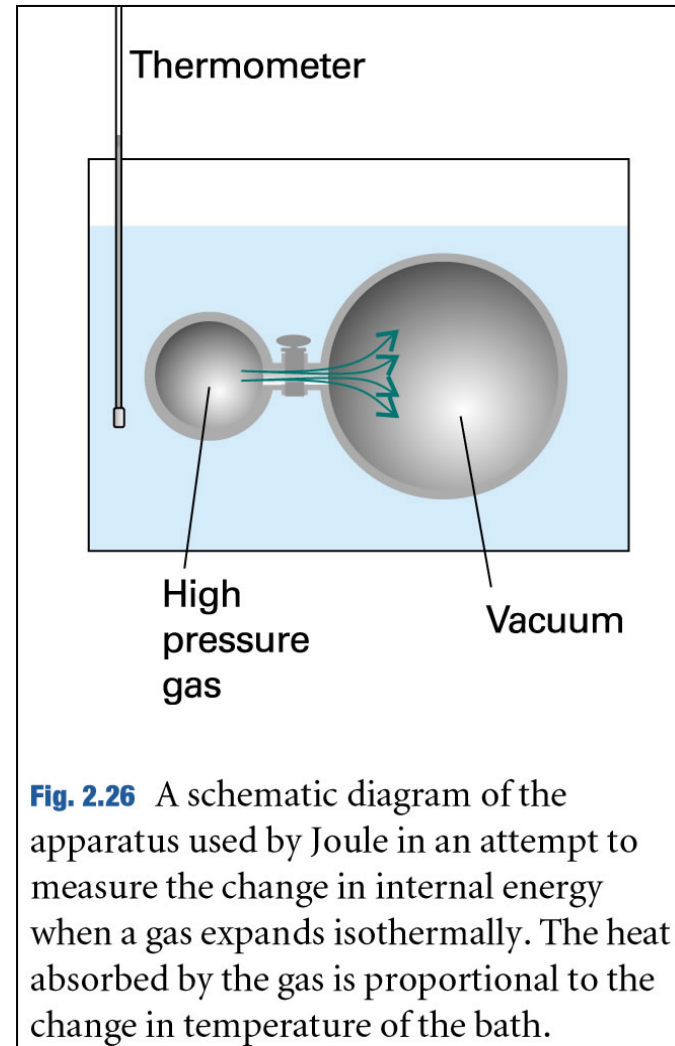
Result : no change in T

Thermodynamic implications of this experiment?

$w = 0$, (No work was done into a vacuum)

No change in T of bath $\rightarrow$ no heat transfer from the system

$: q = 0$

Thus $\Delta U = 0$ and finally, $\pi_T = 0$

Fig. 2.26 A schematic diagram of the apparatus used by Joule in an attempt to measure the change in internal energy when a gas expands isothermally. The heat absorbed by the gas is proportional to the change in temperature of the bath.

2.11 Changes in internal energy

(c) Changes in internal energy at constant pressure

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

$$\left(\frac{\partial U}{\partial T}\right)_p = \pi_T \left(\frac{\partial V}{\partial T}\right)_p + C_V \qquad \text{at constant } p$$

The expansion coefficient : $\quad \alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p \qquad \kappa_T = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_T$

Thus, we obtain $\quad \left(\frac{\partial U}{\partial T}\right)_p = \alpha \pi_T V + C_V$

For a perfect gas, $\quad \left(\frac{\partial U}{\partial T}\right)_p = C_V \quad$ since $\pi_T = 0$

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

2.11 Changes in internal energy

For a perfect gas

$$C_P - C_V = \left(\frac{\partial H}{\partial T}\right)_P - \left(\frac{\partial U}{\partial T}\right)_P \qquad \text{since} \qquad H = U + PV = U + nRT$$

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

$$C_P - C_V = \frac{\alpha^2 TV}{k_T}$$

2.12 The Joule-Thomson effect

Constant enthalpy (isenthalpic) process

cooled by adiabatic expansion

► We regard H as a function of p and T

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

$$\left(\frac{\partial H}{\partial p}\right)_T = -\frac{1}{(\partial p / \partial T)_H (\partial T / \partial H)_p}$$ **Euler chain relation**

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

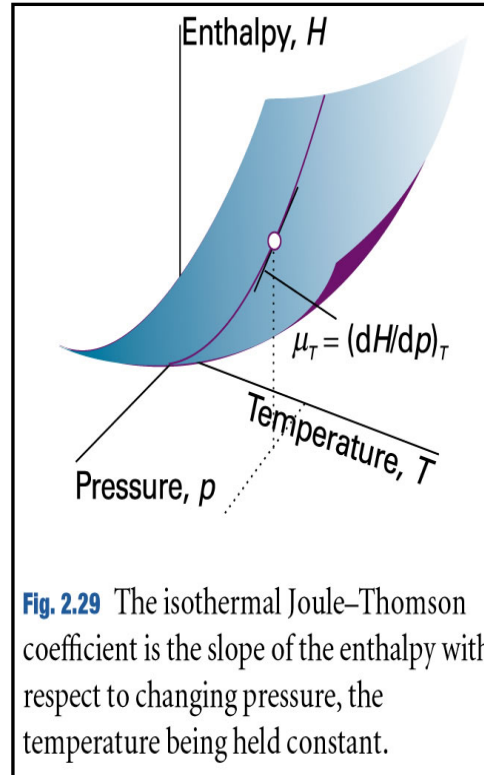$$\mu = \left(\frac{\partial T}{\partial p}\right)_H \qquad \mu = \text{Joule - Thomson coefficien t}$$

Fig. 2.29 The isothermal Joule–Thomson coefficient is the slope of the enthalpy with respect to changing pressure, the temperature being held constant.
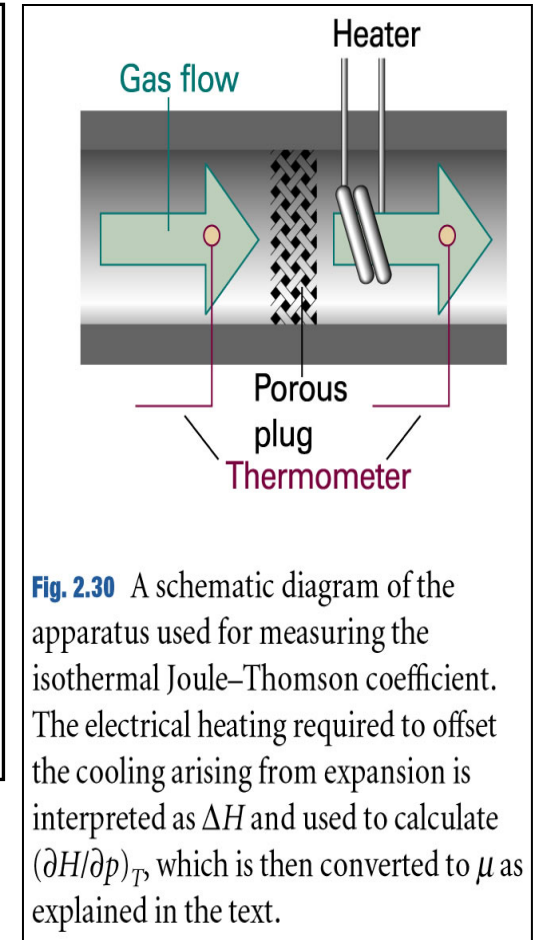
$\mu_T = (dH/dp)_T$

Enthalpy, H

Temperature, T

Pressure, p

Fig. 2.30 A schematic diagram of the apparatus used for measuring the isothermal Joule–Thomson coefficient. The electrical heating required to offset the cooling arising from expansion is interpreted as ΔH and used to calculate $(\partial H/\partial p)_T$, which is then converted to μ as explained in the text.

Heater
Gas flow
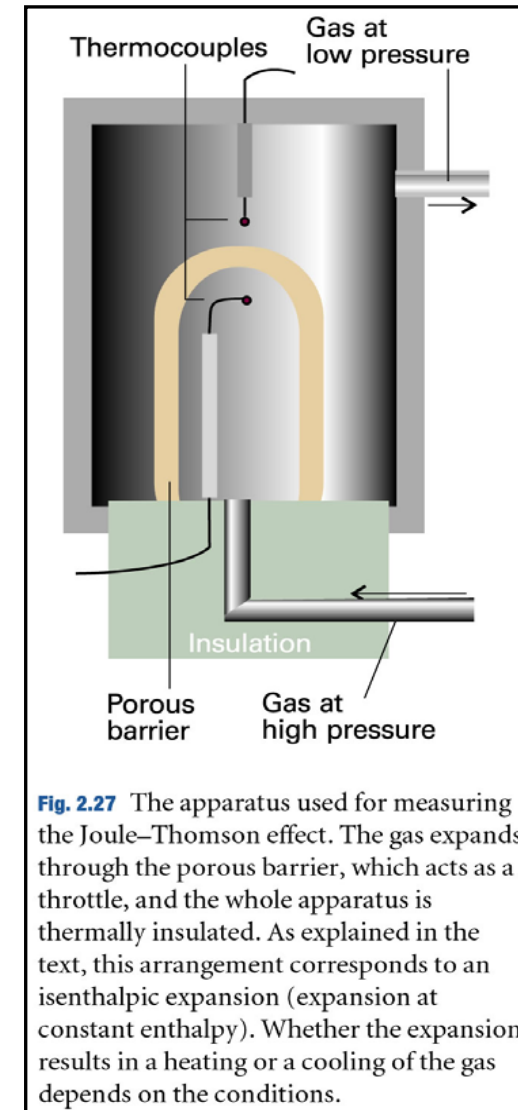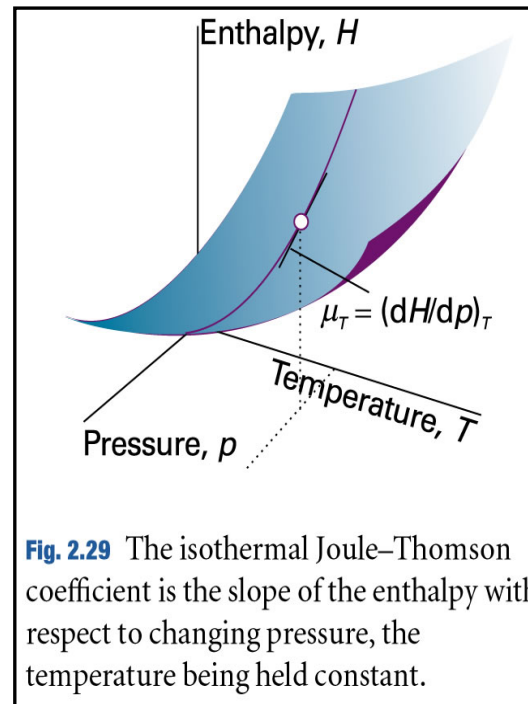Porous
plug
Thermometer

2.12 The Joule-Thomson effect

► Let a gas expand through a porous barrier from one constant pressure to another. (adiabatic process)

► The difference in temperature being proportional to the pressure difference

Modern method of measuring μ :

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

$$\mu_T = -C_p\mu$$

$\mu_T = $ isothermal Joule - Thomson coefficient

Enthalpy, H

$\mu_T = (dH/dp)_T$

Temperature, T

Pressure, p

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

Thermocouples — Gas at low pressure

Insulation

Porous barrier — Gas at high pressure

Fig. 2.27 The apparatus used for measuring the Joule–Thomson effect. The gas expands through the porous barrier, which acts as a throttle, and the whole apparatus is thermally insulated. As explained in the text, this arrangement corresponds to an isenthalpic expansion (expansion at constant enthalpy). Whether the expansion results in a heating or a cooling of the gas depends on the conditions.

2.12 The Joule-Thomson effect

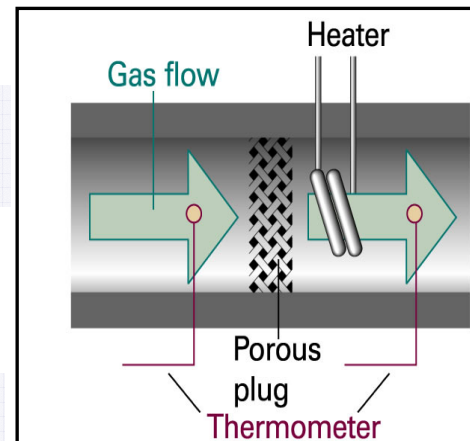To measure μ_t , the gas is pumped continuously at a steady pressure through a heat exchanger

$\downarrow$

The gas flow through a porous plug

$\downarrow$

The steep pressure drop is measured

$\downarrow$

The cooling effect is exactly offset by an electric heater

Fig. 2.30 A schematic diagram of the apparatus used for measuring the isothermal Joule–Thomson coefficient. The electrical heating required to offset the cooling arising from expansion is interpreted as ΔH and used to calculate $(\partial H/\partial p)_T$, which is then converted to μ as explained in the text.
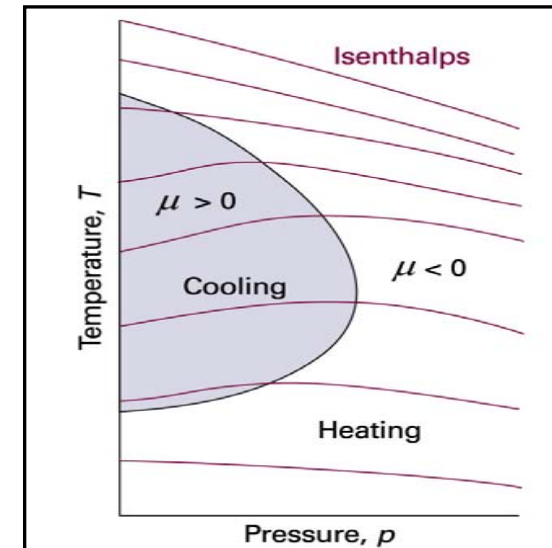
Fig. 2.31 The sign of the Joule–Thomson coefficient, μ, depends on the conditions. Inside the boundary, the shaded area, it is positive and outside it is negative. The temperature corresponding to the boundary at a given pressure is the 'inversion temperature' of the gas at that pressure. For a given pressure, the temperature must be below a certain value if cooling is required but, if it becomes too low, the boundary is crossed again and heating occurs. Reduction of pressure under adiabatic conditions moves the system along one of the isenthalps, or curves of constant enthalpy. The inversion temperature curve runs through the points of the isenthalps where their slope changes from negative to positive.

2.12 The Joule-Thomson effect

► Gases that show a heating effect $(\mu < 0)$ at one temperature show a cooling effect $(\mu > 0)$ when the temperature is below their upper inversion temperature, T_I

Fig. 2.32 The inversion temperatures for three real gases, nitrogen, hydrogen, and helium.