

COURSE CODE: SC202 (CHEMISTRY)

COURSE INSTRUCTOR: DR. SANGITA TALUKDAR (S21) &
DR. DEBARATI MITRA (S22)

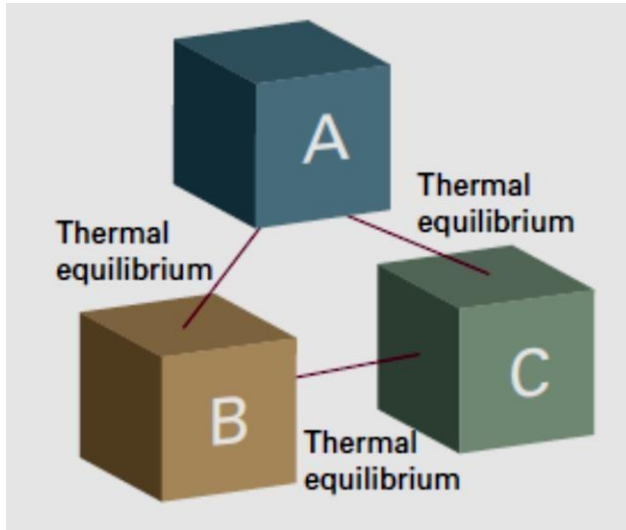
DEPT. OF SCIENCE AND MATHEMATICS

IITG, GUWAHATI

LECTURE-THERMODYNAMICS FIRST LAW

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Chemical Thermodynamics



Zeroth Law of thermodynamics:

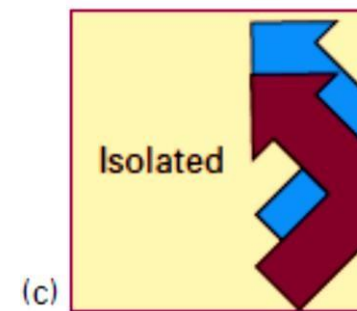
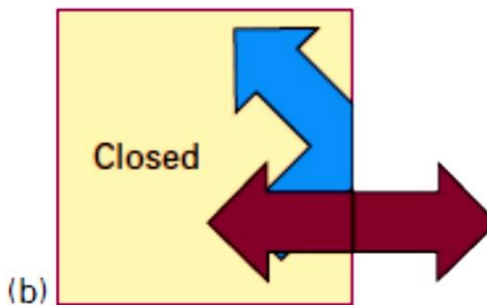
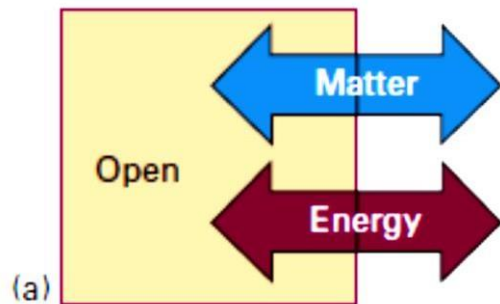
The Zeroth Law of thermodynamics states that :

If A is in thermal equilibrium with B, and B is in thermal equilibrium with C, then C is also in thermal equilibrium with A.

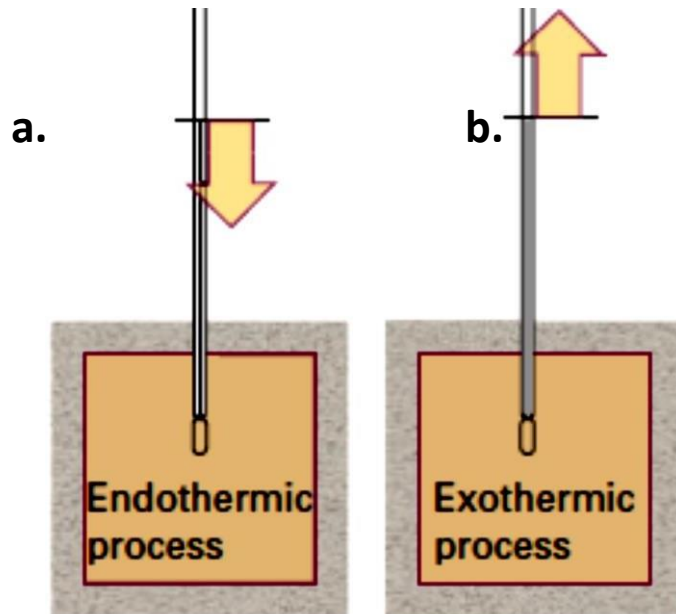
Fig. 1 The experience summarized by the Zeroth Law of thermodynamics is that, if an object A is in thermal equilibrium with B and B is in thermal equilibrium with C, then C is in thermal equilibrium with A.

• The Basic Concepts

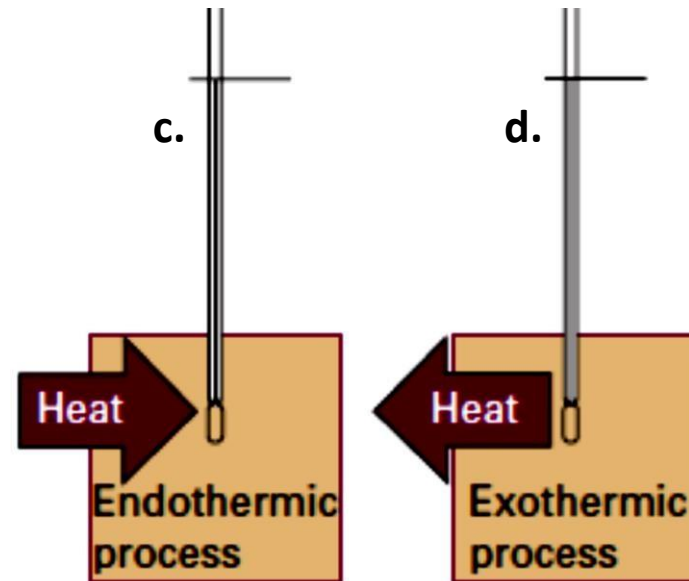
- The system is the part of the world in which we have a special interest. It may be a reaction vessel, an engine, an electrochemical cell, a biological cell, and so on.
- The surroundings comprise the region outside the system and are where we make our measurements.
- If matter can be transferred through the boundary between the system and its surroundings, the system is classified as **open**.
- If matter cannot pass through the boundary, the system is classified as **closed**. Both open and closed systems can exchange energy with their surroundings.
- An **isolated system** is a **closed system** that has neither mechanical nor thermal contact with its surroundings.



- An **exothermic process** is a process that releases energy as heat into its surroundings. All combustion reactions are exothermic.
- An **endothermic process** is a process in which energy is acquired from its surroundings as heat. An example of an endothermic process is the vaporization of water.
- Boundaries that do permit the transfer of energy as heat are called **diathermic**; those that do not are called **adiabatic**.



(a) When an endothermic process occurs in an adiabatic system, the temperature falls; (b) if the process is exothermic, the temperature rises.



(c) When an endothermic process occurs in a diathermic container, energy enters as heat from the surroundings, and the system remains at the same temperature. (d) If the process is exothermic, energy leaves as heat, and the process is isothermal.

In thermodynamics, the total energy of a system is called its **internal energy**, U . The internal energy is **the total kinetic and potential energy** of the molecules in the system. If we denote the change in internal energy as ΔU , when a system changes from an initial state i with internal energy U_i to a final state f of internal energy U_f , then

$$\Delta U = U_f - U_i$$

- The internal energy is a **state function** in the sense that its value depends only on the current state of the system. Changing any one of the state variables, such as the pressure, results in a change in internal energy.
- The internal energy is an **extensive property** of a system and is measured in joules ($1 \text{ J} = 1 \text{ kg m}^2 \text{ s}^{-2}$).
- The molar internal energy, U_m , is the internal energy divided by the amount of substance in a system, $U_m = U/n$; it is an **intensive property** and commonly reported in kilojoules per mole (kJ mol^{-1}).

Extensive property: An extensive property is a property that **depends** on the **amount** of matter in a sample.

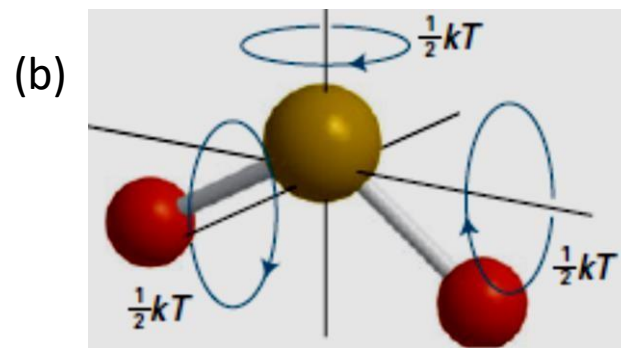
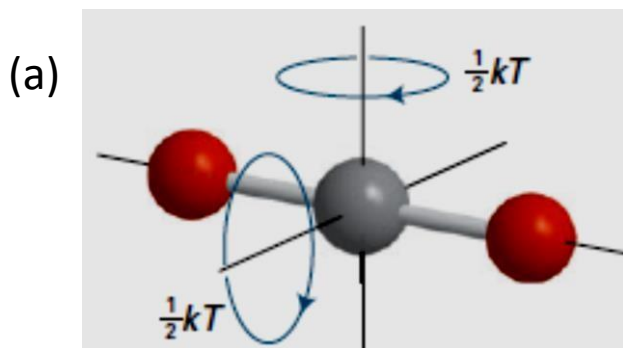
Intensive property: An intensive property, is a physical property of a system that **does not depend** on the **system size** or the **amount** of material in the system.

Molecular interpretation of internal energy

According to the ‘equipartition theorem’ of classical mechanics, the average energy of each quadratic contribution to the energy is $\frac{1}{2}kT$. The mean energy of the atoms, free to move in three dimensions is $\frac{3}{2}kT$ and the total energy of a monatomic perfect gas is $\frac{3}{2}NkT$, or nRT (because $N = nN_A$ and $R = N_A k$; and N_A = Avogadro constant & k = Boltzmann constant). We can therefore write:

$$U_m(T) = U_m(0) + \frac{3}{2}RT \text{ (monatomic gas; translation only)}$$

where $U_m(0)$ is the molar internal energy at $T = 0$, when all translational motion has ceased and the sole contribution to the internal energy arises from the internal structure of the atoms. This equation shows that the **internal energy of a perfect gas increases linearly with temperature**. At 25°C , $\frac{3}{2}RT = 3.7 \text{ kJ mol}^{-1}$, so translational motion contributes about 4 kJ mol^{-1} to the molar internal energy of a gaseous sample of atoms or molecules.



(a) A linear molecule can rotate about two axes perpendicular to the line of the atoms. (b) A nonlinear molecule can rotate about three perpendicular axes.

For a gas that consists of linear molecules, such as N_2 and CO_2 , we need to take into account the effect of rotation and vibration. A **linear molecule**, such as N_2 and CO_2 , can rotate around two axes perpendicular to the line of the atoms, so it has **two rotational modes** of motion, each contributing a term $1/2kT$ to the internal energy. Therefore, the mean rotational energy is kT and the rotational contribution to the molar internal energy is RT . By adding the translational and rotational contributions, we obtain:

$$U_{\text{m}}(T) = U_{\text{m}}(0) + 5/2RT \text{ (linear molecule; translation and rotation only)}$$

A **nonlinear molecule**, such as CH_4 or H_2O , can rotate around **three axes** so each mode of motion contributes a term $1/2kT$ to the internal energy. Therefore, the mean rotational energy is $3/2kT$ and there is a rotational contribution of $3/2RT$ to the molar internal energy. That is,

$$U_{\text{m}}(T) = U_{\text{m}}(0) + 3RT \text{ (nonlinear molecule; translation and rotation only)}$$

- The internal energy of nonlinear gas increases twice as rapidly with temperature compared with the monatomic gas. Thus, for a gas consisting of 1 mol of nonlinear molecules to undergo the same rise in temperature as compared to 1 mol of monatomic gas, twice as much energy must be supplied.
- There are no intermolecular interactions in a perfect gas, so the distance between the molecules has no effect on the energy. Hence, *the internal energy of a perfect gas is independent of the volume it occupies.*

The **First Law of thermodynamics** is expressed as follows:

The internal energy of an isolated system is constant.

There is no ‘perpetual motion machine’—a machine that does work without consuming fuel or using some other source of energy.

These remarks can be summarized mathematically as follows. If we write w for the work done on a system, q for the energy transferred as heat to a system, and ΔU for the resulting change in internal energy, then it follows that

$$\Delta U = q + w$$

**Mathematical statement
of the First Law**

If an electric motor **produced** 15 kJ of energy each second **as mechanical work** and lost 2 kJ as heat to the surroundings, then the change in the internal energy of the motor each second is

$$\Delta U = -2 \text{ kJ} - 15 \text{ kJ} = -17 \text{ kJ}$$

Suppose that, when a spring was wound, 100 J of **work was done on it** but 15 J escaped to the surroundings as heat.

The change in internal energy of the spring is **85 J**.

Expansion work

If we write w for the work done on a system, q for the energy transferred as heat to a system, and ΔU for the resulting change in internal energy, then it follows that

$$\Delta U = q + w \longrightarrow (1)$$

For infinitesimal changes in the internal energy dU , if the work done on a system is dw and the energy supplied to it as heat is dq , then we have,

$$dU = dq + dw \longrightarrow (2)$$

The general expression for work

The work required to move an object by a distance dz against an opposing force of magnitude F is

$$dw = -Fdz \longrightarrow (3)$$

The **negative sign** tells us that, when the system moves an object **against** an **opposing** force of magnitude F , and there are no other changes, then the **internal energy** of the system doing the work will **decrease**.

Let us consider the arrangement shown in Fig 1, in which one wall of a system is a massless, frictionless, rigid, perfectly fitting piston of area A . If the external pressure is p_{ex} , the magnitude of the force acting on the outer face of the piston is $F = p_{\text{ex}}A$. When the system expands through a distance dz against an external pressure p_{ex} , it follows that the work done is $d\mathbf{w} = -p_{\text{ex}}A\mathbf{dz}$. The quantity $A\mathbf{dz}$ is the change in volume, dV , in the course of the expansion. Therefore, the work done when the system expands by dV against a pressure p_{ex} is

$$d\mathbf{w} = -p_{\text{ex}}dV \longrightarrow (4) \quad \text{Expansion work}$$

To obtain the total work done when the volume changes from an initial value V_i to a final value V_f we integrate this expression between the initial and final volumes:

$$w = - \int_{V_i}^{V_f} p_{\text{ex}} dV \longrightarrow (5)$$

The force acting on the piston, $p_{\text{ex}}A$, is equivalent to the force arising from a weight that is raised as the system expands. If the system is **compressed** instead, then the same weight is lowered in the surroundings and eqn (5) can still be used, but now $V_f < V_i$.

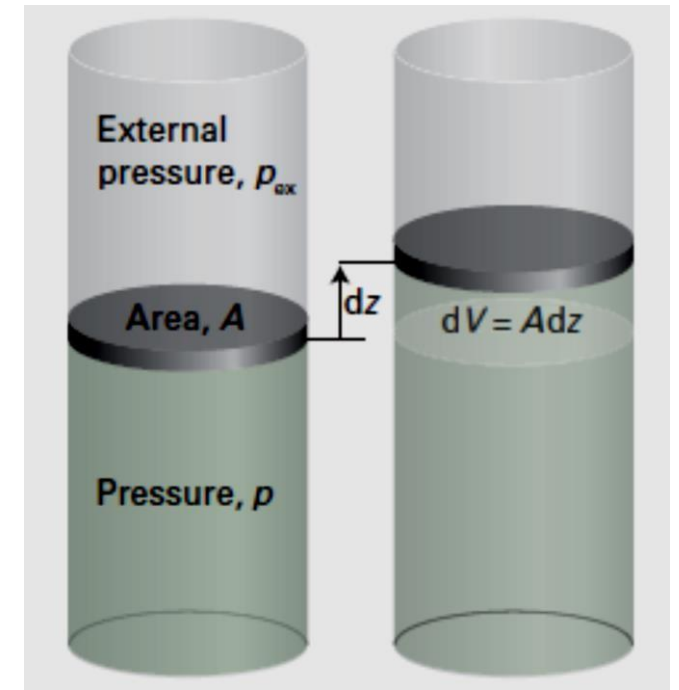


Fig. 1: When a piston of area A moves out through a distance dz , it sweeps out a volume $dV = Adz$. The external pressure p_{ex} is equivalent to a weight pressing on the piston, and the force opposing expansion is $F = p_{\text{ex}}A$.

(b) Free expansion

Free expansion is expansion against **zero opposing force**. It occurs when $p_{\text{ex}} = 0$. According to eqn (4), $dw = 0$ for each stage of the expansion. Hence, overall:

$$w = 0$$

Work of free expansion

$$\longrightarrow (6)$$

That is, **no work** is done when a system expands **freely**. Expansion of this kind occurs when a gas expands into a vacuum.

(c) Expansion against constant pressure

We can evaluate eqn (5) by taking the constant p_{ex} outside the integral:

$$w = -p_{\text{ex}} \int_{V_i}^{V_f} dV = -p_{\text{ex}}(V_f - V_i)$$

$$\longrightarrow (7)$$

Therefore, if we write the change in volume as $\Delta V = V_f - V_i$,

$$w = -p_{\text{ex}}\Delta V$$

Expansion work against
constant external pressure

$$\longrightarrow (8)$$

This result is illustrated graphically in Fig. 2, which makes use of the fact that an integral can be interpreted as an area. The magnitude of w , denoted $|w|$, is equal to the area beneath the horizontal line at $p = p_{\text{ex}}$ lying between the initial and final volumes. A **p, V -graph** is used to illustrate expansion work is called an **indicator diagram**.

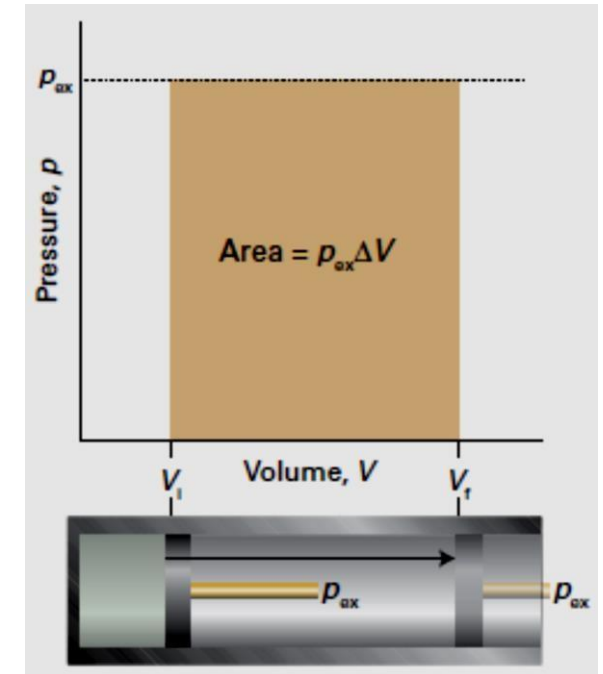


Fig. 2: The work done by a gas when it expands against a constant external pressure, p_{ex} , is equal to the shaded area in this example of an indicator diagram.

A **reversible change** in thermodynamics is a change that can be reversed by **an infinitesimal** modification of a variable. To achieve reversible expansion, we set p_{ex} equal to p at each stage of the expansion. When we set $p_{\text{ex}} = p$, eqn (4) becomes,

$$dw = -p_{\text{ex}}dV = -pdV \quad \boxed{\text{Reversible expansion work}} \longrightarrow (9)$$

The total work of reversible expansion from an initial volume V_i to a final volume V_f is therefore

$$w = - \int_{V_i}^{V_f} p dV \longrightarrow (10)$$

(e) Isothermal reversible expansion

Consider the isothermal, reversible expansion of a perfect gas. Because the equation of state is $pV = nRT$, so $p = nRT/V$, with V the volume at that stage of the expansion. The **temperature T is constant in an isothermal expansion**, so (together with n and R) it may be taken outside the integral. It follows that the **work of reversible isothermal expansion** of a perfect gas from V_i to V_f at a temperature T is

$$w = -nRT \int_{V_i}^{V_f} \frac{dV}{V} = -nRT \ln \frac{V_f}{V_i} \quad \boxed{\text{Reversible, isothermal expansion work of a perfect gas}} \longrightarrow (11)$$

Problem 1: Calculate the work done when 50 g of iron reacts with hydrochloric acid to produce $\text{FeCl}_2(\text{aq})$ and hydrogen in (a) a closed vessel of fixed volume (b) an open beaker at 25°C .

In (a), the volume cannot change, so no expansion work is done and $w = 0$. In (b), the gas drives back the atmosphere and therefore $w = -p_{\text{ex}}\Delta V$. We can neglect the initial volume because the final volume (after the production of gas) is so much larger and $\Delta V = V_f - V_i \approx V_f = nRT/p_{\text{ex}}$, where n is the amount of H_2 produced. Therefore,

$$w = -p_{\text{ex}}\Delta V \approx -p_{\text{ex}} \times \frac{nRT}{p_{\text{ex}}} = -nRT$$

Because the reaction is $\text{Fe}(\text{s}) + 2 \text{HCl}(\text{aq}) \rightarrow \text{FeCl}_2(\text{aq}) + \text{H}_2(\text{g})$, we know that 1 mol H_2 is generated when 1 mol Fe is consumed, and n can be taken as the amount of Fe atoms that react. Because the molar mass of Fe is 55.85 g mol^{-1} , it follows that

$$\begin{aligned} w &\approx -\frac{50 \text{ g}}{55.85 \text{ g mol}^{-1}} \times (8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) \times (298 \text{ K}) \\ &\approx -2.2 \text{ kJ} \end{aligned}$$

Problem 2: Calculate the expansion work done when 50 g of water is electrolyzed under constant pressure at 25°C .

Heat transactions

In general, the change in internal energy of a system is

$$dU = dq + dw_{\text{exp}} + dw_e \longrightarrow (12)$$

where dw_e is work **in addition** to the expansion work, dw_{exp} . For instance, dw_e might be the electrical work of driving a current through a circuit. A system kept at constant volume can do no expansion work, so $dw_{\text{exp}} = 0$. If the system is also **incapable of doing any other kind of work** (if it is not, for instance, an electrochemical cell connected to an electric motor), then $dw_e = 0$ too. Under these circumstances:

$$dU = dq_v \quad \boxed{\text{Heat transferred at constant volume}} \longrightarrow (13)$$

For a measurable change,

$$\Delta U = dq_v \longrightarrow (14)$$

- The energy transferred **as heat at constant volume is equal to the change in internal energy of the system.** Calorimetry is the measurement of heat transactions.
- The heat capacity at constant volume is the slope of the internal energy with respect to temperature.

(a) Calorimetry

Calorimetry is the study of **heat transfer** during physical and chemical processes. A **calorimeter** is a device for **measuring energy transferred as heat**. The most common device for measuring ΔU is an **adiabatic bomb calorimeter**.

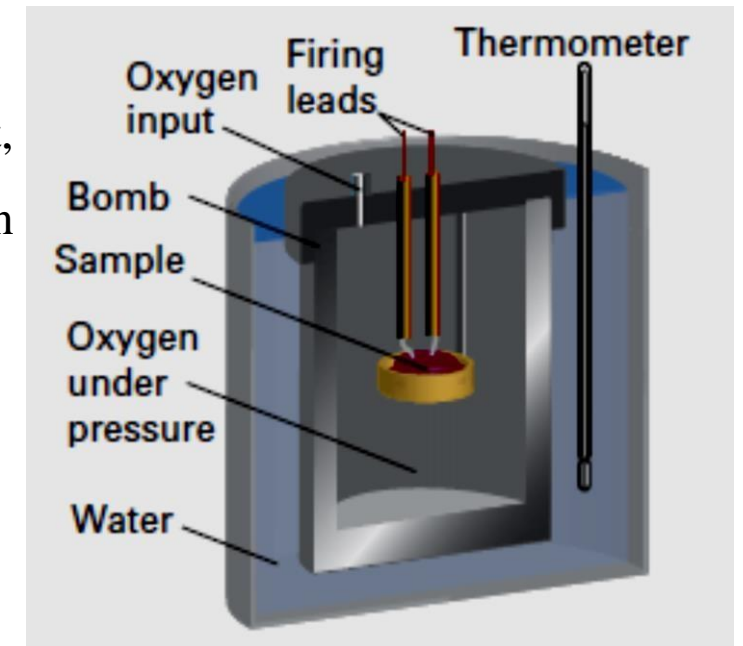
The change in temperature, ΔT , of the calorimeter is proportional to the energy that the reaction releases or absorbs as heat. Therefore, by measuring ΔT we can determine q_v and hence find ΔU . The conversion of ΔT to q_v is best achieved by calibrating the calorimeter using a process of known energy output and determining the **calorimeter constant**, the constant C in the relation

$$q = C\Delta T \longrightarrow (15)$$

The calorimeter constant may be measured electrically by passing a constant current, I , from a source of known potential difference, $\Delta\phi$, through a heater for a known period of time, t .

Then we get,

$$q = It\Delta\phi \longrightarrow (16)$$



(b) Heat capacity

The **heat capacity at constant volume** is denoted by C_V and is defined formally as

$$C_V = \left(\frac{\partial U}{\partial T} \right)_V$$

Definition of heat capacity
at constant volume

→ (17)

The heat capacity of a monatomic perfect gas can be calculated by inserting the expression for the internal energy. There we saw that

$$U_m = U_m(0) + 3/2RT$$

So, from eqn (17)

$$C_{V,m} = d/dT (U_m(0) + 3/2RT) = 3/2R \quad \longrightarrow \quad (18)$$

The numerical value is $12.47 \text{ J K}^{-1} \text{ mol}^{-1}$.

- **Heat capacities are extensive properties:** 100 g of water, for instance, has 100 times the heat capacity than that of 1 g of water.
- The **molar heat capacity at constant volume**, $C_{V,m} = C_V/n$, is the heat capacity per mole of substance, and is an **intensive property**.
- **Specific heat capacity** of a substance is the heat capacity of the sample divided by the mass, usually in grams: $C_{V,s} = C_V/m$. The specific heat capacity of water at room temperature is close to $4.2 \text{ J K}^{-1} \text{ g}^{-1}$.

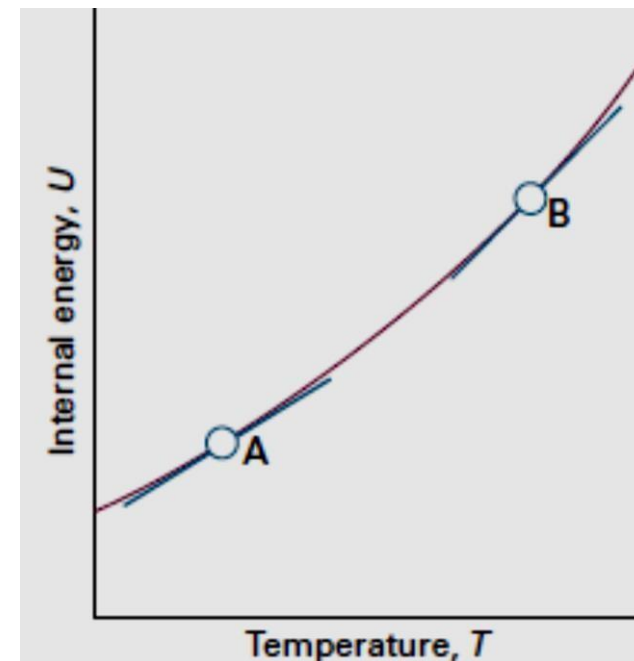


Fig. 3: The internal energy of a system increases as the temperature is raised; this graph shows its variation as the system is heated at constant volume. The slope of the tangent to the curve at any temperature is the heat capacity at constant volume at that temperature.

The heat capacity is used to relate **a change in internal energy to a change in temperature** of a constant-volume system. It follows from eqn (17) that

$$dU = C_v dT \text{ (at constant volume)} \longrightarrow (19)$$

For a measurable change of temperature, ΔT , brings about a measurable increase in internal energy, ΔU , where

$$\Delta U = C_v \Delta T \text{ (at constant volume)} \longrightarrow (20)$$

Because a change in internal energy can be identified with the heat supplied at constant volume, the last equation can also be written

$$q_v = C_v \Delta T \longrightarrow (21)$$

Enthalpy

- (a) Energy transferred as heat at constant pressure is equal to the change in enthalpy of a system.**
- (b) Enthalpy changes are measured in a constant-pressure calorimeter.**
- (c) The heat capacity at constant pressure is equal to the slope of enthalpy with temperature.**

Enthalpy

The **enthalpy**, H , is defined as

$$H = U + pV \longrightarrow (22)$$

where p is the pressure of the system and V is its volume. Because U , p , and V are all state functions, **the enthalpy is a state function.**

The change in enthalpy is equal to the energy supplied as heat at constant pressure (if the system does no additional work):

$$dH = dq \longrightarrow (23)$$

For a measurable change

$$\Delta H = q_p \longrightarrow (24)$$

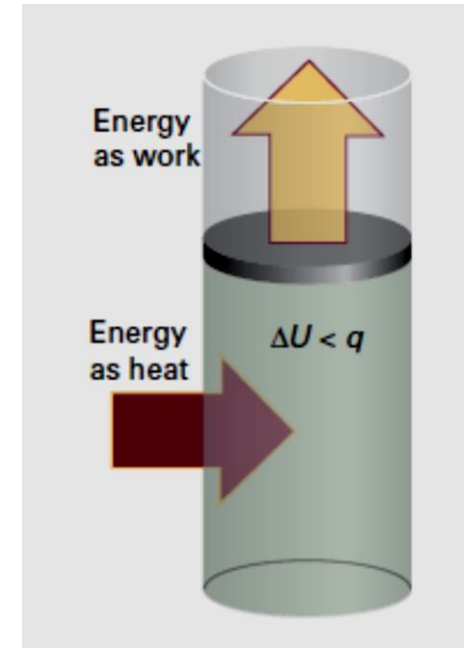


Fig. 4: When a system is subjected to constant pressure and is free to change its volume, some of the energy supplied as heat may escape back into the surroundings as work. In such a case, the change in internal energy is smaller than the energy supplied as heat.

For a general infinitesimal change in the state of the system, U changes to $U + dU$, p changes to $p + dp$, and V changes to $V + dV$, H changes from $U + pV$ to

$$\begin{aligned} H + dH &= (U + dU) + (p + dp)(V + dV) \\ &= U + dU + pV + pdV + Vdp + dpdV \end{aligned}$$

As the last term is the product of two infinitesimally small quantities and therefore can be neglected. As a result, after recognizing $U + pV = H$ on the right, we find that H changes to

$$H + dH = H + dU + pdV + Vdp$$

and hence that

$$dH = dU + pdV + Vdp$$

If we now substitute $dU = dq + dw$ into this expression, we get

$$dH = dq + dw + pdV + Vdp$$

If the system is in equilibrium with its surroundings at a pressure p and does only expansion work, then $dw = -pdV$

$$\text{Hence, } dH = dq + Vdp \longrightarrow (25)$$

At constant pressure, $dp = 0$. Then,

$$dH = dq \text{ (at constant pressure, no additional work)} \longrightarrow (26)$$

Relation between ΔH and ΔU

The enthalpy of a perfect gas is related to its internal energy by using $pV = nRT$ in the definition of H :

$$H = U + pV = U + nRT \longrightarrow (27)$$

This relation implies that the change of enthalpy in a reaction that produces or consumes gas is

$$\Delta H = \Delta U + \Delta n_g RT \longrightarrow (28)$$

where Δn_g is the change in the amount of gas molecules in the reaction.

The **enthalpy of a substance increases as its temperature is raised**. The relation between the increase in enthalpy and the increase in temperature depends on the conditions (for example, constant pressure or constant volume). The **most important condition is constant pressure**, and the slope of the tangent to a plot of enthalpy against temperature at constant pressure is called the **heat capacity at constant pressure**, C_p , at a given temperature

$$C_p = \left(\frac{\partial H}{\partial T} \right)_p \longrightarrow (29)$$

The heat capacity at constant pressure is an **extensive property**. The **molar heat capacity at constant pressure**, $C_{p,m}$, is the heat capacity per mole of material; it is an **intensive property**.

The heat capacity at constant pressure is used to relate the change in enthalpy to a change in temperature. For infinitesimal changes of temperature

$$dH = C_p dT \text{ (at constant pressure)} \longrightarrow (30)$$

If the heat capacity is constant over the range of temperatures of interest, then for a measurable increase in temperature

$$\Delta H = C_p \Delta T \text{ (at constant pressure)} \longrightarrow (31)$$

Because an increase in enthalpy can be equated with the energy supplied as heat at constant pressure, the practical form of the latter equation is

$$q_p = C_p \Delta T \longrightarrow (32)$$

A simple relation between the two heat capacities of a perfect gas:

$$C_p - C_v = nR \longrightarrow (33)$$

The change in internal energy of a perfect gas when the temperature is changed from T_i to T_f and the volume is changed from V_i to V_f can be expressed as

$$\Delta U = C_v(T_f - T_i) = C_v\Delta T \longrightarrow (34)$$

Because the expansion is adiabatic, we know that $q = 0$; because $\Delta U = q + w$, it then follows that $\Delta U = w_{\text{ad}}$. Therefore, by equating the two expressions we have obtained for ΔU , we obtain

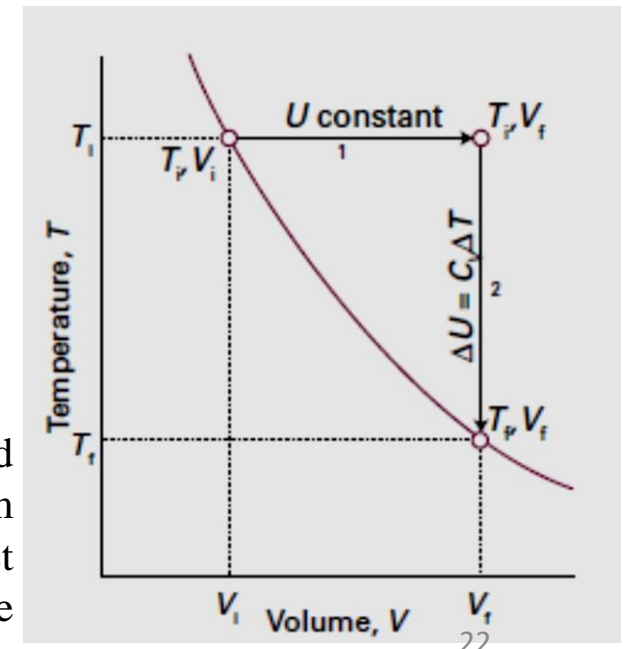
$$w_{\text{ad}} = C_v\Delta T \longrightarrow (35)$$

That is, the work done during an adiabatic expansion of a perfect gas is proportional to the temperature difference between the initial and final states.

The initial and final temperatures of a perfect gas that undergoes reversible adiabatic expansion can be calculated from

$$T_f = T_i \left(\frac{V_i}{V_f} \right)^{1/\gamma} \longrightarrow (36)$$

Fig: 5: To achieve a change of state from one temperature and volume to another temperature and volume, we may consider the overall change as composed of two steps. In the first step, the system expands at constant temperature; there is no change in internal energy if the system consists of a perfect gas. In the second step, the temperature of the system is reduced at constant volume. The overall change in internal energy is the sum of the changes for the two steps.



where $c = C_{v,m}/R$. By raising each side of this expression to the power c , an equivalent expression is

$$V_i T_i^c = V_f T_f^c \longrightarrow (37)$$

This result is often summarized in the form

$$VT^c = \text{constant} \longrightarrow (38)$$

Problem: Consider the adiabatic, reversible expansion of 0.020 mol Ar, initially at 25°C, from 0.50 dm³ to 1.00 dm³. The molar heat capacity of argon at constant volume is 12.48 J K⁻¹ mol⁻¹, so $c = 1.501$. The final temperature (T_f) is

$$T_f = (298 \text{ K}) \times \left(\frac{0.50 \text{ dm}^3}{1.00 \text{ dm}^3} \right)^{1/1.501} = 188 \text{ K}$$

It follows that $\Delta T = -110 \text{ K}$ and therefore, $w = \{(0.020 \text{ mol}) \times (12.48 \text{ J K}^{-1} \text{ mol}^{-1})\} \times (-110 \text{ K}) = -27 \text{ J}$

Problem: Calculate the final temperature, the work done, and the change of internal energy when ammonia is used in a reversible adiabatic expansion from 0.50 dm³ to 2.00 dm³, the other initial conditions being the same.

The pressure of a perfect gas that undergoes **reversible adiabatic expansion** from a volume V_i to a volume V_f is related to its initial pressure by

$$p_f V_f^\gamma = p_i V_i^\gamma \longrightarrow (39)$$

where $\gamma = C_{p,m}/C_{v,m}$.

$$pV^\gamma = \text{constant.} \longrightarrow (40)$$

For a monatomic perfect gas, $C_{p,m} = 5/2R$, so $\gamma = 5/3$ (as $C_p - C_v = R$).

For a gas of nonlinear polyatomic molecules, $C_{v,m} = 3R$, so $\gamma = 4/3$.

The curves of pressure versus volume for adiabatic change are known as **adiabats**.

Problem : When a sample of argon (for which $\gamma = 5/3$) at 100 kPa expands reversibly and adiabatically to twice its initial volume the final pressure will be

$$p_f = \left(\frac{V_i}{V_f} \right)^\gamma p_i = \left(\frac{1}{2} \right)^{5/3} \times (100 \text{ kPa}) = 31.5 \text{ kPa}$$

Thermochemistry

The study of the **energy transferred as heat during the course of chemical reactions** is called **thermochemistry**.

Thermochemistry is a branch of thermodynamics because a reaction vessel and its contents form a system and chemical reactions, result in **the exchange of energy between the system and the surroundings**.

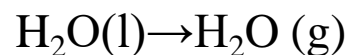
Because the release of heat signifies a decrease in the enthalpy of a system, an exothermic process is the one for which $\Delta H < 0$. Conversely, because the absorption of heat results in an increase in enthalpy, an endothermic process has $\Delta H > 0$.

For, exothermic process: $\Delta H < 0$ and endothermic process: $\Delta H > 0$.

Changes in enthalpy are normally reported for processes taking place under a set of standard conditions. The **standard enthalpy change**, ΔH^ϕ , is the change in enthalpy for a process in which **the initial and final substances are in their standard states**:

The **standard state** of a substance **at a specified temperature is its pure form at 1 bar**.

As an example of a standard enthalpy change, the *standard enthalpy of vaporization*, $\Delta_{\text{vap}}H^\phi$, is the enthalpy change per mole when a pure liquid at 1 bar vaporizes to a gas at 1 bar, as in



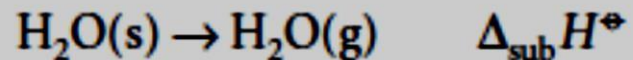
$$\Delta_{\text{vap}}H^\phi(373 \text{ K}) = +40.66 \text{ kJ mol}^{-1}$$

(a) Enthalpies of physical change

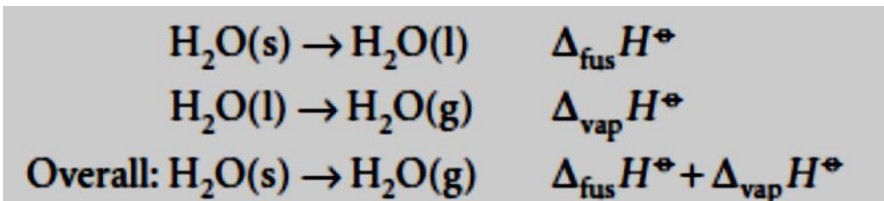
- The standard enthalpy change that accompanies a change of physical state is called the **standard enthalpy of transition** and is denoted $\Delta_{\text{trs}}H^\phi$.
- The **standard enthalpy of vaporization**, $\Delta_{\text{vap}}H^\phi$, is one example.
- The **standard enthalpy of fusion**, $\Delta_{\text{fus}}H^\phi$, the standard enthalpy change accompanying the conversion of a solid to a liquid, as in



Because **enthalpy is a state function**, a change in enthalpy is **independent** of the path between the two states. This feature is of great importance in thermochemistry, for it implies that the same value of ΔH^ϕ will be obtained however the change is brought about between the same initial and final states. For example, we can predict the conversion of a solid to a vapour either as occurring by sublimation (the direct conversion from solid to vapour)



or as occurring in two steps, first fusion (melting) and then vaporization of the resulting liquid:



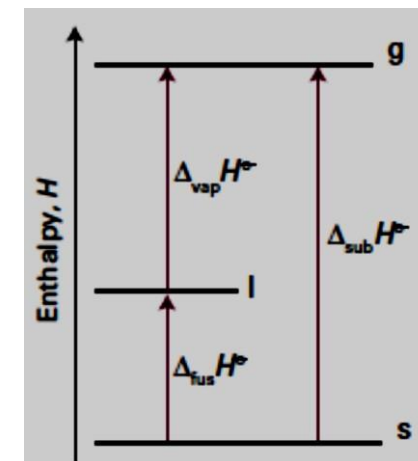
Because the overall result of the **indirect path** is the same as that of the **direct path**, the overall enthalpy change is the **same** in each case, and we can conclude that (for processes occurring at the same temperature)

$$\Delta_{\text{sub}} H^{\ominus} = \Delta_{\text{fus}} H^{\ominus} + \Delta_{\text{vap}} H^{\ominus}$$

The vaporization of a solid often involves a large increase in energy, especially when the solid is ionic and the strong Coulombic interaction of the ions must be overcome in a process such as $\text{MX(s)} \rightarrow \text{M}^{\text{+}}(\text{g}) + \text{X}^{\text{-}}(\text{g})$

The **lattice enthalpy**, ΔH_{L} , is the change in standard molar enthalpy for this process. The lattice enthalpy is equal to the lattice internal energy at $T = 0$; at normal temperatures they differ by only a few kilojoules per mole, and the difference is normally neglected.

Experimental values of the lattice enthalpy are obtained by using a **Born–Haber cycle**, a **closed path of transformations starting and ending at the same point**, one step of which is the formation of the solid compound from a gas of widely separated ions.



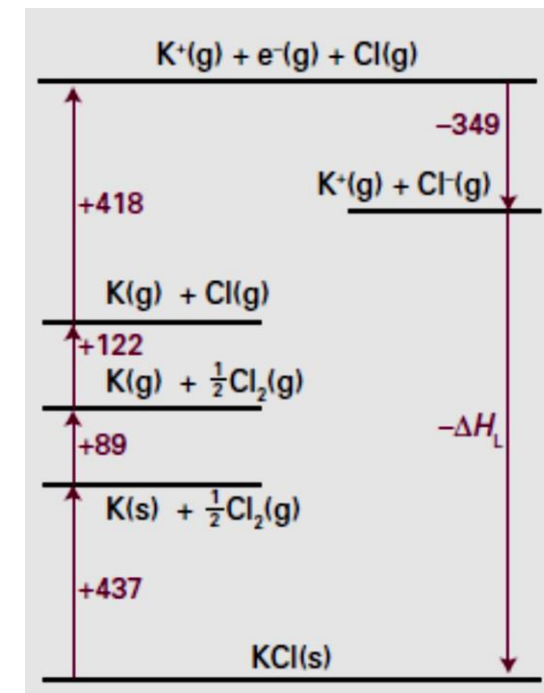
A typical Born–Haber cycle, for potassium chloride, consists of the following steps (for convenience, starting at the elements):

	$\Delta H^\ominus/(\text{kJ mol}^{-1})$	
1. Sublimation of K(s)	+89	[dissociation enthalpy of K(s)]
2. Dissociation of $\frac{1}{2}$ Cl ₂ (g)	+122	$[\frac{1}{2} \times \text{dissociation enthalpy of Cl}_2(\text{g})]$
3. Ionization of K(g)	+418	[ionization enthalpy of K(g)]
4. Electron attachment to Cl(g)	−349	[electron gain enthalpy of Cl(g)]
5. Formation of solid from gas	$-\Delta H_L/(\text{kJ mol}^{-1})$	
6. Decomposition of compound	+437	[negative of enthalpy of formation of KCl(s)]

Because the sum of these enthalpy changes is equal to zero, we can infer from

$$89 + 122 + 418 - 349 - \Delta H_L/(\text{kJ mol}^{-1}) + 437 = 0$$

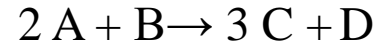
that $\Delta H_L = +717 \text{ kJ mol}^{-1}$. ●



(b) Enthalpies of chemical change

The **standard reaction enthalpy**, $\Delta_r H^\ominus$ (or ‘standard enthalpy of reaction’)

Thus, for a reaction of the form



the standard reaction enthalpy would be

$$\Delta_r H^\ominus = \{3H_m^\ominus(\text{C}) + H_m^\ominus(\text{D})\} - \{2H_m^\ominus(\text{A}) + H_m^\ominus(\text{B})\} \longrightarrow (41)$$

In general,

$$\Delta_r H^\ominus = \sum_{\text{Products}} \nu H_m^\ominus - \sum_{\text{Reactants}} \nu H_m^\ominus \longrightarrow (42)$$

(c) Hess’s law

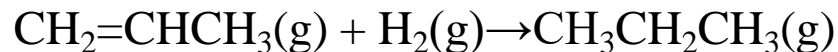
Standard enthalpies of individual reactions can be combined to obtain the enthalpy of another reaction. This application of the First Law is called **Hess’s law**:

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.

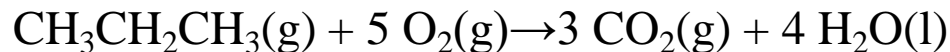
Hess's law

*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.*

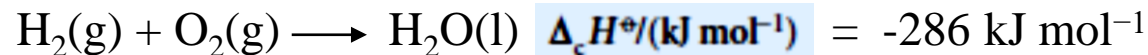
Example 1. The standard reaction enthalpy for the hydrogenation of propene



is -124 kJ mol^{-1} . The standard reaction enthalpy for the combustion of propane

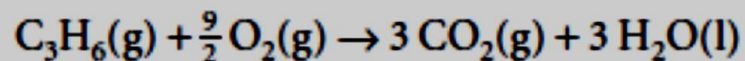


is $-2220 \text{ kJ mol}^{-1}$.



Calculate the standard enthalpy of combustion of propene.

Answer The combustion reaction we require is



This reaction can be recreated from the following sum:

	$\Delta_r H^\ominus / (\text{kJ mol}^{-1})$
$\text{C}_3\text{H}_6(\text{g}) + \text{H}_2(\text{g}) \rightarrow \text{C}_3\text{H}_8(\text{g})$	-124
$\text{C}_3\text{H}_8(\text{g}) + 5 \text{ O}_2(\text{g}) \rightarrow 3 \text{ CO}_2(\text{g}) + 4 \text{ H}_2\text{O}(\text{l})$	-2220
$\text{H}_2\text{O}(\text{l}) \rightarrow \text{H}_2(\text{g}) + \frac{1}{2} \text{ O}_2(\text{g})$	+286
<hr/>	
$\text{C}_3\text{H}_6(\text{g}) + \frac{9}{2} \text{ O}_2(\text{g}) \rightarrow 3 \text{ CO}_2(\text{g}) + 3 \text{ H}_2\text{O}(\text{l})$	-2058

Example 2. Calculate the enthalpy of hydrogenation of benzene from its enthalpy of combustion and the enthalpy of combustion of cyclohexane.

	$\Delta_f H^\ominus / (\text{kJ mol}^{-1})$	$\Delta_c H^\ominus / (\text{kJ mol}^{-1})$
Benzene, $\text{C}_6\text{H}_6(\text{l})$	+49.0	−3268
Cyclohexane		−3920