

Part 1: Equilibrium

2. The First Law: the concepts

Bilingual

Program



2. The First Law: the concepts

This chapter introduces the basic concepts of thermodynamics. It concentrates on the conservation of energy. The target concept of the chapter is enthalpy, which is a very useful book-keeping property for keeping track of the heat output of physical processes and chemical reactions at constant pressure.



2. The First Law: the concepts

The basic concepts

2.1 Work, heat, and energy

2.2 The First Law

Work and heat

2.3 Expansion work

2.4 Heat transactions

2.5 Enthalpy

2.6 Adiabatic changes

Thermochemistry

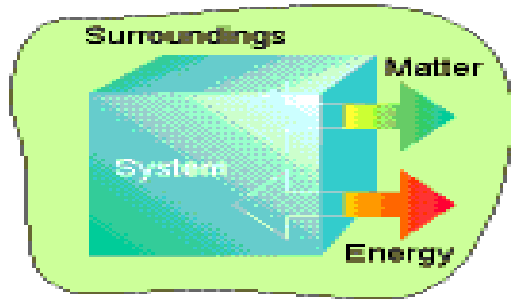
2.7 Standard enthalpy changes

2.8 Standard enthalpies of formation

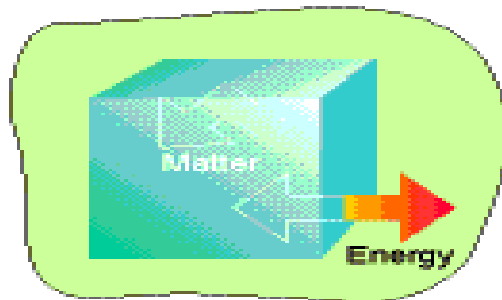
2.9 The temperature dependence of reaction enthalpies



2.1 Work, heat, and energy



(a) Open



(b) Closed



(c) Isolated

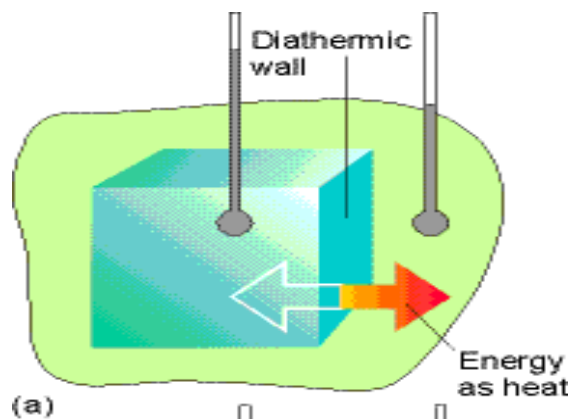
(a). Open system
can exchange matter and energy with its surroundings.

(b). Closed system *
can exchange energy with its surroundings, but it cannot exchange matter.

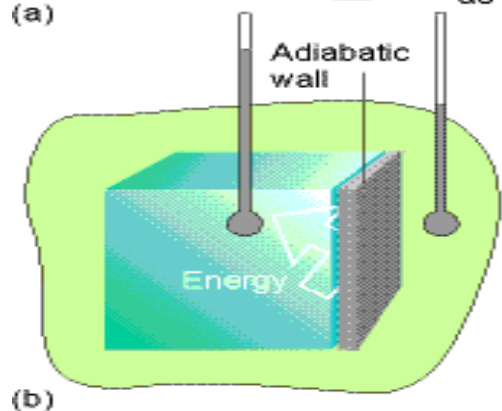
(c). An isolated system can exchange neither energy nor matter with its surroundings.



2.1 Work, heat, and energy



(a). A **diathermic system** is one that allows energy to escape as heat through its boundary if there is a difference in temperature between the system and its surroundings.



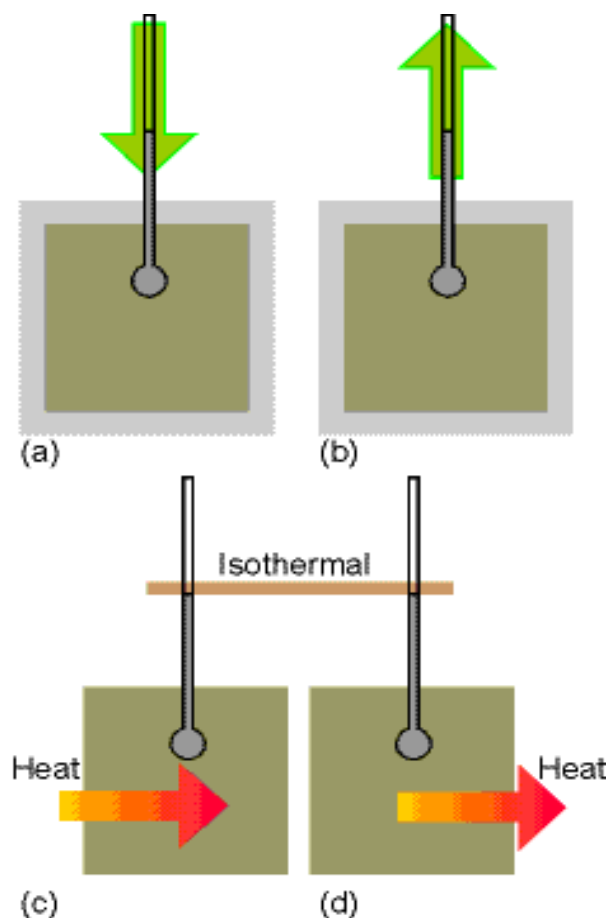
(b). An **adiabatic system** is one that does not permit the passage of energy as heat through its boundary even if there is a temperature difference between the system and its surroundings.



2.1 Work, heat, and energy

Exothermic process: one that releases energy as heat.

Endothermic process: one that absorbs energy as heat.

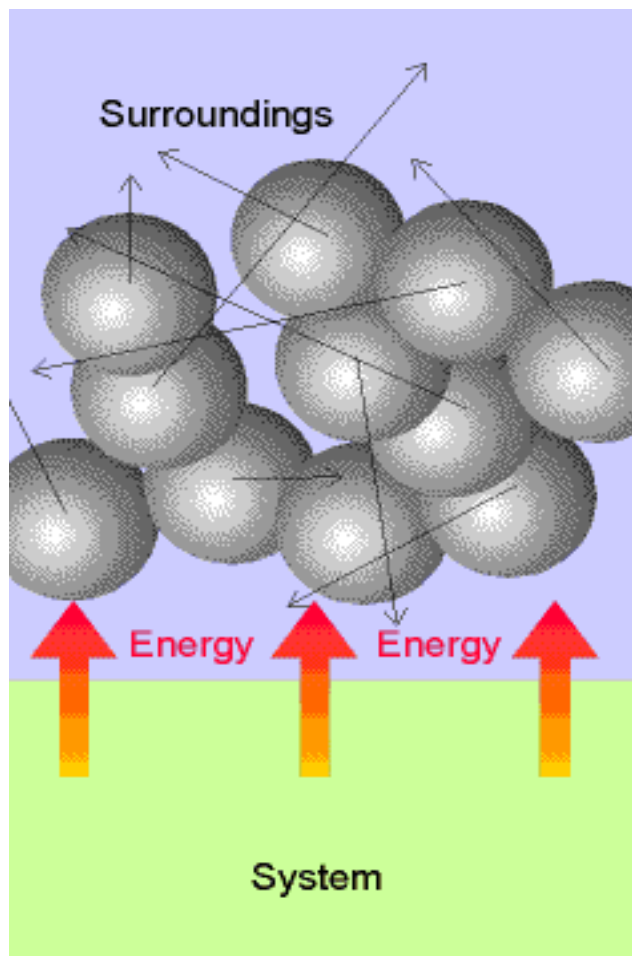


(a) When an endothermic process occurs in an adiabatic system, the temperature falls; **(b)** if the process is exothermic, then the temperature rises. **(c)** When an endo-thermic process occurs in a diathermic container, energy enters as heat from the surroundings, and the system remains at the same temperature; **(d)** if the process is exothermic, then energy leaves as heat, and the process is isothermal.



2.1 Work, heat, and energy

Heat-molecular interpretation

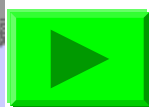
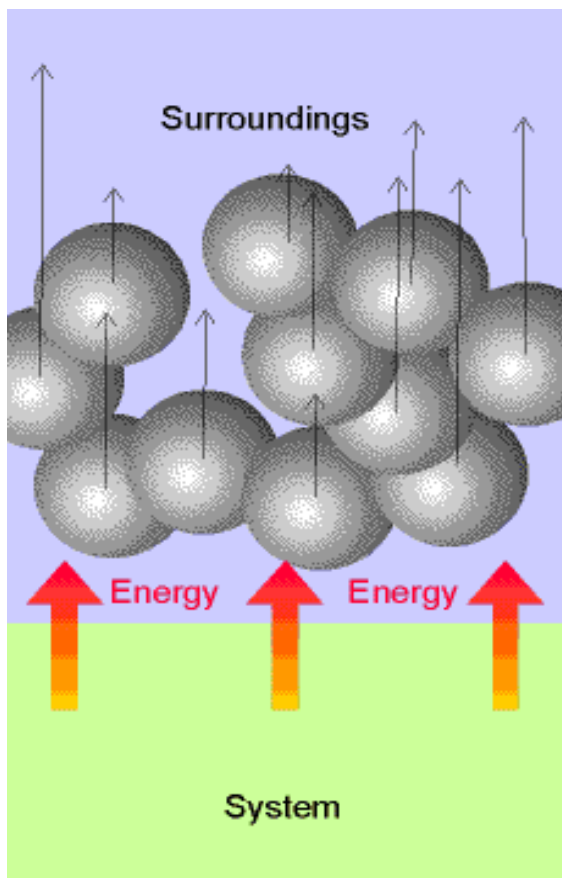


Heat is the transfer of energy that makes use of chaotic molecular motion. The chaotic motion of molecules is called **thermal motion**. When a system heats its surroundings, molecules of the system stimulate the thermal motion of the molecules in the surroundings.



2.1 Work, heat, and energy

Work-molecular interpretation



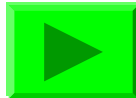
Work is the transfer of energy that makes use of organized motion. When a system does work, it stimulates orderly motion in the surroundings



The basic concepts

2.1 Work, heat, and energy

2.2 The First Law

- 1). The internal energy 
- 2). The conservation of energy
- 3). The formal statement of the First Law



2.2 The First Law

1). The internal energy

The internal energy, U : the total energy of a system is called its internal energy; it is the total kinetic and potential energy of the molecules composing the system.

The internal energy is a **state function**. It is an extensive property.

Internal energy, heat, and work are measured in the same units, the **Joule (J)**.



2.2 The First Law

2). The conservation of energy

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

$$\Delta U = q + w \text{ — the First Law of thermodynamics}$$

The internal energy of a system may be changed either by doing work on the system or by heating it.

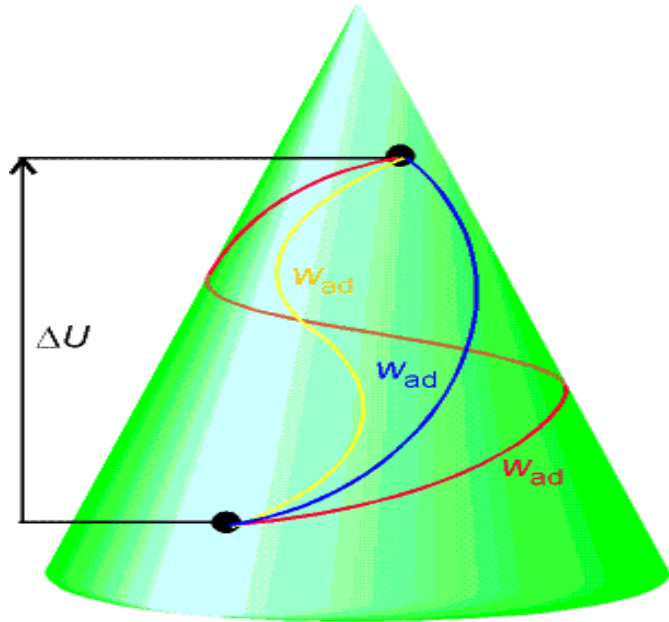
$w > 0$ or $q > 0$, energy is transferred to the system as work or heat.

$w < 0$ or $q < 0$, energy is lost from the system as work or heat.



2.2 The First Law

3). The formal statement of the First Law



The same quantity of work must be done on an adiabatic system to achieve the same change of state even though different means of achieving that work may be used.

$$h = A_f - A_i = \Delta A$$

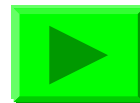
The work needed to change an adiabatic system from one specified state to another specified state is the same however the work is done.

$$w_{ad} = U_f - U_i = \Delta U$$



Work and heat

2.3 Expansion work



- 1). The general expression for work
- 2). Free expansion
- 3). Expansion against constant pressure
- 4). Reversible expansion
- 5). Isothermal reversible expansion

2.4 Heat transactions

2.5 Enthalpy

2.6 Adiabatic changes



2.3 Expansion work

Infinitesimal form

If the work done on a system is dw and the energy supplied to it as heat is dq , the infinitesimal change of internal energy dU is:

$$dU = dq + dw$$



2.3 Expansion work

1). The general expression for work

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

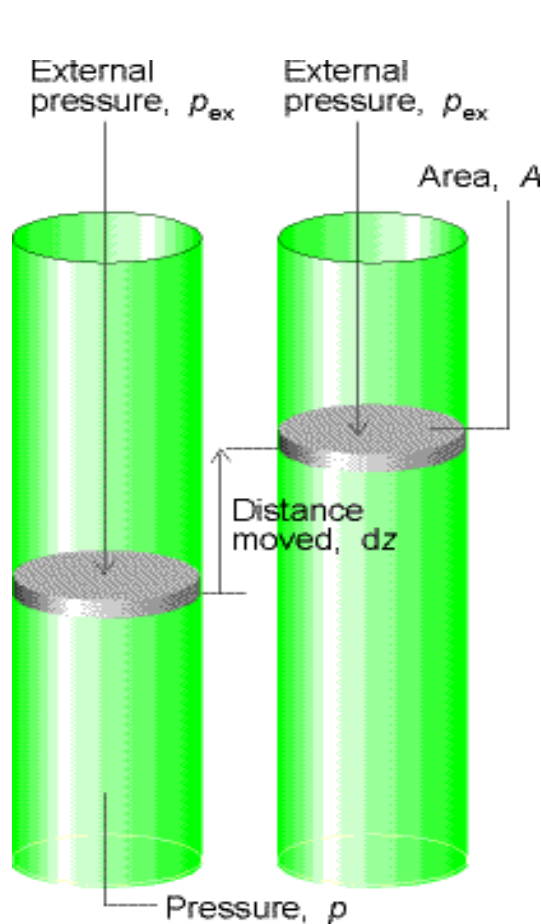
$$dw = -F dz$$

The **negative sign** presents that when the system moves an object against an opposing force, the internal energy of the system doing the work will decrease



2.3 Expansion work

1). The general expression for work



the area of the piston, A

the external pressure, p_{ex}

the force on the outer face, $F = p_{\text{ex}} A$.

When the system expands through a distance dz against p_{ex} , the work done:

$$dw = - p_{\text{ex}} A dz$$

where $A dz$ is the change in volume, dV , in the course of the expansion.



2.3 Expansion work

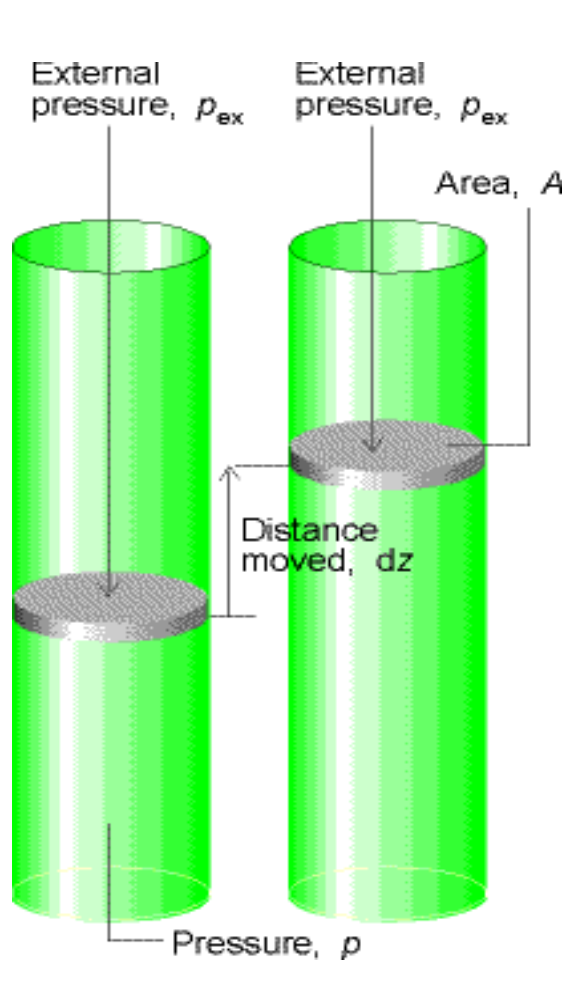
1). The general expression for work

The work done when the system expands by dV against a pressure p_{ex} is

$$dw = -F dz = -p_{\text{ex}} dV$$

The total work done, w :

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





2.3 Expansion work

In general, the work done on a system can be expressed in the form $dw = -Fdz$, where F is a 'generalized force' and dz is a 'generalized displacement'.

Varieties of work

Type of w	dw	Comments	Units
Expansion	$-p_{\text{ex}}dV$	p_{ex} dV	Pa m^3
Surface expansion	$\gamma d\sigma$	γ $d\sigma$	Nm^{-1} m^2
Extension	$f dl$	f dl	N m
Electrical	φdq	φ dq	V C



2.3 Expansion work

2). Free expansion

Free expansion: the expansion against zero opposing force.

$$p_{\text{ex}} = 0 \quad \longrightarrow \quad dw = 0 \text{ for each stage of the expansion}$$
$$w = 0$$

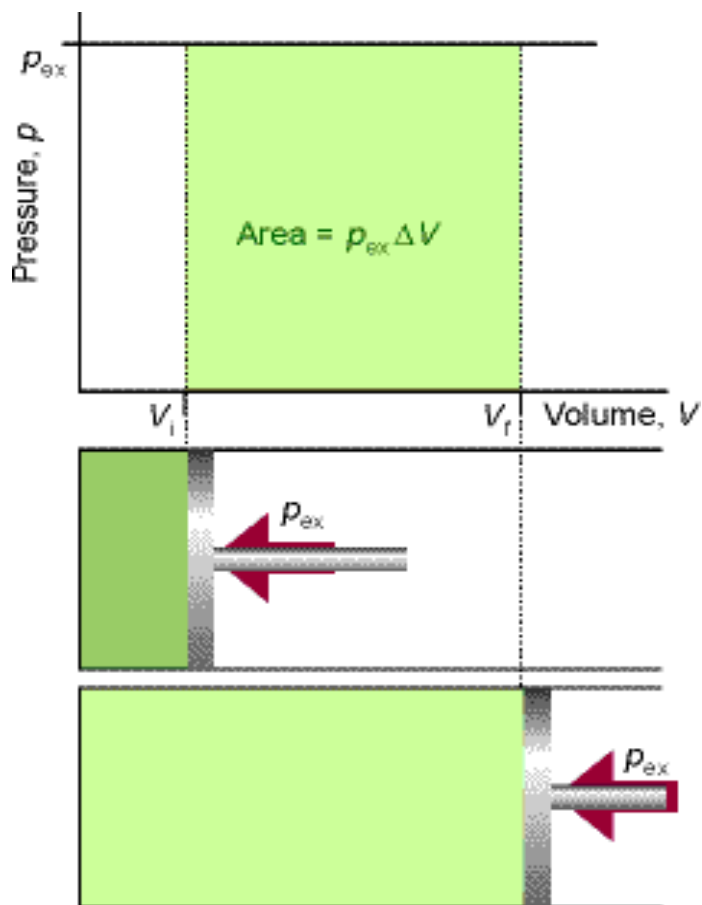
No work is done when a system expands freely.

Expansion of this kind occurs when a system expands into a vacuum.



2.3 Expansion work

3). Expansion against constant pressure



For an expansion of the external pressure constant throughout of the expansion

$$\begin{aligned} w &= -p_{\text{ex}} \int_{V_i}^{V_f} dV \\ &= -p_{\text{ex}} (V_f - V_i) = -p_{\text{ex}} \Delta V \end{aligned}$$

The magnitude of w , is equal to the area beneath the horizontal line at $p = p_{\text{ex}}$ lying between the initial and final volumes.



2.3 Expansion work

4). Reversible expansion

A reversible change in thermodynamics is a change that can be reversed by an infinitesimal modification of a variable. The key word 'infinitesimal' sharpens the everyday meaning of the word 'reversible' as something that can change direction.



2.3 Expansion work

4). Reversible expansion

To achieve a **reversible expansion**, set the external pressure p_{ex} equal to the pressure of the confined gas p at each stage of the expansion, $p_{\text{ex}} = p$

$$dw_{\text{rev}} = -p_{\text{ex}} dV = -p dV$$

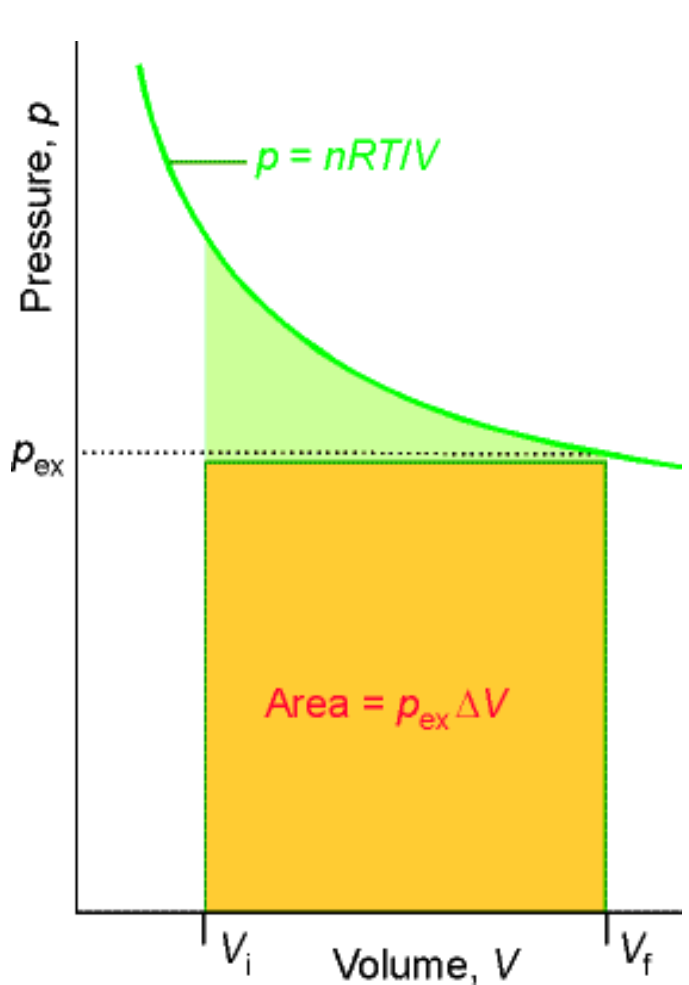
$$w = -\int_{V_i}^{V_f} p dV$$

This equation is for the reversible expansion. The integral can be evaluated once we know how the pressure of the confined gas depends on its volume.



2.3 Expansion work

5). Isothermal reversible expansion



For the isothermal, reversible expansion of a perfect gas:

$$\begin{aligned}w_{\text{rev},T} &= -nRT \int_{V_i}^{V_f} \frac{dV}{V} \\ &= -nRT \ln \frac{V_f}{V_i}\end{aligned}$$



Example

Calculate the work done when 50 g of iron reacts with hydrochloric acid in (a) a closed vessel of fixed volume, (b) an open beaker at 25 °C.

Method: We need to judge the magnitude of the volume change, and then to decide how the process occurs. If there is no change in volume, there is no expansion work however the process takes place. If the system expands against a constant external pressure, the work can be calculated. A general feature of processes in which a condensed phase changes into a gas is that the volume of the former may usually be neglected relative to that of the gas it forms.



Example

Answer: In (a) the volume cannot change, so no work is done and $w = 0$. In (b) the gas drives back the atmosphere and therefore $w = -p_{\text{ex}} \Delta V$. If neglect the initial volume, $\Delta V = V_{\text{f}} - V_{\text{i}} \approx V_{\text{f}} = nRT / p_{\text{ex}}$, where n is the amount of H_2 produced.

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



Example

The reaction is



Because 1 mol H_2 is generated when 1 mol Fe is consumed

$$\begin{aligned} w &= -nRT \\ &= -\frac{50\text{g}}{55.85\text{g mol}^{-1}} (8.314 \text{ J K}^{-1} \text{ mol}^{-1})(298.15\text{K}) \\ &= -2.2\text{kJ} \end{aligned}$$



2.4 Heat transactions

The change in internal energy of a system generally is

$$dU = dq + dw_{\text{exp}} + dw_e$$

$$dU = dq$$

at constant volume, no additional work. For a measurable change:

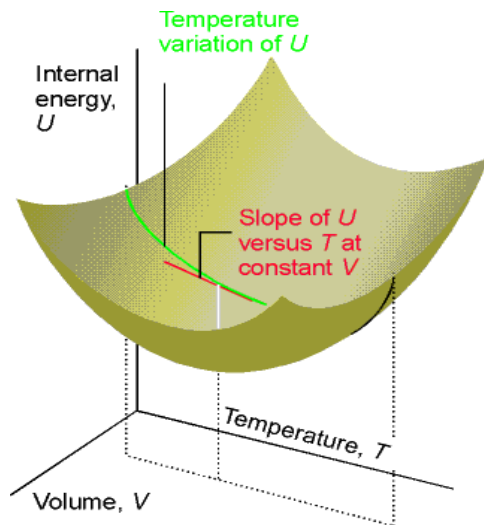
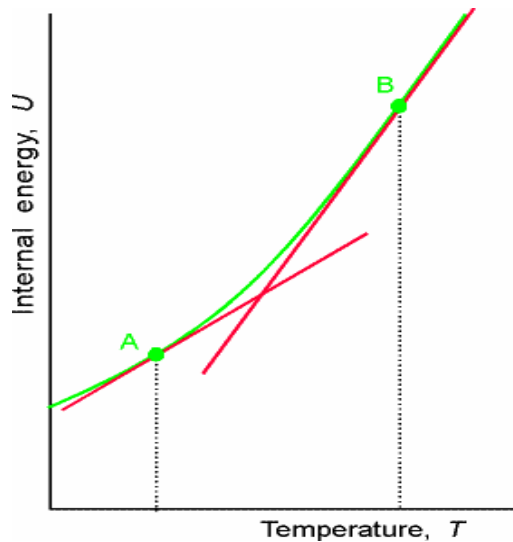
$$\Delta U = q_V$$

where the subscript means a change at constant volume.



2.4 Heat transactions

Heat capacity



The internal energy of a substance increases when its temperature is raised. The slope of the curve at any T is called the **heat capacity**, C_V , of the system at that T .

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

C_V – Extensive properties

$C_{V,m}$ – Intensive properties



2.4 Heat transactions

Heat capacity

A change in internal energy to a change in temperature of a constant-volume system follows:

$$dU = C_V dT \text{ (at constant } V \text{)}$$

An infinitesimal change in T brings about an infinitesimal change in U , and the constant of proportionality is C_V at constant V . If C_V is independent of T over the range of temperatures of interest, a measurable change in internal ΔU

$$\Delta U = C_V \Delta T \text{ (at constant } V \text{)}$$



2.4 Heat transactions

Heat capacity

Because a change in U can be identified with the heat supplied at constant V , the above equation is then

$$q_V = C_V \Delta T$$

This relation provides a simple way of measuring C_V of a sample. The ratio of the heat supplied to T rise it causes is the **heat capacity** of the sample.



2.5 Enthalpy

1). The definition of enthalpy

The change in internal energy is not equal to the heat supplied when the system is free to change its volume. Under these circumstances some of the energy supplied as heat to the system is returned to the surroundings as expansion work. However, we shall now show that in this case the heat supplied at constant pressure is equal to the change in another thermodynamic property of the system, the **enthalpy**, H .



2.5 Enthalpy

1). The definition of enthalpy

The enthalpy, a state function, is defined as:

$$H = U + pV$$

The change in enthalpy between any pair of initial and final states is independent of the path between them, and

ΔH is equal to the heat supplied at constant pressure to a system:

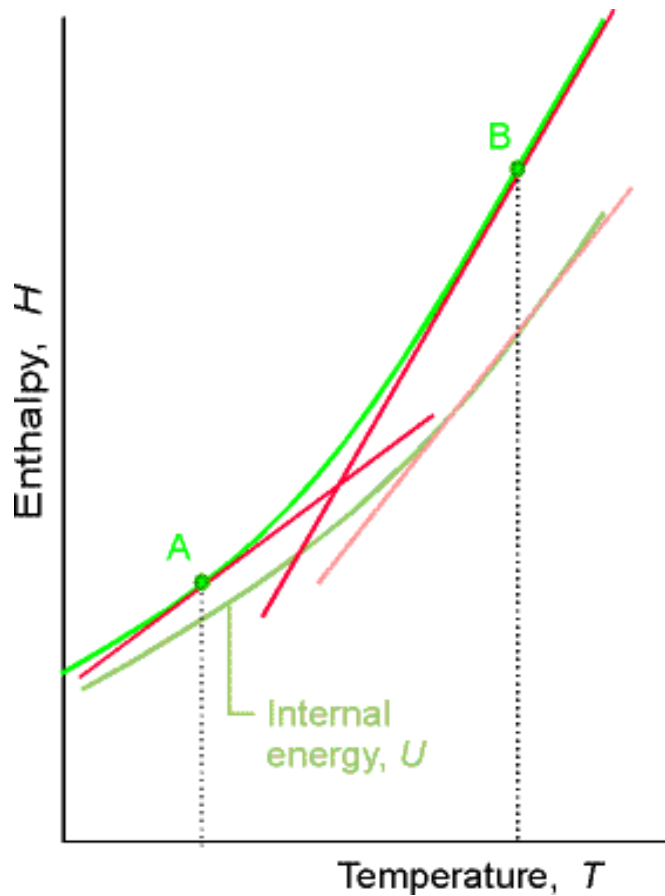
$$dH = dq \text{ (at constant pressure, no additional work)}$$

$$\text{or } \Delta H = q_p$$



2.5 Enthalpy

2). The variation of enthalpy with temperature



The H of a substance increases as its T is raised. The relation between the increase in H and the increase in T depends on the conditions. The most important condition is constant p , and the slope of a graph of H against T at constant p is called the heat capacity at constant p , C_p

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



2.5 Enthalpy

2). The variation of enthalpy with temperature

For infinitesimal changes of temperature:

$$dH = C_p dT \text{ (at constant } p \text{)}$$

If the heat capacity is constant over the range of temperatures of interest:

$$\Delta H = C_p \Delta T \text{ (at constant } p \text{)}$$

$$q_p = C_p \Delta T$$



2.5 Enthalpy

3). The relation between heat capacities

In most cases the heat capacity at constant p of a system is larger than its heat capacity at constant V .

For the two heat capacities of a perfect gas:

$$C_p - C_V = nR$$

$$C_{p,m} - C_{V,m} = R$$



Example - Relating ΔH and ΔU

The internal energy change when 1.0 mol CaCO_3 in the form of calcite converts to aragonite is +0.21 kJ. Calculate the difference between the enthalpy change and the change in internal energy when the pressure is 1.0 bar given that the densities of the solids are 2.71 gcm^{-3} and 2.93 gcm^{-3} , respectively.



Example - Relating ΔH and ΔU

Method: The starting point for the calculation is the relation between the enthalpy of a substance and its internal energy. The difference between the two quantities can be expressed in terms of the pressure and the difference of their molar volumes calculated by $\rho = M/V_m$.



Example - Relating ΔH and ΔU

Answer: The change in enthalpy when the transformation occurs is

$$\begin{aligned}\Delta H &= H(\text{aragonite}) - H(\text{calcite}) \\ &= \{U(\text{a}) + pV(\text{a})\} - \{U(\text{c}) + pV(\text{c})\} \\ &= \Delta U + p\{V(\text{a}) - V(\text{c})\} \\ &= \Delta U + p\Delta V\end{aligned}$$



Example - Relating ΔH and ΔU

For the volume of 1.0 mol CaCO_3 (100 g) and $\rho = M/V_m$:

$$V(\text{a}) = 100(\text{g}) / 2.93(\text{gcm}^{-3}) = 34 \text{ cm}^3$$

$$V(\text{c}) = 100(\text{g}) / 2.71(\text{gcm}^{-3}) = 37 \text{ cm}^3$$

$$\begin{aligned} p\Delta V &= 1.0 \times 10^{-5} \text{ Pa} \times (34 - 37) \times 10^{-6} \text{ m}^3 \\ &= -0.3 \text{ Pam}^3 = -0.3 \text{ J} \end{aligned}$$



$$\Delta H - \Delta U = -0.3 \text{ J}$$



Example - Calculating a change in enthalpy

Water is heated to boiling under a pressure of 1.0 atm. When an electric current of 0.50 A from a 12 V supply is passed for 300 s through a resistance in thermal contact with it, it is found that 0.798 g of water is vaporized. Calculate the molar internal energy and enthalpy changes at the boiling point (373.15 K).



Example - Calculating a change in enthalpy

Method: Because the vaporization occurs at constant pressure, the enthalpy change is equal to the heat supplied by the heater. Therefore, calculate the heat supplied and express that as an enthalpy change; then convert the result to a molar enthalpy change by division by the amount of H_2O molecules vaporized. To convert from enthalpy change to internal energy change, we assume that the vapour is a perfect gas.



Example - Calculating a change in enthalpy

Answer: The enthalpy change is

$$q_p = I \mathcal{V} t = (0.50\text{A}) \times (12\text{V}) \times (300\text{s}) = +1.8\text{J}$$

$$\Delta H = q_p = 1.8\text{J}$$

Because 0.798 g of water is 0.0443 mol H₂O, the enthalpy of vaporization per mole of H₂O is

$$\Delta H_m = q_p = \frac{1.8\text{J}}{0.0443\text{mol}} = +41\text{kJmol}^{-1}$$

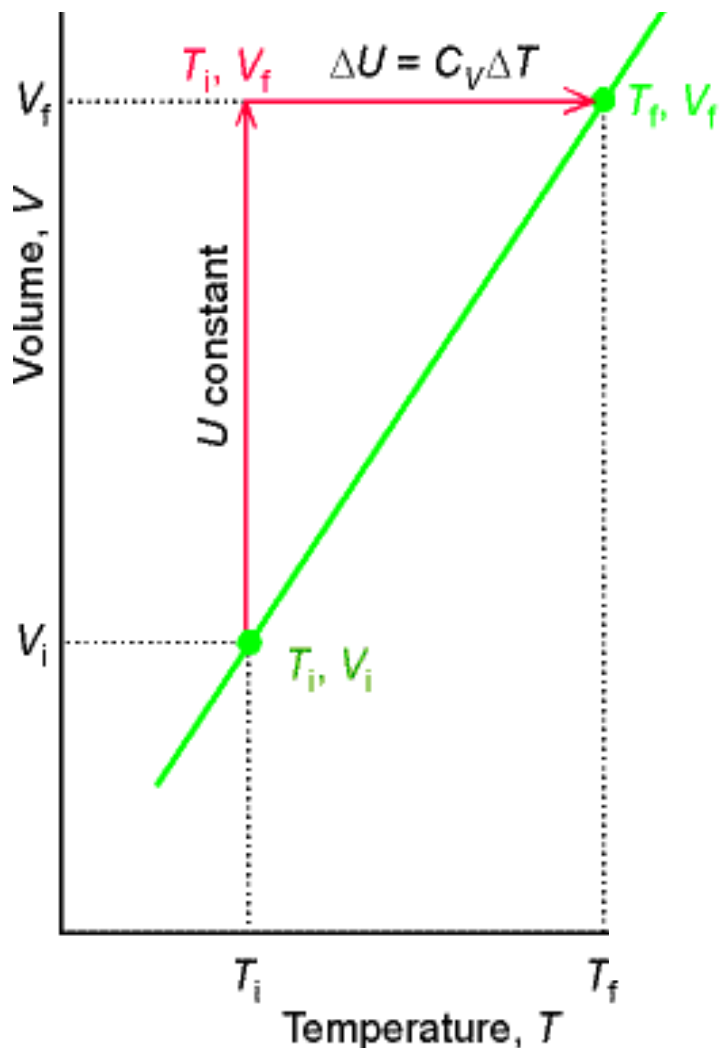
In the process H₂O (l) → H₂O(g) the change in the amount of gas molecules $\Delta n = +1$ mol

$$\Delta U_m = \Delta H_m - RT = +38\text{kJmol}^{-1}$$



2.6 Adiabatic changes

1). The work of adiabatic change



The change in internal energy:

$$\Delta U = C_V (T_f - T_i) = C_V \Delta T$$

For adiabatic expansion

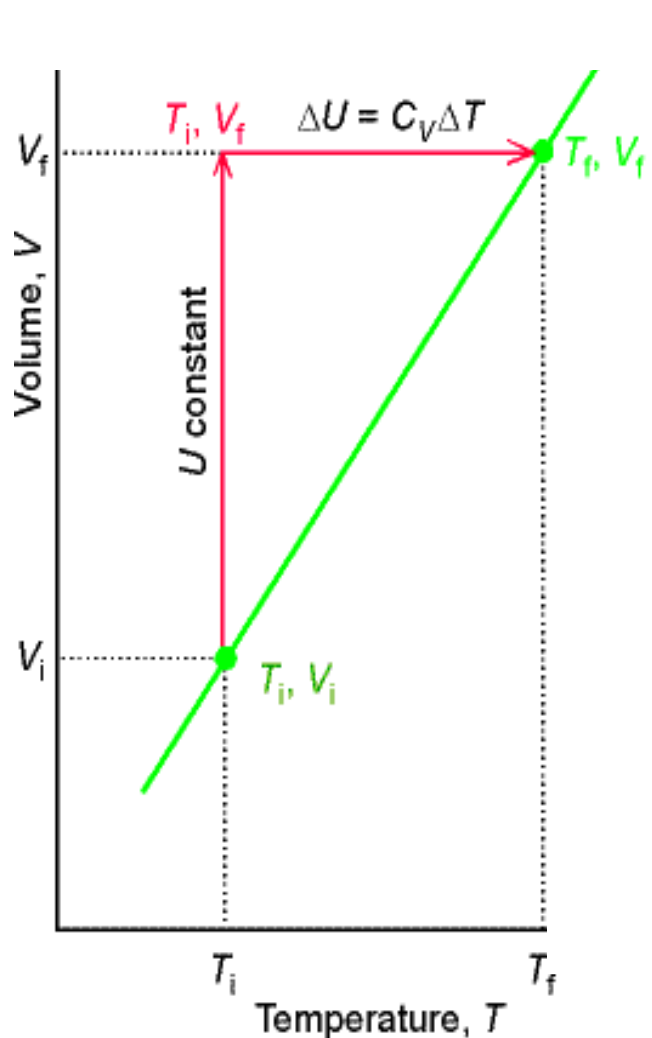
$$q=0, \Rightarrow \Delta U = w_{\text{ad}}$$

$$w_{\text{ad}} = C_V \Delta T$$



2.6 Adiabatic changes

1). The work of adiabatic change



For the reversible:

$$V_f T_f^c = V_i T_i^c, \quad c = \frac{C_{V,m}}{R}$$

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



2.6 Adiabatic changes

2). Heat capacity ratio and adiabats

The change in pressure resulting from an adiabatic, reversible expansion of a perfect gas:

$$pV^\gamma = \text{constant}$$

The heat capacity ratio is defined as:

$$\gamma = \frac{C_{p,m}}{C_{V,m}}$$



2.6 Adiabatic changes

2). Heat capacity ratio and adiabats

Since the heat capacity at constant pressure is greater than the heat capacity at constant volume

$$\gamma > 1$$

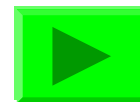
For a perfect gas, it follows that:

$$\gamma = \frac{C_{V,m} + R}{C_{V,m}}$$



Thermochemistry

2.7 Standard enthalpy changes



- 1). The standard enthalpy change
- 2). Enthalpies of physical change
- 3). Enthalpies of chemical change
- 4). Hess's law

2.8 Standard enthalpies of formation

2.9 The T dependence of reaction enthalpies



Thermochemistry

Thermochemistry: a branch of thermodynamics, concentrating on the heat produced or required by chemical reactions.

Process releasing heat-exothermic:

$$\Delta H < 0.$$

Process absorbing heat endothermic:

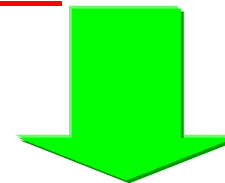
$$\Delta H > 0.$$



2.7 Standard enthalpy changes

1). The standard enthalpy change

The standard enthalpy change, ΔH^\ominus , the change in enthalpy for a process in which the initial and final substances are in their standard states.



The standard state: of the pure form a substance at 1 bar and at a specified temperature.

Conventionally, $T=298.15$ K (25 °C)



2.7 Standard enthalpy changes

2). Enthalpies of physical change

The standard enthalpy of transition, $\Delta_{\text{trs}}H^\ominus$: the standard enthalpy change accompanying a change of physical state.

The standard enthalpy of vaporization - enthalpy change per mole when a pure liquid at 1 bar vaporizes to a gas at 1 bar:



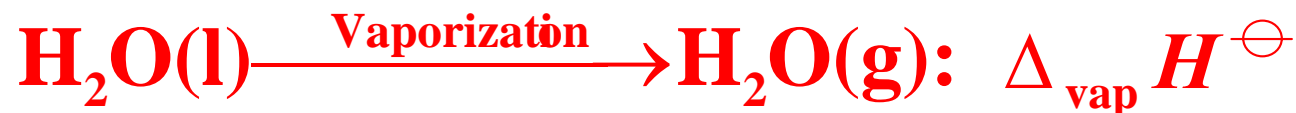
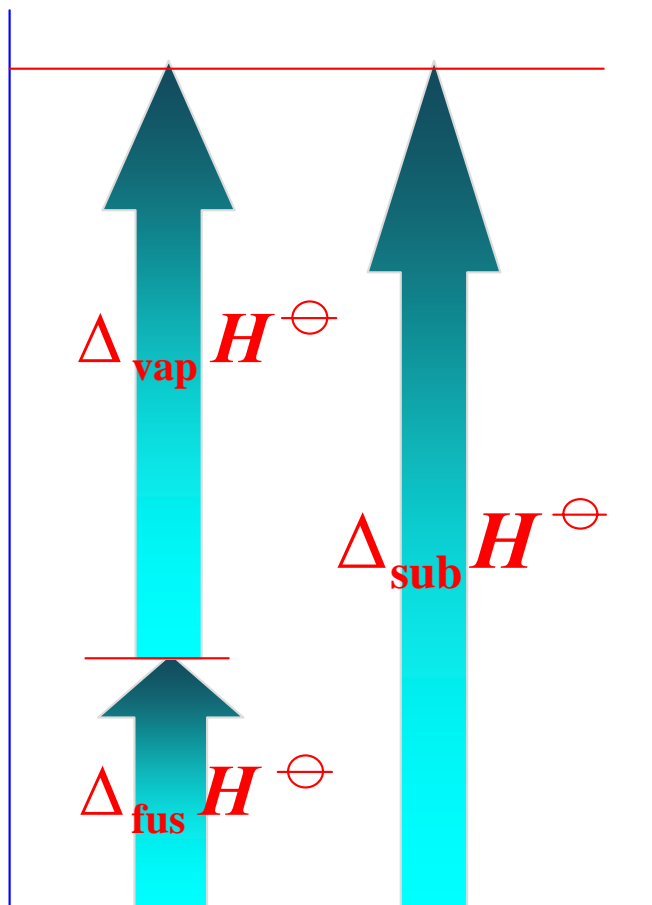
The standard enthalpy of fusion - enthalpy change accompanying the conversion of a solid to a liquid





2.7 Standard enthalpy changes

2). Enthalpies of physical change

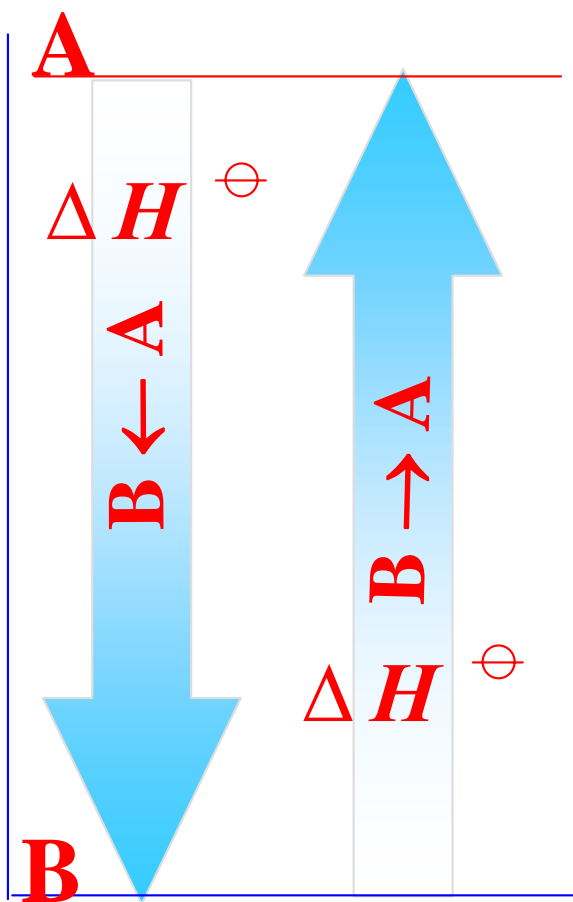


$$\Delta_{\text{sub}} H^{\ominus} = \Delta_{\text{fus}} H^{\ominus} + \Delta_{\text{vap}} H^{\ominus}$$



2.7 Standard enthalpy changes

2). Enthalpies of physical change



$$\Delta H^{\ominus}(\text{A} \rightarrow \text{B}) = -\Delta H^{\ominus}(\text{B} \rightarrow \text{A})$$

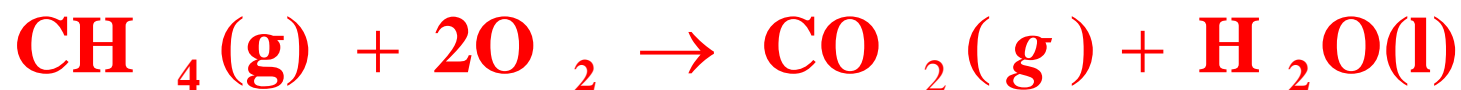


2.7 Standard enthalpy changes

3). Enthalpies of chemical change

The standard reaction enthalpy, $\Delta_r H^\ominus$ the change in enthalpy when reactants in their standard states change to products in their standard states.

e.g.



$$\Delta_r H^\ominus = -890 \text{ kJmol}^{-1}$$



2.7 Standard enthalpy changes

3). Enthalpies of chemical change

The standard enthalpy of combustion, $\Delta_c H^\ominus$ the standard reaction enthalpy for the complete oxidation of an organic compound to CO_2 and H_2O .

e.g.



$$\Delta_c H^\ominus = -2808 \text{ kJmol}^{-1}$$



2.7 Standard enthalpy changes

3). Enthalpies of chemical change

The standard molar enthalpy, H_m^\ominus

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

$$\Delta_r H^\ominus = \sum_J \nu_J H_m^\ominus(\text{J})$$

ν — the stoichiometric coefficients;

$H_m^\ominus(\text{J})$ — the standard molar enthalpy of species **J**



2.7 Standard enthalpy changes

4). 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.



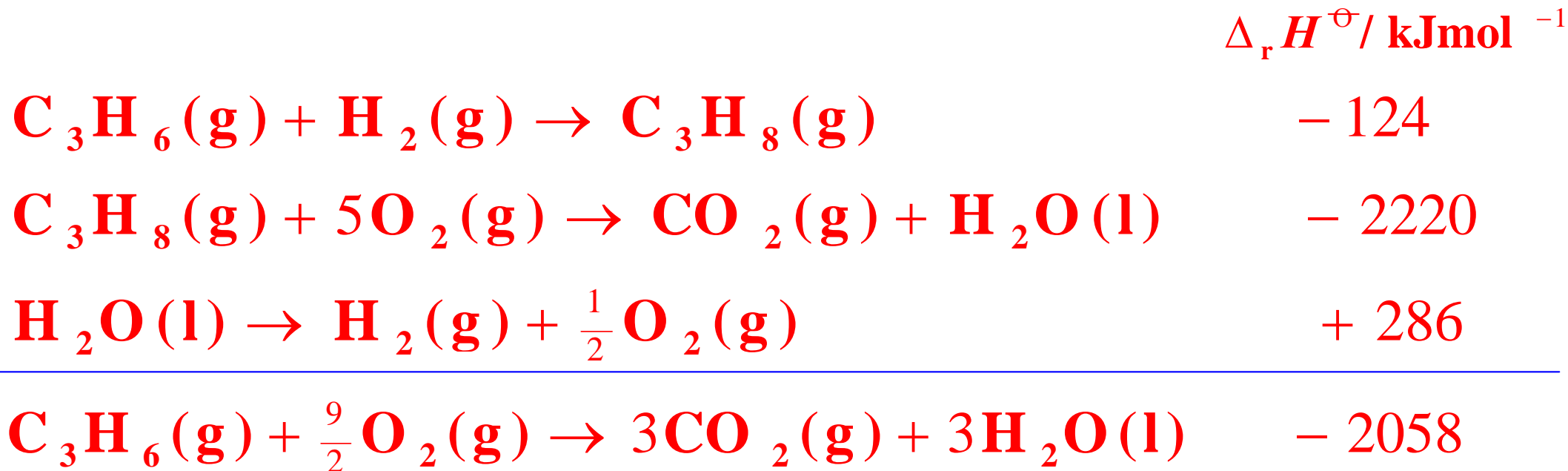
2.7 Standard enthalpy changes

e.g.



Calculate the standard enthalpy of combustion of propane.

This reaction can be recreated from the following sum





2.8 Standard enthalpy of formation

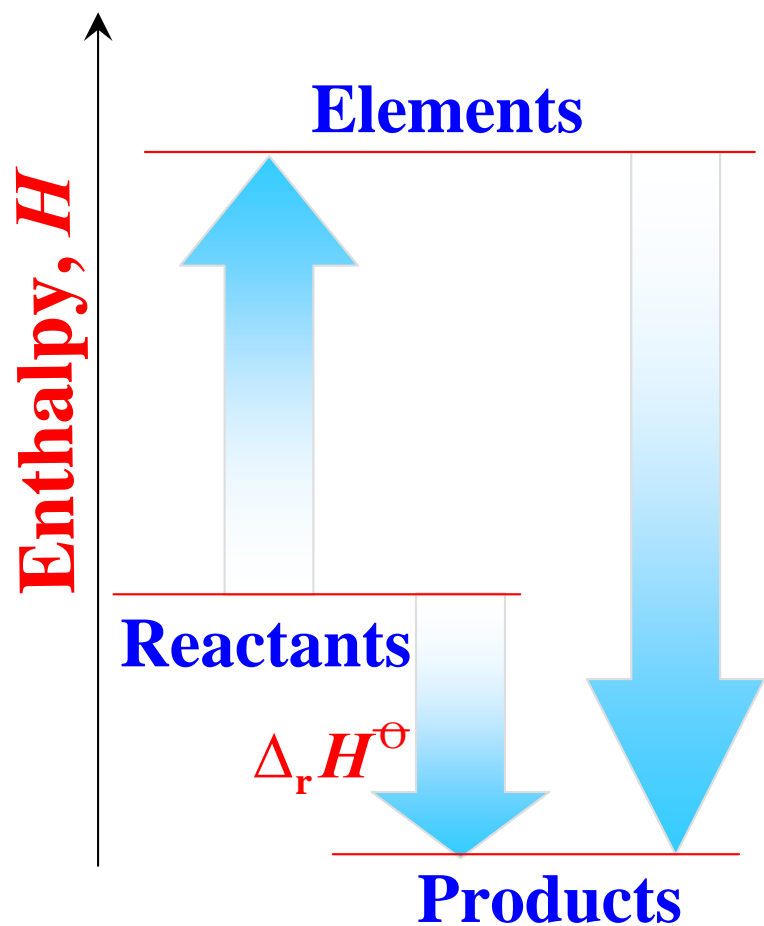
The **standard enthalpy of formation**, $\Delta_f H^\ominus$ **is the standard reaction enthalpy for the formation of the compound from its elements in their reference states.**

The reference state of an element is its most stable state at the specified temperature and 1 bar.



2.8 Standard enthalpy of formation

The reaction enthalpy in terms of enthalpies of formation



$$\Delta_r H^\ominus = \sum_{\text{Products}} \nu H_f^\ominus - \sum_{\text{Reactants}} \nu H_f^\ominus$$

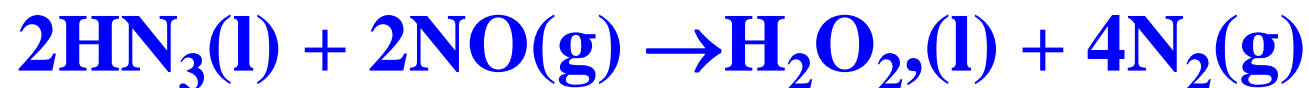
$$\Delta_r H^\ominus = \sum_{\text{J}} \nu_{\text{J}} H_f^\ominus (\text{J})$$



2.8 Standard enthalpy of formation

Illustration

The standard reaction enthalpy of



is calculated as follows:

$$\begin{aligned}\Delta_{\text{r}}H^{\ominus} &= \left\{ H_{\text{f}}^{\ominus}(\text{H}_2\text{O}_2, \text{l}) + 4H_{\text{f}}^{\ominus}(\text{N}_2, \text{g}) \right\} \\ &\quad - \left\{ 2H_{\text{f}}^{\ominus}(\text{HN}_3, \text{l}) + 2H_{\text{f}}^{\ominus}(\text{NO}, \text{g}) \right\} \\ &= \{-187.78 + 4(0)\} - \{2(264.0) + 2(90.25)\} \\ &= -892.3 \text{ kJmol}^{-1}\end{aligned}$$



2.9 The temperature dependence of reaction enthalpies

□ Kirchhoff ' law

The estimation from C_p and $\Delta_r H^\ominus$ at some other T

Standard reaction enthalpies at different T can be estimated from heat capacities and reaction enthalpy at some other T . If a substance is heated from T_1 to T_2 ,

From $dH = C_p dT$ (at constant p)



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

The standard enthalpy changes:

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



2.9 The temperature dependence of reaction enthalpies

□ Kirchhoff ' law

Where $\Delta_r C_p^\ominus$ is the difference of the molar heat capacities of products and reactants under standard conditions weighted by the the stoichiometric coefficients:

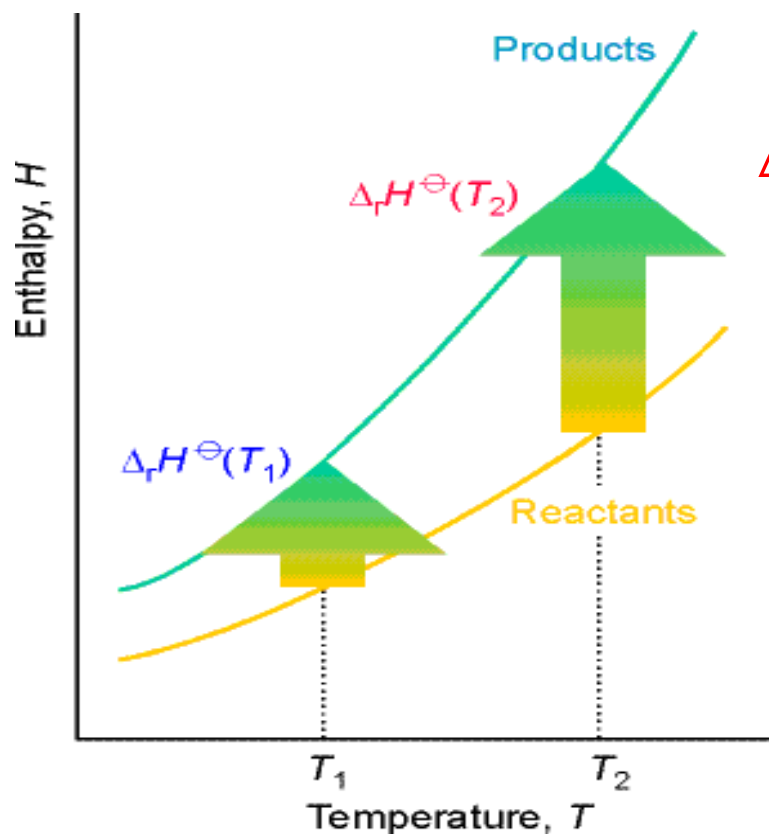
$$\Delta_r C_p^\ominus = \sum_{\text{Products}} \nu C_{p,m}^\ominus - \sum_{\text{Reactants}} \nu C_{p,m}^\ominus$$

More generally,
$$\Delta_r C_p^\ominus = \sum_J \nu_J C_{p,m}^\ominus (J)$$



2.9 The temperature dependence of reaction enthalpies

The change in reaction enthalpy reflects the difference in the changes of the enthalpies.



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

$$\Delta_r C_p^\ominus = \sum_{\text{Products}} \nu C_{p,m}^\ominus - \sum_{\text{Reactants}} \nu C_{p,m}^\ominus$$



Part 1: Equilibrium

1. The properties of gases
2. The First Law: the concepts
3. The First Law: the machinery
4. The Second Law: the concepts
5. The Second Law: the machinery
6. Physical transformations of pure substances
7. Simple mixtures
8. Phase diagrams
9. Chemical equilibrium
10. Electrochemistry