
Energetics

Section 1

Thermodynamics

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Thermodynamics

Energy is one of the most fundamental and universal concepts of physical science, but one that is remarkably difficult to define in way that is meaningful to most people. This perhaps reflects the fact that energy is not a “thing” that exists by itself, but is rather an attribute of matter (and also of electromagnetic radiation) that can manifest itself in different ways. It can be observed and measured only indirectly through its effects on matter that acquires, loses, or possesses it.

1.1 System and Surroundings

The thermodynamic view of the world requires that we be very precise about using certain words. The two most important of these are **system** and **surroundings**. A **thermodynamic system** is that part of the world towards which we are directing our attention. Everything that is not a part of the system constitutes the **surroundings**. The system and surroundings are separated by a **boundary**. If our system is one mole of a gas in a container, then the boundary is simply the inner wall of the container itself. The boundary need not be a physical barrier; for example, if our system is a factory or a forest, then the boundary can be wherever we wish to define it. We can even focus our attention on the dissolved ions in an aqueous solution of a salt, leaving the water molecules as part of the surroundings. The single property that the boundary must have is that it be clearly defined, so we can unambiguously say whether a given part of the world is in our system or in the surroundings.



1.2 Types of System

Open system

A system, which can exchange matter as well as energy with the surroundings, is called an open system. All reactions carried out in open containers are examples of open systems. Evaporation of water in a beaker or hot coffee in a cup represents an open system.

Closed system

A system, which can exchange energy but not mass with the surroundings, is called a closed system. For example, boiling water in a closed steel vessel is an example of a closed system.

Isolated system

A system, which can neither exchange mass nor energy with surroundings, is called an isolated system. They are also called insulated systems. Hot coffee (in contact with its vapour) in a closed and insulated thermos is an example of isolated system. The tea in a closed Thermos bottle approximates an isolated system over a short time interval.

1.3 State of the system

The *properties* of a system are those quantities such as the **pressure, volume, temperature**, and its composition, which are in principle measurable and capable of assuming definite values. There are of course many properties other than those mentioned above; the density and thermal conductivity are two examples. However, the pressure, volume, and temperature have special significance because they determine the values of all the other properties; they are therefore known as **state properties** because if their values are known then the system is in a definite *state*

For instance, in a system consisting of an ideal gas, the state may be defined by only three variables such as temperature (T), pressure (P) and volume (V). The values of other variables such as amount of gas, density, etc. will be definite and can be easily calculated

Change of state

In dealing with thermodynamics, we must be able to define the change in the state of a system when it undergoes some process. This is done by specifying changes in the values of the different state properties using the symbol Δ (*delta*) as illustrated here for a change in the volume:

$$\Delta V = V_{final} - V_{initial}$$

We can compute similar delta-values for changes in P , V , n_i (the number of moles of component i), and the other state properties we will meet later.

1.4 Heat and Work

Heat and work are both measured in energy units, so they must both represent energy. How do they differ from each other, and from just plain “energy” itself?

First, recall that energy can take many forms: mechanical, chemical, electrical, radiation (light), and thermal, or heat. So heat is a form of energy, *but it differs from all the others in one crucial way*. All other forms of energy are inter-convertible: mechanical energy can be completely converted to electrical energy, and the latter can be completely converted to heat (Can you think of a process exemplifying these changes?). However, complete conversion of heat into other forms of energy is impossible.

There is another special property of heat that you already know about: thermal energy can be transferred from one body (i.e., one system) to another. We often refer to this as a “flow” of heat. Moreover, you know that heat can only flow from a system at a higher temperature to one at a lower temperature. This special characteristic is often used to distinguish heat from other modes of transferring energy across the boundaries of a system.

Work, like energy, can take various forms: mechanical, electrical, gravitational, etc. All have in common the fact that they are the product of two factors, an *intensity term* and a *capacity term*. For example, the simplest form of mechanical work arises when an object moves a certain distance against an opposing force. Electrical work is done when a body having a certain charge moves through a potential difference.

Type of work	Intensity factor	Capacity factor	Expression
Mechanical	Force	change in distance	$f\Delta x$
Gravitational	Gravitational potential (a function of height)	mass	mgh
Electrical	Potential difference	quantity of charge	$Q\Delta V$

Performance of work involves a transformation of energy; thus when a book drops to the floor, gravitational work is done (a mass moves through a gravitational potential difference), and the potential energy the book had before it was dropped is converted into kinetic energy which is ultimately dispersed as heat.

Heat and work are best thought of as processes by which energy is exchanged, rather than as energy itself. That is, heat “exists” only when it is flowing, work “exists” only when it is being done.

When two bodies are placed in thermal contact and energy flows from the warmer body to the cooler one, we call the process “heat”. A transfer of energy to or from a system by any means other than heat is called “work”.

1.5 Internal Energy

Every substance possesses a definite quantity of energy, under a given set of factors such as chemical nature of the substance, temperature and pressure. The total energy contained in a system or substance is called its internal energy or intrinsic energy. It is represented by the symbol 'E' or 'U'. Stated differently, it is the sum of different forms of energies found in the components of the system

How can we know how much internal energy a system possesses? The answer is that we cannot, at least not on an absolute basis; all scales of energy are arbitrary. The best we can do is measure changes in energy. However, we are perfectly free to define zero energy as the energy of the system in some arbitrary *reference state*, and then say that the internal energy of the system in any other state is the difference between the energies of the system in these two different states.

You will find out soon that we use the sign ΔU indicating the difference between U_2 and U_1

1.6 First Law of Thermodynamics

This law is one of the most fundamental principles of the physical world. Also known as the *Law of Conservation of Energy*, it states that energy cannot be created or destroyed; it can only be redistributed or changed from one form to another.

A way of expressing this law that is generally more useful in Chemistry is that any change in the internal energy of a system is given by the sum of the heat q that flows across its boundaries and the work w done on the system by the surroundings.

$$\Delta U = \Delta Q + W$$

This says that there are two kinds of processes, heat and work, that can lead to a change in the internal energy of a system. Since both heat and work can be measured and quantified, this is the same as saying that any change in the energy of a system must result in a corresponding change in the energy of the world outside the system- in other words; energy cannot be created or destroyed.

Sign conventions

W is positive, when work is done on the system.

W is negative, when work is done by the system.

Q is positive, when heat is supplied to the system.

Q is negative, when heat is lost by the system.

IMPORTANT: The sign conventions are a little different in Thermodynamics in Physics & Chemistry. Physics deals with force, hence when work ($F \cdot ds$) is done by the system then it is taken as positive, whereas Chemistry deals with Energy, hence, when Heat (Q) is supplied to a system it increases internal energy and is taken as positive

Example A gas is cooled and loses 65 J of heat. The gas contracts as it cools and work done on the system equal to 22 J is exchanged with the surroundings. What are Q , W and ΔE ?

Solution: System loses heat hence, $Q = -65 \text{ J}$

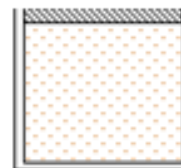
Also gas contracts and work is done on the system, $W = 22 \text{ J}$

$$\Delta E = Q + W = -65 + 22 = -43 \text{ J}$$

Pressure-Volume Work

The kind of work most frequently associated with chemical change occurs when the volume of the system changes owing to the disappearance or formation of gaseous substances. This is sometimes called expansion work or PV -work, and it can most easily be understood by reference to the simplest form of matter we can deal with, the hypothetical *ideal gas*.

The figure shows a quantity of gas confined in a cylinder by means of a massless piston. Let at any instant pressure of the gas is P and piston displaces by a distance dx . Area of the piston is A .



Work done = $F \cdot ds$

$$dw = F \cdot dx = F dx = P A dx = P dV$$

By convention, work done by the system (in this case, the gas) on the surroundings is negative, so the work is given by:

$$dw = -PdV$$

$$\text{or } W = - \int_{V_1}^{V_2} PdV$$

Example 3000 J of heat is given to a gas at constant pressure of $2 \times 10^5 \text{ N/m}^2$. If its volume increases by 10 litres during the process find the change in the internal energy of the gas.

Solution: $\Delta Q = 3000 \text{ J}$

$$W = P\Delta V = (2 \times 10^5 \text{ N/m}^2)(10 \times 10^{-3} \text{ m}^3) = 2 \times 10^3 \text{ J}$$

$$\Delta U = \Delta Q - W = 3000 - 2000 = 1000 \text{ J}.$$

Different processes

1.7 Reversible Process and Irreversible Process

A process which is carried out infinitesimally slowly is called a **reversible process**. At every stage, the system remains in equilibrium. By reversing the conditions, the processes can be reversed. The basic assumption of carrying out a process infinitesimally slowly is that the properties of a system (P, V & T) don't change with during the process.

Under the same assumption, if a process is carried out rapidly, it cannot be reversed and is called **irreversible process**

1.8 Types of Processes

Isobaric (Constant pressure): It is the process in which the pressure of gas remains same at each instant.

Work done in constant pressure process is given as:

$$W = - \int_{V_1}^{V_2} PdV = -P \int_{V_1}^{V_2} dV = -P(V_2 - V_1)$$

From first law: $\Delta U = q - P\Delta V$

Isochoric (Constant volume): Volume of the gas remains constant. So the work done will be zero.

From first law: $\Delta U = q$

Isothermal (constant temperature): In this case temperature of the gas remains same.

Work done in case of ideal gas in isothermal process is:

$$W = - \int_{V_1}^{V_2} PdV = - \int_{V_1}^{V_2} \left(\frac{nRT}{V} \right) dV = -nRT \int_{V_1}^{V_2} \frac{dV}{V} = -nRT \ln \left(\frac{V_2}{V_1} \right) = -nRT \ln \left(\frac{P_1}{P_2} \right)$$

As temperature is constant, we have change in internal energy as **zero**

So from first law: $\Delta U = q - nRT \ln \left(\frac{V_2}{V_1} \right) = 0$ or $q = nRT \ln \left(\frac{V_2}{V_1} \right)$

Adiabatic Process It is the process in which there will be no exchange of heat between system and surroundings. In adiabatic process for an ideal gas, we have $PV^\gamma = K$ (constant)

Work done in case of ideal gas is:

$$\begin{aligned} W &= - \int_{V_1}^{V_2} PdV = - \int_{V_1}^{V_2} \frac{K}{V^\gamma} dV = -K \left[\frac{V^{1-\gamma}}{1-\gamma} \right]_{V_1}^{V_2} = \frac{K}{\gamma-1} \left(\frac{1}{V_2^{\gamma-1}} - \frac{1}{V_1^{\gamma-1}} \right) \\ &= \frac{1}{\gamma-1} \left(\frac{K}{V_2^{\gamma-1}} - \frac{K}{V_1^{\gamma-1}} \right) \\ &= \frac{1}{\gamma-1} (P_2 V_2 - P_1 V_1) = \frac{1}{\gamma-1} (nRT_2 - nRT_1) = \frac{nR\Delta T}{\gamma-1} \end{aligned}$$

Example Calculate the work done (in kilo joule) done during a reaction in which the volume expands from 10 L to 20 L against an external pressure of 5.0 atm.

Solution: Expansion work, $W = -P_{ext} (\Delta V)$

$$W = -5 \times (20 - 10) L atm = -50 L atm = -5.0623 kJ$$

The negative sign indicates that the expanding system loses work energy and does work on the surroundings.

Example A certain volume of dry air at NTP is expanded reversibly to four times its volume (a) isothermally (b) adiabatically. Calculate the final pressure and temperature in each case, assuming ideal behaviour. $\left(\frac{C_p}{C_v} \text{ for air} = 1.4 \right)$

Solution: Let V_1 be the initial volume of dry air at NTP.

(a) Isothermal expansion: During isothermal expansion, the temperature remains the same throughout. Hence, final temperature will be 273 K.

Since $P_1 V_1 = P_2 V_2$

$$P_2 = \frac{P_1 V_1}{V_2} = \frac{1 \times V_1}{4V_1} = 0.25 atm$$

(b) Adiabatic expansion:

$$\frac{T_1}{T_2} = \left(\frac{V_2}{V_1}\right)^{\gamma-1}$$

$$\frac{273}{T_2} = \left(\frac{4V_1}{V_1}\right)^{1.4-1} = 4^{0.4}$$

$$T_2 = \frac{273}{4^{0.4}} = 4^{0.4}$$

Final pressure

$$\frac{P_1}{P_2} = \left(\frac{V_2}{V_1}\right)^{\gamma}$$

$$\frac{1}{P_2} = \left(\frac{4V_1}{V_1}\right)^{1.4} = 4^{1.4}$$

$$P_2 = \frac{1}{4^{1.4}} = 0.143 \text{ atm}$$

Example Calculate the amount of work done by 2 mole of an ideal gas at 298 K in reversible isothermal expansion from 10 litre to 20 litre

Solution: Amount of work done in reversible isothermal expansion

$$w = -2.303nRT \log \frac{V_2}{V_1}$$

Given $n = 2$, $R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$, $T = 298 \text{ K}$, $V_2 = 20 \text{ L}$ and $V_1 = 10 \text{ L}$

Substituting the values in above equation

$$W = -2.303 \times 2 \times 8.314 \times 298 \log \frac{10}{10}$$

$$= -3434.9 \text{ J}$$

i.e., work is done by the system.

1.9 Heat changes at constant pressure: the ENTHALPY

Most chemical processes are accompanied by changes in the volume of the system, and therefore involve both heat and work terms. If the process takes place at a constant pressure, then the work is given by $P\Delta V$ and the change in internal energy will be

$$\Delta U = Q - P\Delta V$$

Thus the amount of heat that passes between the system and the surroundings is given by

$$Q = \Delta U + P\Delta V$$

Since both ΔU and ΔV in above equation are state functions, then Q_p , the heat that is absorbed or released when a process takes place at constant pressure, must also be a state function and is known as the **enthalpy change ΔH** .

$$\Delta H \equiv Q_p = \Delta U + P\Delta V$$

So enthalpy is defined as, $H = U + PV$, another state function.

The difference between ΔH and ΔU is not usually significant for systems consisting of only solids or liquids. Solids and liquids do not suffer any significant volume changes upon heating. The difference, however, becomes significant when gases are involved. Let us consider a reaction involving gases. If V_A is the total volume of the gaseous reactants, V_B is the total volume of the gaseous products, n_A is the number of moles of gaseous reactants and n_B is the number of moles of gaseous products, all at constant pressure and temperature, then using the ideal gas law, we write

$$PV_A = n_A RT \text{ and } PV_B = n_B RT$$

$$\text{or, } p\Delta V = \Delta n_g RT$$

$$\text{or, } \Delta H = \Delta U + \Delta n_g RT$$

Example For the reaction $C(\text{graphite}) + \frac{1}{2} O_2(g) \longrightarrow CO(g)$

At 298 K and 1 atm, $\Delta H = -26.4$ k cal. What is ΔE , if the molar volume of graphite is 0.0053 L? ($R = 0.002$ k cal mol⁻¹ K⁻¹)

Solution: Here $\Delta n_g = 1 - \frac{1}{2} = \frac{1}{2}$

We can neglect molar volume of graphite.

Using $\Delta H = \Delta E + \Delta n_g RT$

$$\Delta E = -26.4 - \frac{1}{2} \times 0.002 \times 298 = -26.7 \text{ k cal}$$

1.10 The Heat Capacity

For systems in which no change in composition (chemical reaction) occurs, things are even simpler: to a very good approximation, the enthalpy depends only on the temperature. This means that the temperature of such a system can serve as a direct measure of its enthalpy. The functional relation between the internal energy and the temperature is given by the *heat capacity* measured at constant pressure:

$$C_p = \frac{dH}{dT}$$

(or $\Delta H/\Delta T$ if you don't care for calculus!)

An analogous quantity relates the heat capacity at constant *volume* to the internal energy:

$$C_v = \frac{dU}{dT}$$

The difference between C_p and C_v is of importance only when the **volume** of the system changes significantly— that is, when different numbers of moles of gases appear on either side of the chemical equation. For reactions involving only liquids and solids, C_p and C_v are for all practical purposes identical.

Heat capacity can be expressed in joules or calories per mole per degree (molar heat capacity), or in joules or calories per gram per degree; the latter is called the *specific heat capacity* or just the *specific heat*

Example For Ag, \bar{C}_p ($\text{JK}^{-1}\text{mol}^{-1}$) is given by $23.43 + 0.00628T$. calculate ΔH if 3 mol of silver are raised from 25°C to its melting point 961°C under 1 atm pressure.

Solution: At constant P for 1 mole,

$$\Delta H = \int_{T_1}^{T_2} \bar{C}_p dT = \int_{T_1}^{T_2} (23.43 + 0.00628T) dT$$

$$\Delta H = 23.43(T_2 - T_1) + \frac{1}{2}(0.00628)(T_2^2 - T_1^2) \text{Jmol}^{-1}$$

$$\text{Since, } T_1 = 273.15 + 25 = 298.15\text{K and } T_2 = 273.15 + 961 = 1234.15\text{K}$$

$$T_2 - T_1 = 936\text{K}$$

$$\begin{aligned} \Delta H &= 23.43(936) + \frac{1}{2}(0.00628)[(1234.15)^2 - (298.15)^2] = 21930 + 4500 \\ &= 26430 \text{ J/mol} \end{aligned}$$

$$\text{For 3 mol, } \Delta H = 3(26430)\text{J} = 79290 \text{ J}$$

1.11 Extensive and Intensive Properties

In thermodynamics, a distinction is made between extensive properties and intensive properties. An extensive property is a property whose value depends on the quantity or size of matter present in the system. For example, mass, volume, internal energy, enthalpy, heat capacity, etc are extensive properties.

Those properties which do not depend on the quantity or size of matter present are known as intensive properties. For example temperature, density, pressure etc are intensive properties

Relationship between C_p and C_v for an ideal gas

We have $H = U + PV = U + RT$ (for one mole of a gas)

Differentiating it, $\frac{dH}{dt} = \frac{dU}{dt} + R$

Or $C_p = C_v + R$

Example 1 mol of CO_2 gas at 300 K is expanded under adiabatic condition such that its volume becomes 27 times.

(a) What is final temperature? b) What is work done?

$\gamma = 1.33$ and $C_v = 6 \text{ cal mol}^{-1}$ for CO_2

Solution: For adiabatic condition $T_2/T_1 = (V_1/V_2)^{\gamma-1}$

$$T_2 = (1/27)^{1.33-1} \times 300 = 100 \text{ K}$$

Thus, $T_2 < T_1$, hence cooling takes place due to the expansion under adiabatic condition .

(a) $\Delta E = q + w$

$q = 0$ (for adiabatic condition)

$$\Delta E = w$$

Work is done at the cost of internal energy ;if gas expands , we have negative sign hence internal energy decreases .

$$w = -\Delta E = -C_v (T_2 - T_1) = -6 \times (100 - 300) = 1200 \text{ cal}$$

Example 1 m^3 of neon gas ($C_v = \frac{3}{2}R$) at 273.2 K and 10 atm undergoes three different expansions to a final pressure of 1 atm. Calculate the final volume and the work done in three different expansions.

(a) Isothermal reversible expansion,

(b) Adiabatic reversible expansion and

(c) Irreversible adiabatic expansion.

Solution:

$$(a) \text{ Final volume, } V_2 = \frac{P_1 V_1}{P_2} = \frac{(1)(10)}{(1)} = 10 \text{ m}^3$$

The work done by the gas in expanding equals the heat absorbed by the gas from its surroundings.

$$\therefore -w = q = nRT \ln \frac{V_2}{V_1}; \text{ since } n = \frac{PV}{RT}$$

$$n = \frac{10 \times 10^3}{0.0821 \times 273.2} = 446.1 \text{ mol}$$

$$-w = (446.1)(8.314)(273.2)(2.303) \log_{10} 10 = 2333.5 \text{ kJ}$$

(b) For adiabatic reversible expansion,

$$V_2 = \left(\frac{P_1}{P_2}\right)^{\frac{1}{\gamma}} \cdot V_1$$

$$\gamma = \frac{C_p}{C_v} = \frac{\frac{3}{2}R + R}{\frac{3}{2}R} = \frac{5}{3}$$

$$\therefore V_2 = (10)^{3/5} (1) = 3.9813^3$$

The final temperature is obtained from

$$P_2 V_2 = nRT_2$$

$$T_2 = \frac{P_2 V_2}{nR} = \frac{(1)(3.981 \times 10^3)}{(446.1)0.821} \\ = 108.8K$$

For an adiabatic process, $q = 0$ & $\Delta E = w$.

Also, since C_V is constant

$$w = nC_V(T_2 - T_1) = \left(n \frac{3}{2} R\right) (T_2 - T_1) \\ = (446.1) \left(\frac{3}{2} R\right) (108.8 - 273.2) = -914.1 \text{ kJ}$$

(c) For irreversible adiabatic expansion,

Form equation (xvi), we have

$$-C_V(T_2 - T_1) = nR P_2 \left(\frac{T_2}{P_2} - \frac{T_1}{P_1}\right) \\ -\frac{3}{2}(T_2 - 273.2) = nR (1) \left(\frac{T_2}{1} - \frac{273.2}{10}\right) \\ \therefore T_2 = 174.8K \\ \therefore \Delta E = w = \frac{3}{2} nR (174.8 - 273.2) = -547.4 \text{ kJ}$$

Note that there is considerably less cooling of the gas and less work is done by the gas in the irreversible adiabatic expansion than in the reversible adiabatic expansion.

Example A sample of argon gas at 1 atm pressure and 27°C expands reversibly and adiabatically from 1.25 dm³ to 2.50 dm³. calculate the enthalpy change in this process, $C_{v,m}$ for argon is 12.48 J K⁻¹ mol⁻¹.

Solution:

For a reversible expansion of an ideal gas, we have:

$$T_2 V_2^{\gamma-1} = T_1 V_1^{\gamma-1} \text{ where } \gamma = \frac{C_{p,m}}{C_{v,m}}$$

For a monoatomic gas (assumed to be ideal)

$$\gamma = \frac{C_{p,m}}{C_{v,m}} = \frac{C_{v,m} + R}{C_{v,m}} = 1 + \frac{R}{C_{v,m}} = 1 + \frac{8.314}{12.48} = 1.662$$

$$\text{Hence, } T_2 = \left(\frac{V_1}{V_2}\right)^{\gamma-1} T_1 = \left(\frac{1.25}{2.50}\right)^{0.6662} (300 \text{ K}) = 189.0 \text{ K.}$$

The enthalpy change in the given process would be $\Delta H = n C_{p,m} \Delta T$

$$\text{where } n = \frac{pV}{RT} = \frac{(101.325 \text{ kPa})(1.25 \text{ dm}^3)}{(8.314 \text{ J K mol}^{-1})(300 \text{ K})} = 0.0508 \text{ mol}$$

$$C_{p,m} = C_{v,m} + R = (12.48 + 8.314) \text{ J K}^{-1} \text{ mol}^{-1} = 20.794 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$\Delta T = T_f - T_1 = (189.0 - 300) \text{ K} = -111 \text{ K}$$

$$\text{Hence, } \Delta H = n C_{p,m} \Delta T = (0.0508 \text{ mol})(20.794 \text{ J K}^{-1} \text{ mol}^{-1})(-111 \text{ K})$$

$$= -117.25 \text{ J}$$

Example Five mol of an ideal gas at 293 K are expanded thermally from an initial pressure 0.4 kPa to a final pressure of 0.1 kPa against an external pressure of 0.1 kPa.

(a) Calculate the $Q, w, \Delta E$ and ΔH .

(b) Calculate the corresponding value of $Q, W, \Delta E$ and ΔH if the above process is carried out reversibly.

Solution:

(a) For an isothermal expansion against a constant, pressure we have

$$\begin{aligned} W &= P_{ext}(V_2 - V_1) \\ &= -P_{ext} \left(\frac{nRT}{P_2} - \frac{nRT}{P_1} \right) = -P_{ext} \left(\frac{1}{P_1} - \frac{1}{P_2} \right) = -9135 \text{ J} \end{aligned}$$

Since temperature is constant.

$$\Delta E = 0, \Delta H = 0, q = -W = 9135 \text{ J}$$

(b) For isothermal reversible expansion:

$$-W = 2.303 nRT \log \frac{P_1}{P_2} = 2.0303 \times 5 \times 8.314 \times 293 \log \frac{0.4}{0.1}$$

$$\Rightarrow W = -16888 \text{ J}$$

$$\Delta E = \Delta H = 0, q = -W = 16888 \text{ J}$$

Example 0.4 mol of mono-atomic gas fills a 1 dm³ container to a pressure of 10.0 kPa. It is expanded reversibly and adiabatically until a pressure of 0.1 kPa. What are final volume and temperature? What is the work done in expansion?

Solution:

Since mono-atomic gas is being expanded adiabatically

$$\Rightarrow P_1 V_1^\gamma = P_2 V_2^\gamma \left[\gamma = \frac{5}{3} \text{ for monoatomic gas} \right]$$

$$\Rightarrow (V_2)^{5/3} = \frac{P_1 V_1^y}{P_2} = \frac{1.0 \times (1)^{5/3}}{0.1} = 10$$

$$\Rightarrow V_2 = 3.98 \text{ dm}^3.$$

Also $P_2 V_2 = nR T_2$

$$\Rightarrow T_2 = \frac{P_2 V_2}{nR} = \frac{0.1 \times 3.98}{0.4 \times 8.314} = 0.12 \text{ K}$$

The work done during expansion under adiabatic condition:

$$W = \frac{-(P_1 V_1 - P_2 V_2)}{(\gamma - 1)} = \frac{-1(1 \times 1 - 3.98)}{(5/3 - 1)}$$

$$= -0.903 \text{ kPa dm}^3 \quad [\because 1 \text{ kPa} = 10^3 \text{ Pa}, 1 \text{ dm}^3 = 10^{-3} \text{ m}^3, \text{ Pa} = \text{N/m}^2].$$

$$= -903 \text{ J}$$

Example The heat of formation of methane at 25° and at constant pressure is -17.9

kcal. Calculate its heat of formation at constant volume

Solution: $C(s) + 2H_2(g) \rightarrow CH_4(g)$

$$\Delta H = -17.9 \text{ kcal } 25^\circ \text{ C}$$

$$\Delta H = \Delta E + \Delta nRT$$

$$\Delta n = -1$$

$$R = 2 \text{ cal} = 2 \times 10^{-3} \text{ kcal}$$

$$T = 298$$

$$\Delta E = -17.149 \text{ kcal}$$

Section 2

Thermochemistry

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Thermochemistry

2.1 Enthalpy Changes

In Thermochemistry, all substances are said to possess a heat content or enthalpy, H . For a reaction carried out at constant pressure (usually at atmospheric pressure in an open container), and if no other work is involved, the heat absorbed or evolved is called the enthalpy change.

The enthalpy change of reaction is the heat exchange (either absorption or release) with the surroundings at constant pressure before and after the reaction.

$$\Delta H = (\text{sum of enthalpies of products}) - (\text{sum of enthalpies of reactants})$$

$$\Delta H = H_p (\text{enthalpy of products}) - H_r (\text{enthalpy of reactants})$$

2.2 Endothermic and Exothermic Reactions

With respect to enthalpy change, reactions can be classified into exothermic and endothermic reactions.

Exothermic reactions are reactions in which the energy required to break the bonds in the reactants is smaller than the energy liberated in forming the bonds in the products. They give out heat to the surroundings.

For an exothermic reaction (heat given out to the surroundings), ΔH is negative.

Endothermic reactions are reactions in which the energy required to break the bonds in the reactants is greater than the energy liberated in forming the bonds in the products. They absorb heat to the surroundings.

For an endothermic reaction (heat absorbed from the surroundings), ΔH is positive.

Average Bond Enthalpy values can be used to calculate the enthalpy change in a reaction.

Enthalpy Change in Reaction = Sum of Bond Enthalpies of Reactants – Sum of Bond Enthalpies of Products

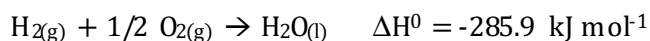
2.3 Standard Enthalpy Change

Standard Enthalpy Change for a reaction, symbolized as ΔH°_{298} , is defined as: The enthalpy change when the molar quantities of reactants shown in a balanced chemical equation completely react to form products under standard conditions.

Standard conditions are as follows:

- a pressure of 1 atmosphere
- a temperature of 298 K
- if solution is used, 1M is specified.
- Elements or compounds in their normal stable state

Example: For the following reaction,



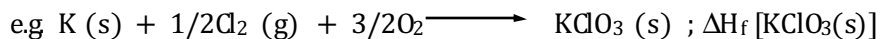
Example For the reaction $\text{H}_2(\text{g}) + 1/2 \text{O}_2(\text{g}) \longrightarrow \text{H}_2\text{O}(\text{l})$; $\Delta H^{\circ} = -68 \text{ kcal}$ at 298 K

What is standard enthalpy of $\text{H}_2\text{O}(\text{l})$?

Solution: $\Delta H^{\circ} = H_p - H_R = H_{\text{H}_2\text{O}}^{\circ} - \left[H_{\text{H}_2}^{\circ} + \frac{1}{2} H_{\text{O}_2}^{\circ} \right]$
 $\Rightarrow H_{\text{H}_2\text{O}}^{\circ} = -68 \text{ kcal mol}^{-1}$

2.4 Standard enthalpy change of Formation ΔH_f°

The heat change when 1 mole of a pure substance in the specified state is formed from its elements in their standard states at 1 atm and 298K.



- ✓ The standard state of a substance is its most stable form at 1 atm and 298K.
- ✓ The more negative the value of ΔH_f , the more stable the substance is compared to its constituent elements from which it is formed.

2.5 Standard enthalpy change of Combustion ΔH_c°

The heat change when 1 mole of the substance is completely burnt in oxygen under standard conditions.



∴ ΔH_c is always negative - heat is evolved.

∴ Complete combustion: C must burn to give CO_2 , not CO. S must burn to give SO_3 .

Example $\Delta H_{\text{combustion}}^0 (\text{CH}_4, \text{g}) = -890.36 \text{ kJ/mol}; H_f^0 (\text{CO}_2, \text{g}) = -393.51 \text{ KJ/mol};$

$$H_f^0 (\text{H}_2\text{O}, \text{l}) = -285.83 \text{ kJ/mol};$$

$$H_f^0 (\text{CH}_4, \text{g}) = ?$$

Solution: $\text{CH}_4 (\text{g}) + 2\text{O}_2 (\text{g}) \rightarrow \text{CO}_2 (\text{g}) + 2\text{H}_2\text{O} (\text{l})$

$$\Delta H_{\text{combustion}}^0 = H^0 (\text{CO}_2, \text{g}) + 2H^0 (\text{H}_2\text{O}, \text{l}) - H^0 (\text{CH}_4, \text{g})$$

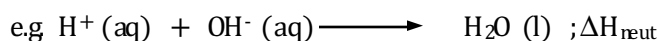
$$\therefore H^0 (\text{CH}_4, \text{g}) = H^0 (\text{CO}_2, \text{g}) + 2H^0 (\text{H}_2\text{O}, \text{l}) - \Delta H_{\text{combustion}}^0$$

$$= -393.51 + 2(-285.83) - (-890.36) = -965.17 + 890.36 = -74.81 \text{ KJ/mol}$$

Later in this lesson using Hess's law we shall find heat of reaction as given below Heat of reaction = \sum Heat of combustion of reactants - \sum Heat of combustion of products.

2.6 Standard enthalpy change of Neutralisation $\Delta H_{\text{neut}}^\theta$

The heat change when an amount of acid or alkali is neutralised to form 1 mole of water under standard conditions.



∴ For reaction involving weak acid and/or weak base - value is less negative because energy is needed to ionise weak acid/base.

Example 150 ml of 0.5 N nitric acid solution at 25.35°C was mixed with 150 ml of 0.5 N sodium hydroxide solution at the same temperature. The final temperature was recorded to be 28.77°C . Calculate the heat of neutralization of nitric acid with sodium hydroxide

Solution: Total mass of solution $150 + 150 = 300$ gram

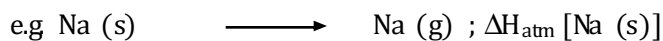
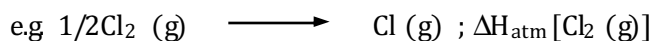
$$Q = 300 \times (28.77 - 25.35) = 300 \times 3.42 = 1026 \text{ cal}$$

$$\therefore \text{heat of neutralization} = \frac{Q}{150} \times 1000 \times \frac{1}{0.5} = \frac{1026}{150} \times 1000 \times \frac{1}{0.5} = 13.68 \text{ kcal}$$

Since, the enthalpy of neutralization is always -ve, so heat of neutralization = -13.68 kcal

2.7 Standard enthalpy change of Atomization $\Delta H_{\text{atm}}^\ominus$

The heat change involved when 1 mole of the gaseous atoms is formed from the element in the standard state under standard conditions.

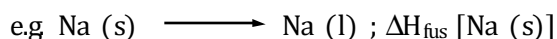


∴ ΔH_{atm} is always positive – heat is absorbed to overcome bonds in the substance. The higher the ΔH_{atm} , the stronger the bond.

∴ Note: For liquids and solids, atomisation includes enthalpies of fusion and vaporisation.

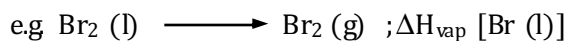
2.8 Molar enthalpy change of Fusion $\Delta H_{\text{fus}}^\ominus$

The energy change when 1 mole of the solid is converted into liquid at its melting point and at 1 atm.



2.9 Molar enthalpy change of Vaporization $\Delta H_{\text{vap}}^\ominus$

The energy change when 1 mole of the liquid is converted into gas at its boiling point and at 1 atm.



∴ ΔH_{fus} and ΔH_{vap} are always positive – heat is absorbed to overcome bonds between the particles (ions, molecules, atoms etc.) in the solid.

2.10 Lattice Energy

The heat change when 1 mole of pure solid ionic compound is formed from its constituent gaseous ions under standard conditions.



∴ L.E. is always negative – because ionic bonds are formed from the attraction of the oppositely charged gaseous ions. The larger the L.E., the stronger the ionic bond.

∴
$$\text{L.E.} \propto \frac{Z_+Z_-}{r_+ + r_-}$$

Example Calculate the lattice energy for the reaction, $Li^+(g) + Cl^-(g) \rightarrow LiCl(s)$ from the following data.

$$\Delta H_{sub}(Li) = 160.67 \text{ kJ mol}^{-1}; \frac{1}{2}D(Cl_2) = 122.17 \text{ kJ mol}^{-1}; I.P.(Li) = 520.07 \text{ kJ mol}^{-1};$$

$$E.A.(Cl) = -365.26 \text{ kJ mol}^{-1} \text{ and } \Delta H_f^0(LiCl) = -401.66 \text{ kJ mol}^{-1}.$$

Solution: Applying the equation (xix),

$$-Q = \Delta H_{sub} + \frac{1}{2}D + I.P. - E.A. - U$$

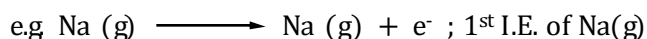
And substituting the respective value gives

$$-401.66 = 160.67 + 122.17 + 520.07 - 365.26 - U$$

$$\therefore U = 839.31 \text{ kJ mol}^{-1}$$

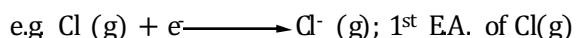
2.11 First Ionisation Energy 1st I.E.

The energy change to remove 1 mole of electrons from 1 mole of gaseous atoms (X) to form 1 mole of gaseous ions (X⁺).



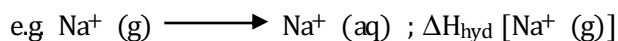
2.12 First Electron Affinity 1st E.A.

The energy change to add 1 mole of electrons to 1 mole of gaseous atoms (X) to form 1 mole of gaseous ions (X⁻).



2.13 Standard Enthalpy of Hydration ΔH_{hyd}^{\ominus}

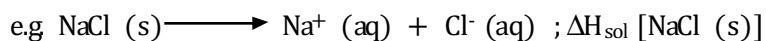
The heat change when 1 mole of the gaseous ion is hydrated under standard conditions.



∴ ΔH_{hyd} is always negative – heat is evolved as ion-solvent bonds are formed between the solute (ion) and the solvent particles.

2.14 Standard Enthalpy of Solution $\Delta H_{\text{sol}}^\ominus$

The heat change when 1 mole of the solute is completely dissolved in enough solvent so that no further heat change takes place on adding more solvent (i.e. infinite dilution) under standard conditions.



∴ When ionic solids dissolve in water, heat is either evolved or absorbed. The process of solution involves:

- 1) an input of energy to overcome the electrostatic forces holding the ions in the lattice. This involves bond-breaking.

Energy required = L.E.

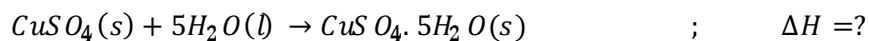
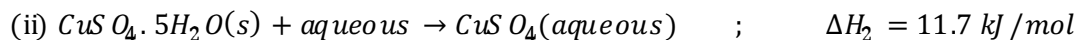
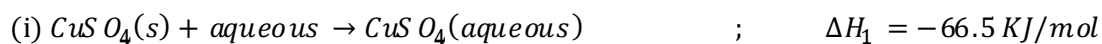
- 2) an output of energy as ion-solvent bonds are formed between the solute (ion) and the solvent particles.

Energy = $\Delta H_{\text{hyd}}(\text{cation}) + \Delta H_{\text{hyd}}(\text{anion})$

$$\therefore \Delta H_{\text{sol}} = -\text{L.E.} + [\Delta H_{\text{hyd}}(\text{cation}) + \Delta H_{\text{hyd}}(\text{anion})]$$

Example The enthalpies of solution of anhydrous CuSO_4 and hydrated $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ are -66.5 and 11.7 kJ mol^{-1} respectively. Calculate the enthalpy of hydration of CuSO_4 to $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$.

Solution: Given that



$$\Delta H = \Delta H_1 - \Delta H_2 = -66.5 - 11.7 = -78.2 \text{ kJ}$$

2.15 Bond Energy (BE)

The bond energy of X-Y bond is the average energy absorbed when 1 mole of X-Y bonds are broken.

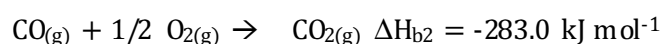
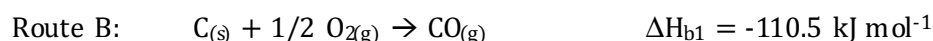
The stronger the bond, the higher the bond energy.

2.16 Hess's Law

The total enthalpy change accompanying a chemical change is independent of the route by which the chemical change takes place. Therefore, the overall change in enthalpy is the same, whichever route is followed.

Example:

The enthalpy change for the oxidation of carbon (graphite) to carbon dioxide is the same whether it is carried out Route A (1 stage) or Route B (2 stages)



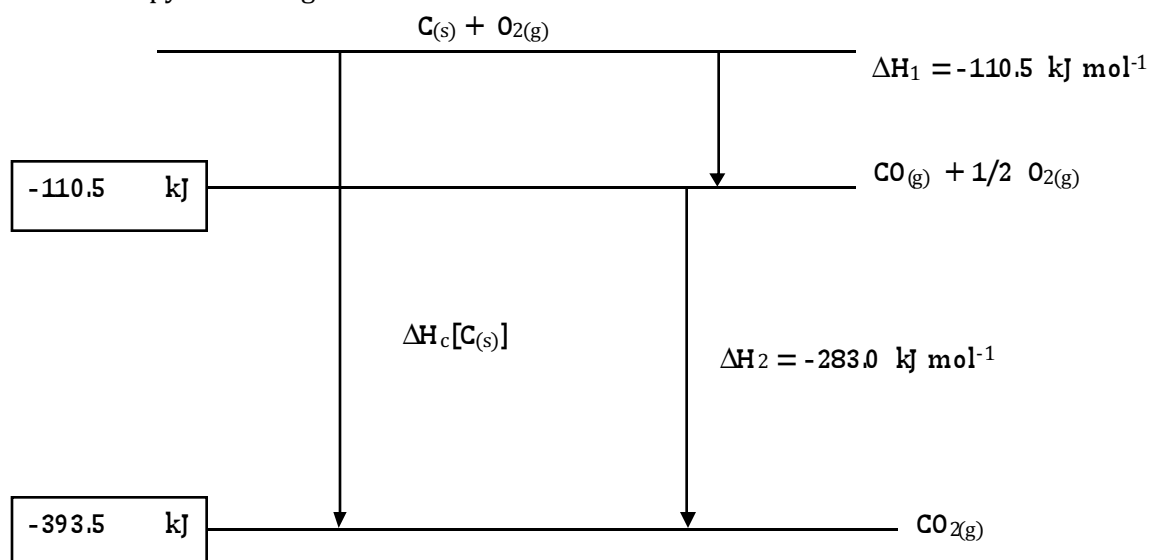
$$\Delta H_{b1} + \Delta H_{b2} = (-110.5) + (-283.0) = -393.5 \text{ kJ mol}^{-1}$$

2.17 Enthalpy Level Diagram and Enthalpy Cycle

The enthalpy change of a reaction can be represented by an enthalpy level diagram or enthalpy cycle.

Enthalpy Level Diagram

The enthalpy level diagram for the oxidation of carbon is shown below:



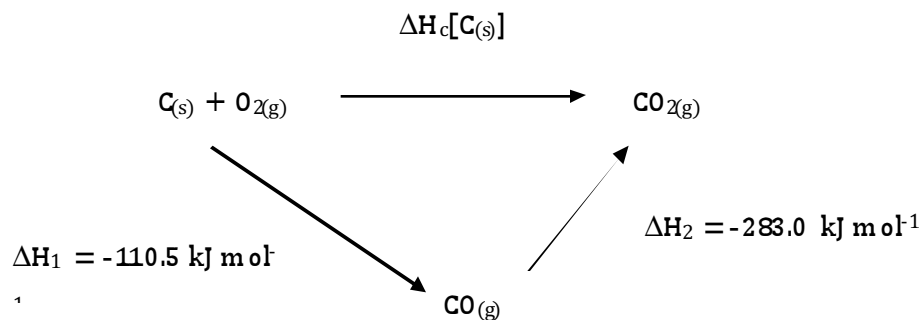
Note: On drawing an enthalpy diagram.

1. Draw a line at 0 to represent the enthalpy level of elements.

2. Draw a line above or below this zero line to represent the enthalpy level of reactants.
3. Draw another line to represent the enthalpy level of intermediate products.
4. Draw another line to represent the enthalpy level of final products.

Enthalpy Cycle (Born-Haber Cycle)

The enthalpy cycle for the oxidation of carbon is shown below:



Note: On drawing the enthalpy cycle (Born-Haber cycle)

1. Relate the various equations involved in a reaction.
2. Write the equations in the form of a cycle and check if the cycle can 'flow' in one direction.

The required enthalpy change can be found by following the path

Reactants \longrightarrow intermediate products \longrightarrow Final products

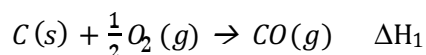
and doing simple arithmetic calculation.

The Use of Hess's Law in determining Enthalpy Changes

Some reactions proceed very slowly or involve formation of side products. Hess's Law can be used to determine the enthalpy changes of such reactions which cannot be determined directly by calorimetry experiments.

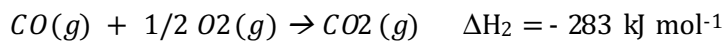
Example 1:

It is difficult to determine the enthalpy change for

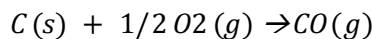


because some graphite may oxidized completely to $\text{CO}_{2(g)}$

This enthalpy change should be determined indirectly by calorimetry experiments using Hess's Law. Since



These two values can be determined relatively easily in calorimetry experiments. The enthalpy change for

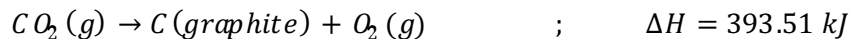
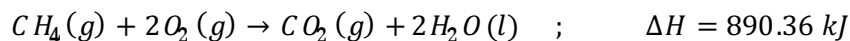


ΔH_1 can be determined indirectly from these two values, using Hess's Law

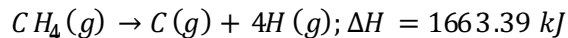
$$\Delta H_{\text{comb.}} [C(s)] = \Delta H_1 + \Delta H_2$$

$$\Delta H_1 = \Delta H_{\text{comb.}} [C(s)] - \Delta H_2 = (-393.5) - (-283) = -110.5 \text{ kJ mol}^{-1}$$

Example Calculate bond energy of C - H bond from the following data

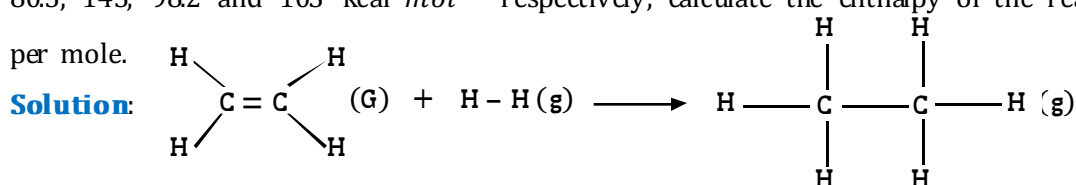


Solution: Adding all the equations, we get



$$\therefore \text{B. E. of C - H bond} = \frac{1663.39}{4} = 415.85 \text{ kJ mol}^{-1}$$

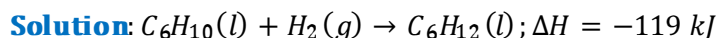
Example Given that the average bond energies of C - C, C = C, C - H and H - H bonds are 80.5, 145, 98.2 and 103 kcal mol⁻¹ respectively, calculate the enthalpy of the reaction per mole.



$$\Delta H_{\text{reaction}} = (\epsilon_{\text{H-H}} + \epsilon_{\text{C=C}}) - (2\epsilon_{\text{C-H}} + \epsilon_{\text{C-C}})$$

$$\Delta H_{\text{reaction}} = (103 + 145) - (196.4 + 80.5) = 248 - 276.9 = -28.9 \text{ kcal/mol}$$

Example The standard molar enthalpies of formation of cyclohexane (l) and benzene (l) at 25°C are -156 and 49 kJ mol⁻¹ respectively. The standard enthalpy of hydrogenation of cyclohexene (l) at 25°C is -119 kJ mol⁻¹. Use these data to estimate the magnitude of resonance energy of benzene.



(This involves breaking up of double bonds and addition of three H₂ molecules.)

Enthalpy change of equation (i) can be given as

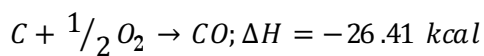
$$\Delta H = -357 = \Delta H_f(C_6H_{12}, l) - \Delta H_f(C_6H_6, l)$$

$$\Delta H_f(C_6H_6, l) = -156 + 357 = 201 \text{ KJ}$$

$$\begin{aligned} \therefore \text{resonance energy} &= \text{observed } \Delta H_f - \text{calculated } \Delta H_f \text{ of } C_6H_6 \\ &= 49 - 201 = -152 \text{ kJ} \end{aligned}$$

Example When 12.0 g of carbon reacted with oxygen to form CO and CO_2 at $25^\circ C$ and constant pressure, 75.0 kcal of heat was liberated and no carbon remained. Calculate the mass of oxygen needed for it and moles of CO and CO_2 formed. Given $\Delta H_f CO_2 = -94.05$ and $\Delta H_f CO = -26.41 \text{ kcal mole}^{-1}$

Solution: Here $C + O_2 \rightarrow CO_2; \Delta H = -94.05 \text{ kcal}$



Let a mole of carbon reacts to form CO_2 and b moles of carbon reacts to form CO.

Since 12 g or 1 mole carbon is used up

$$a + b = \frac{12}{12} = 1 \quad \dots\dots\dots (1)$$

$$a \times 94.05 + b \times 26.41 = 75$$

$$a = 0.718 \text{ i.e. mole of } CO_2 \text{ formed} \quad \dots\dots\dots (2)$$

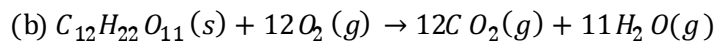
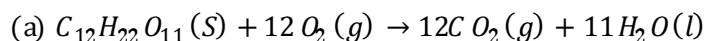
$$b = 0.282 \text{ i.e. mole of } CO \text{ formed}$$

$$\text{Also moles of } O_2 \text{ used for this change} = 0.718 + \frac{0.282}{2} = 0.859$$

$$\text{Thus weight of } O_2 \text{ used} = 0.859 \times 32 = 27.49 \text{ gm}$$

Example When maltose, $C_{12}H_{22}O_{11}(s)$ burns in a calorimetric bomb at 298 K yielding water and carbon dioxide, the heat of combustion is - 1350 Kcal/mol. Calculate the heat of combustion of maltose at constant pressure if the water vapour resulting from the combustion is (a) condensed and (b) not condensed.

Solution: The combustion reaction of maltose can be shown for (a) and (b) as follows.



Case A: when water is condensed

It is given that

$$\Delta H_v = -1350 \text{ K cal/mol}$$

$$\Delta n = 0, R = 1.987 \times 10^{-3} \text{ kcal mol}^{-1} K^{-1}$$

$$T = 298 \text{ K}$$

On inserting these value in the expression

$$\Delta H_p = \Delta H_v + \Delta nRT$$

$$\Delta H_p = -1350 + 0 \times RT = -1350 \text{ kcal/mol}$$

Case B: When water is not condensed

It is given that,

$$\Delta H_v = -1350 \text{ kcal/mol}$$

$$\Delta n = (12 + 11 - 12) = 11$$

$$R = 1.987 \times 10^{-3} \text{ kcal/mol}$$

$$T = 298 \text{ K}$$

On inserting these values in the expression

$$\Delta H_p = \Delta H_v + \Delta nRT$$

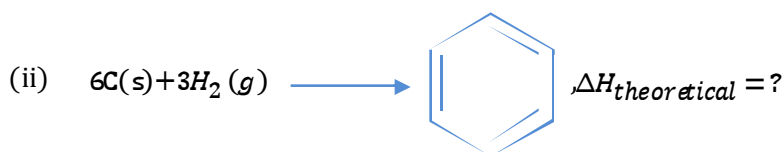
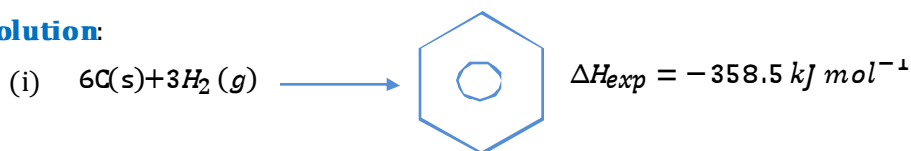
$$\Delta H_p = [-1350 + (11 \times 1.987 \times 10^{-3} \times 298)] \text{ kcal}$$

$$\Delta H_p = -1343 \text{ kcal/mol}$$

Example Calculate the resonance energy of C_6H_6 using kekule formula for C_6H_6 form the following data.

- (i) ΔH_f^0 for $C_6H_6 = -358.5 \text{ kJ mol}^{-1}$
- (ii) Heat of atomization of $C = 716.8 \text{ kJ mol}^{-1}$
- (iii) Bond energy of $C-H$, $C=C$ and $H-H$ are 490, 340, 620, 436.9 kJ mol^{-1} respectively.

Solution:



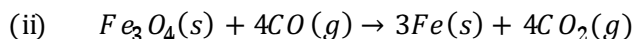
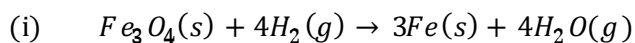
$$\begin{aligned} \Delta H_{theoretical} &= [6\Delta H_{C(s) \rightarrow C(g)} + 3\Delta H_{H-H}] - [3\Delta H_{C=C} + 3\Delta H_{C-C} + 6H_{C-H}] \\ &= [6 \times 716.8 + 3 \times 436.9] - [3 \times 620 + 3 \times 340 + 6 \times 490] \\ &= -208.5 \text{ kJ mol}^{-1} \end{aligned}$$

\therefore Resonance energy

$$= \Delta H_{exp} - \Delta H_{theoretical}$$

$$= -358.5 - (-208.5) = -150.0 \text{ kJ mol}^{-1}$$

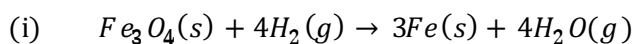
Example Magnetite Fe_3O_4 is reduced iron by hydrogen or carbon monoxide as



Calculate the enthalpy change involved during the reduction to get 1 g of iron. Data given are

Substance	$Fe_3O_4(s)$	$CO(g)$	$CO_2(g)$	$H_2O(g)$
$\Delta H_f (298 K)$	1117.1	110.5	393.5	242.8
	[kJ/mol]			

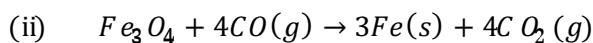
Solution:



$$\Delta H_i = 4\Delta H_f(H_2O, g) - \Delta H_f(Fe_3O_4, s)$$

$$= 4 \times 241.8 - 1117.1 = -149.9$$

$$\begin{aligned} \text{Enthalpy change during the reduction to get 1 g of iron} &= \frac{149.9}{3 \times 56} = 0.89226 \text{ kJ/g} \\ &= 892.26 \text{ J/g} \end{aligned}$$



$$\Delta H_2 = 4\Delta H_f(CO_2, g) - 4\Delta H_f(CO, g) - \Delta H_f(Fe_3O_4, s)$$

$$= 4 \times 393.5 - 4 \times 110.5 - 1117.1 = 14.9 \text{ kJ}$$

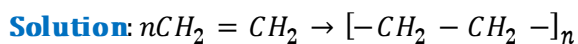
Enthalpy change during the reduction to get 1 g of iron

$$= \frac{14.9}{3 \times 56} = 0.08869 \frac{\text{kJ}}{\text{g}} = 88.69 \text{ J/g}$$

Example Using the data (all values are in kJ/mol at 25°C) given below

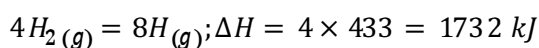
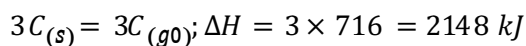
- Enthalpy of polymerization of ethylene = - 72
- Enthalpy of formation of benzene (l) = 49
- Enthalpy of vaporization of benzene (l) = 144
- Resonance energy of benzene (l) - 152
- Heat of formation of gaseous atoms from the elements in their standard state
 $H = 218, C = 715$
- Average bond energy of C - H bond = 415.

Calculate the bond energy of C - C and C = C bonds.

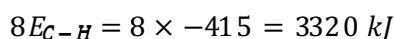
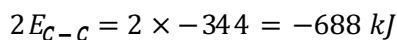


For breakage of each double bond, there is formation of two single bonds.

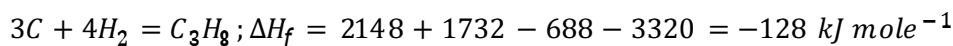
$$\Delta H = n[\epsilon_{C-C} - 2\epsilon_{C=C}]$$



The bond energies are

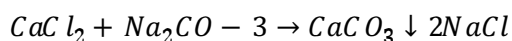


Adding,

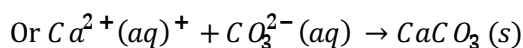
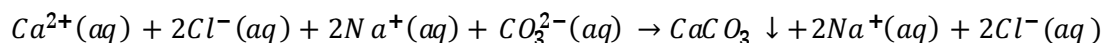


Example Calculate the enthalpy change when infinitely dilute solution of $CaCl_2$ and Na_2CO_3 mixed. ΔH_f° for Ca^{2+} (aq), CO_3^{2-} (aq) and $CaCO_3$ (s) are -129.80 , -161.65 , $-288.5 \text{ kcal mole}^{-1}$ respectively.

Solution: on mixing $CaCl_2$ (aq) and Na_2CO_3



Solution are very dilute and thus 100% dissociation occurs

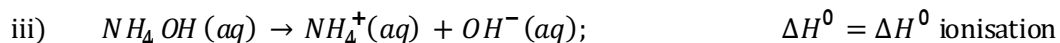
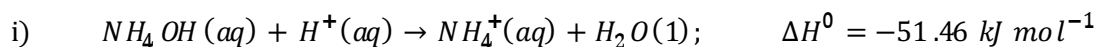


$$\therefore \Delta H = \sum H_{products}^\circ - \sum H_{reactants}^\circ \text{ or } \Delta H = \Delta H_f^\circ CaCO_3 - [\Delta H_f^\circ Ca^{2+} + \Delta H_f^\circ CO_3^{2-}]$$

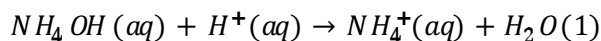
$$\therefore \Delta H^\circ \text{ of compound} = \Delta H^\circ \text{ formation} = -288.5 - (-129.8 - 161.65) = 2.95 \text{ kcal}$$

Example The enthalpy of neutralization of ammonium hydroxide by hydrochloric acid is $51.46 \text{ kJ mol}^{-1}$. Calculate the enthalpy of ionization of ammonium hydroxide.

Solution:



On adding (ii) and (iii), we get



$$\text{or } \Delta H^\circ = -57.32 + \Delta H_{ionisation}^\circ$$

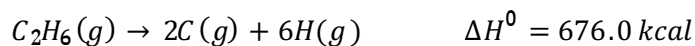
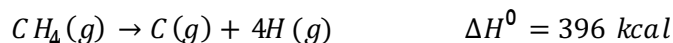
from equation (i), we have

$$\Delta H^\circ = -51.46 \text{ kJ mol}^{-1}$$

$$\text{Hence } (-57.32 + \Delta H_{ionisation}^\circ) \text{ kJ mol}^{-1} = -51.46 \text{ kJ mol}^{-1}$$

$$\text{Or } \Delta H_{ionisation}^\circ = +5.86 \text{ kJ mol}^{-1}$$

Example The enthalpy change for the following processes at 25°C and under constant pressure of one atmosphere are as follows:

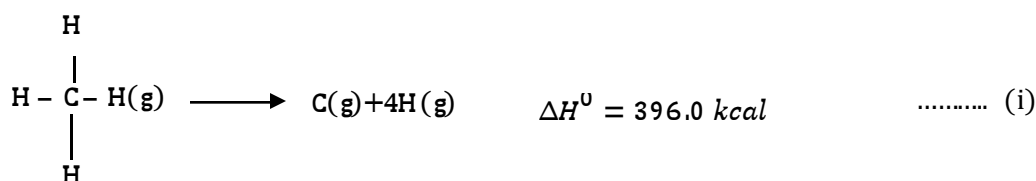


Calculate C - C bond energy in the molecule of C_2H_6 .

If molar heat of sublimation of carbon, $\text{C}(s)$ and molar heat of dissociation of $\text{H}_2(g)$ are 171.8 and 104.1 kcal respectively. Calculate the standard heat of formation of ethane, $\text{C}_2\text{H}_6(g)$.

Solution:

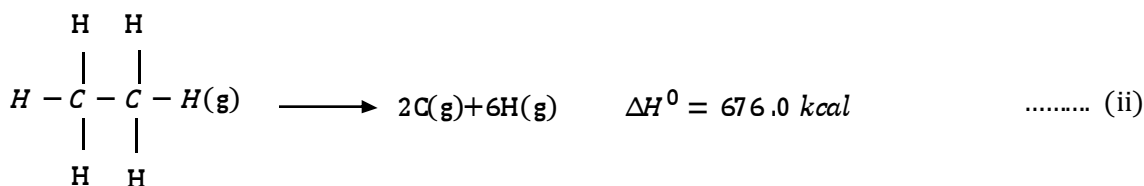
It is given that



That is, $4 \times \text{B.E of } \text{C} - \text{H} = 396 \text{ kcal}$

$$\therefore \text{B.E of } \text{C} - \text{H} = \frac{396}{4} \text{ kcal} = 99.0 \text{ kcal}$$

Again,



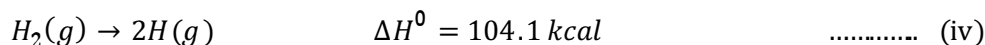
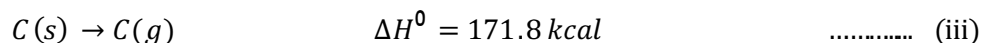
It means that

$$6 \times \text{B.E of } \text{C} - \text{H} + \text{B.E. of } \text{C} - \text{C} = 676.0 \text{ kcal}$$

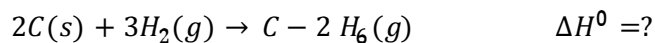
Or, $6 \times 99.0 + \text{B.E of } \text{C} - \text{C} = 676.0 \text{ kcal}$

$$\therefore \text{B.E of } \text{C} - \text{C} = (676.0 - 594) \text{ kcal} = 82.0 \text{ kcal}$$

That is $\text{B.E. of } \text{C} - \text{C} = 82.0 \text{ kcal}$

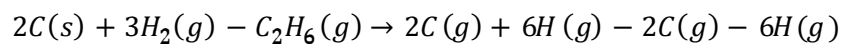


ΔH° for the following reaction is to be found,

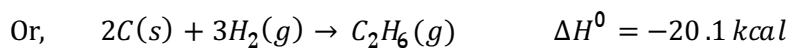


Equation (iii) $\times 2$ + equation (iv) $\times 3$ - equation (ii)

On doing so,



$$\Delta H^0 = [(2 \times 171.8) + 3 \times 104.1 - 676] \text{ kcal}$$



That is, heat of formation of $C_2H_6(g)$, $\Delta H^0 = -20.1 \text{ kcal}$

Section 3

Spontaneity

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3.1 Spontaneous Change

We must now address why reactions occur, and what controls the equilibrium position of a reaction. To do this, we must introduce the idea of a spontaneous process.

“spontaneous” means occurs by itself \therefore a spontaneous reaction or change occurs by itself (until it reaches equilibrium), whereas a “non-spontaneous” reaction is in a direction away from equilibrium and can thus occur only if we force it to happen by inputting energy.

Let's consider reactions that lie ~100% to one side or the other to help get the points across, and then we will be more general later.

Examples: 1) Sodium metal, Na(s), will spontaneously react with Cl₂ gas to give NaCl, but NaCl will not spontaneously give Na metal and Cl₂ gas unless we input energy.

2) Iron metal will spontaneously rust when exposed to water and oxygen gas, but rust will not spontaneously give Fe metal.

These examples are obvious, but what about:

Which is the spontaneous direction in which the reaction will go by itself, and which is the direction we must force it to go???

Similarly, consider something falling, e.g. a ball or chalk-board eraser

Note: “spontaneousness” (or “spontaneity”) does not tell us anything about rates of reaction, only about whether it will occur by itself.

What factors determine which direction of a reaction is spontaneous? We shall see a little later. First, let's refresh our memories of the 1st Law.

First Law of Thermodynamics = Conservation of Energy

$$\Delta E = q + w$$

E = internal energy of system (sum of potential and kinetic energies)

q = heat

w = work

As chemists, our “system” is usually a reaction in a beaker or flask - everything else is “surroundings”

$$\therefore E_{\text{universe}} = E_{\text{system}} + E_{\text{surroundings}}$$

The universe consists of everything \therefore its energy is constant ($\Delta E_{\text{univ}} = 0$)

$$\therefore \Delta E_{\text{univ}} = \Delta E_{\text{sys}} + \Delta E_{\text{sur}} = 0$$

i.e., ΔE_{sys} and ΔE_{surr} cancel each other out \therefore energy (E) cannot be created or destroyed.

This is the First Law of Thermodynamics

NOTE: First Law does not by itself help us to understand and predict the spontaneous direction, however.

How is E, the internal energy of the system, related to H, the enthalpy we learnt about

$$H = E + PV \quad (P = \text{pressure}, V = \text{volume})$$

$$\Delta H = \Delta E + P\Delta V \quad (\text{at constant pressure})$$

For most reactions (in solution), ΔV is insignificant

$$\therefore \Delta H \approx \Delta E$$

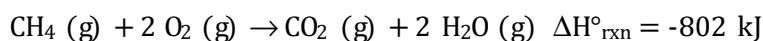
ΔH = enthalpy change = the heat gained or lost at constant pressure.

Can we predict spontaneity from the sign of ΔH ?

i.e., are all exothermic rxns ($\Delta H < 0$) spontaneous?

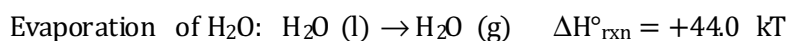
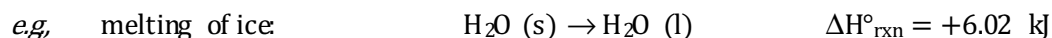
are all endothermic rxns ($\Delta H > 0$) non-spontaneous?

19th century scientists used to think so for a long time, but the answer is NO.



These are spontaneous as written (left to right), and their $\Delta H < 0$ (exothermic). But, in general, $\Delta H < 0$ does not define spontaneity. There are reactions with $\Delta H > 0$ (endothermic) that are also spontaneous.

****spontaneous reactions are usually exothermic, but not always!****



$\Delta H > 0$ for both, yet both occur spontaneously.

\therefore ΔH by itself does not determine spontaneity! We must keep looking to find the law that determines spontaneity.

3.2 Entropy, and the 2nd Law of Thermodynamics

Spontaneity is determined by a thermodynamic function called **ENTROPY** (symbol **S**, units Joules/Kelvin (J/K)). This is the basis of the 2nd law of Thermodynamics and allows us to predict when a process is spontaneous.

First, let's think about entropy.

What is an increase in entropy? Increasing the dispersal of energy or matter over more energy states corresponds to an increase in entropy e.g. dispersing (spreading) energy over more atoms represents an increase in entropy (think of a hot metal in contact with a cold one - the heat will be spread out spontaneously). e.g. dispersing (spreading) matter over a bigger volume represents an increase in entropy (think of a gas in one container distributing between it and an empty container when connected).

Entropy is often related to the idea of DISORDER. Increasing disorder (i.e. decreasing order) is increasing entropy. Spreading (dispersing) heat energy over a bigger amount of metal, or spreading (dispersing) the gas molecules over a greater volume are both examples of going to a situation with greater disorder (smaller order)

Nature has an inherent tendency towards greater dispersal (spreading out) of energy and matter i.e. to greater disorder.

e.g. gas *vs* crystal. A gas is much more disordered than a crystal

A measure of dispersal (or disorder) in a system is ENTROPY (S). Increasing entropy (S) = increasing dispersal (disorder)

i.e. $S_{\text{disordered system}} > S_{\text{ordered system}}$

e.g. $S(\text{gas}) \gg S(\text{crystal})$

S is a state function, like enthalpy H or energy E — it depends on the present state of the system, not how it got there

3.3 Second Law of Thermodynamics

2nd Law of Thermodynamics: In a spontaneous process, the change in the entropy of the universe is positive, i.e. $\Delta S_{\text{universe}} > 0$

i.e. spontaneous processes occur in the direction that increases the entropy of the universe.

True - but doesn't help yet with figuring out which is the spontaneous direction of a reaction - we'll get to that later.

Now, $\Delta S_{\text{universe}} = \Delta S_{\text{system}} + \Delta S_{\text{surroundings}}$

$\therefore \Delta S_{\text{sys}} + \Delta S_{\text{surr}} > 0$ for a spontaneous process

Note: ΔS_{sys} may or may not be > 0 (positive)

ΔS_{surr} may or may not be > 0 (positive)

but $\Delta S_{\text{universe}} \text{ ALWAYS } > 0$ for a spontaneous process

First, let's look at ΔS_{sys} (or ΔS_{rxn}) in detail - we'll return to ΔS_{surr} later

3.4 Calculating Entropy Changes (ΔS°)

Let's also learn to predict the sign of ΔS°

Example 1. $\text{N}_2 (\text{g}) + 3 \text{H}_2 (\text{g}) \rightleftharpoons 2 \text{NH}_3 (\text{g})$

Change in entropy (ΔS°) = S° (products) - S° (reactants)

Prediction: 4 moles of gas \rightarrow 2 moles of gas

(greater disorder \rightarrow less disorder)

(less order \rightarrow more order)

\therefore we predict change in entropy (ΔS°) will be < 0 (negative)

Let's think about ΔS_{surr} more closely.

It turns out that ΔS_{surr} is related to ΔH_{rxn} !

Why? Think about it:

ΔH_{rxn} gives heat (q) to, or takes heat from, the surroundings \therefore the entropy ΔS_{surr} of the surroundings will be changed

(1) If $\Delta H_{\text{rxn}} < 0$ (exothermic), $q_{\text{sys}} < 0$, $q_{\text{surr}} > 0 \therefore \Delta S_{\text{surr}} > 0$

(2) If $\Delta H_{\text{rxn}} > 0$ (endothermic), $q_{\text{sys}} > 0$, $q_{\text{surr}} < 0 \therefore \Delta S_{\text{surr}} < 0$

Thus, heat/enthalpy changes in the system (the reaction) cause S_{surr} to change, and therefore $\Delta S_{\text{surr}} \neq 0$.

$\therefore \Delta S_{\text{surr}}$ depends on $-q_{\text{sys}}$ (i.e. ΔH_{rxn}) and the temperature (T) of surroundings

The relationship is: $\Delta S_{\text{surr}} = -q_{\text{sys}}/T = -\Delta H_{\text{rxn}}/T$

So, ΔS_{surr} is given by ΔH_{rxn} ($= \Delta H_{\text{sys}}$) and the T at which the reaction takes place.

3.5 Entropy Changes at Equilibrium

What is the situation for a reaction that has reached equilibrium?

At equilibrium, no net change is occurring $\therefore \Delta S_{\text{univ}} = 0$

$\therefore \Delta S_{\text{sys}} = -\Delta S_{\text{surr}}$ (because $\Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}} = 0$)

Example: $\text{H}_2\text{O} (\text{l}) \rightleftharpoons \text{H}_2\text{O} (\text{g})$ $\Delta H_{\text{vaporization}} = +40.7 \text{ kJ/mol}$

- this is an equilibrium at 100 °C (373 K)

This is true for both forward and reverse directions \therefore at equilibrium, no movement away from equilibrium in either direction is spontaneous, *i.e.*, no change.

Summary: A reaction is spontaneous if $\Delta S_{\text{univ}} > 0$

$$\text{i.e. } \Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}} > 0$$

For a spontaneous reaction:

if $\Delta H < 0$ (exothermic), $\Delta S_{\text{surr}} > 0$ and ΔS_{sys} can be > 0 or < 0

if $\Delta H > 0$ (endothermic), $\Delta S_{\text{surr}} < 0$ and ΔS_{sys} must be > 0

$$\Delta S_{\text{surr}} = -\Delta H_{\text{sys}}/T$$

At equilibrium, no movement from equilibrium position is spontaneous:

$$\Delta S_{\text{sys}} = -\Delta S_{\text{surr}}$$

Example Predict the sign of ΔS in the system for each of the following process:

- (a) $C O_2 (s) \rightarrow C O_2 (g)$, sublimation of dry ice
- (b) $CaSO_4(s) \rightarrow CaO(s) + SO_3(g)$
- (c) $N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$
- (d) $I_2(s) \rightarrow I_2(aq)$, dissolution of I_2 in water

Solution:

- (a) ΔS is positive since a gas is much more disordered than a solid.
- (b) ΔS is positive since on the product side only one mole of gaseous SO_3 appears which results in an increase in randomness.
- (c) ΔS is negative since the number of moles of gaseous reactants is more than that of gaseous products.
- (d) ΔS is positive; iodine molecules are electrically neutral and form a molecular solid. The dissolution process destroys the order of the crystal and thus randomness increases.

Example A mole of steam is condensed at 100°C, the water is cooled to 0°C and frozen to ice. What is the difference in entropies of the steam and ice? The heats of vaporization and fusion are 540 cal g^{-1} and 80 cal g^{-1} respectively. Use the average heat capacity of liquid water as 1 cal $g^{-1} \text{degree}^{-1}$.

Solution:

Entropy change during condensation of steam

$$\Delta S_1 = \frac{18 \times 540}{373} \text{ cal/}^{\circ} = -26.06 \text{ cal/}^{\circ} C$$

Entropy change during cooling of water from 100°C to 0°C

$$\Delta S_2 = 18 \times 1 \ln \frac{273}{373} \text{ cal}/^{\circ}\text{C} = -5.62 \text{ cal}/^{\circ}\text{C}$$

Entropy change during freezing of water at 0°C

$$\Delta S_3 = \frac{18 \times 80}{273} \text{ cal}/^{\circ}\text{C} = -5.27 \text{ cal}/^{\circ}\text{C}$$

So total entropy change = $-26.06 - 5.62 - 5.27 = -36.95 \text{ cal}/^{\circ}\text{C}$

Hence difference in entropy between steam and ice = $36.95 \text{ cal}/^{\circ}\text{C}$

3.6 Gibbs Free Energy (G)

To avoid having to consider $\Delta S^{\circ}_{\text{sys}}$ and $\Delta S^{\circ}_{\text{surr}}$ all the time, a new thermodynamic quantity was introduced in the 19th century called the Gibbs Free Energy (G).

Since $\Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}}$ and $\Delta S_{\text{surr}} = -\Delta H_{\text{sys}}/T$

$$\therefore \Delta S_{\text{univ}} = \Delta S_{\text{sys}} - \Delta H_{\text{sys}}/T$$

$$\therefore T\Delta S_{\text{univ}} = T\Delta S_{\text{sys}} - \Delta H_{\text{sys}} \quad \text{and} \quad \therefore -T\Delta S_{\text{univ}} = \Delta H_{\text{sys}} - T\Delta S_{\text{sys}} = \Delta G_{\text{sys}}$$

$$\therefore \Delta G_{\text{sys}} = \Delta H_{\text{sys}} - T\Delta S_{\text{sys}} \quad \text{or usually just as} \quad \Delta G = \Delta H - T\Delta S$$

Since $\Delta G_{\text{sys}} = -T\Delta S_{\text{univ}}$ and $\Delta S_{\text{univ}} > 0$ for a spontaneous reaction:

$\Delta G < 0$ (i.e., negative) for a spontaneous reaction.

$\Delta G > 0$ (i.e., positive) for a non-spontaneous reaction.

$\Delta G = 0$ for a process at equilibrium

This is the most convenient form of the 2nd Law of Thermodynamics i.e. saying: $\Delta G_{\text{sys}} < 0$ for a spontaneous reaction is the same as **saying $\Delta S_{\text{univ}} > 0$**

Free Energy is a state function and ΔG° = standard free energy change (kJ/mol). **Note:** since H values not available, G values also are not, and we can only calculate ΔG values. Appendix 3 lists $\Delta G^{\circ}_{\text{form}}$ values for this.

The Meaning of ΔG

For a spontaneous process, ΔG = maximum work (w) the system can do.

For a non-spontaneous process, ΔG = the minimum work that must be done to the system to make the reaction happen. $\therefore \Delta G = w_{\text{max}}$

Since $\Delta G = \Delta H - T\Delta S$ $\therefore \Delta H = \Delta G + T\Delta S$ $\therefore \Delta H = w_{\text{max}} + T\Delta S$

i.e., part of the energy released (ΔH) goes into an entropy change and is not available to do work.

Summary

If $\Delta G < 0$, process is spontaneous and can do work on the surroundings.

If $\Delta G > 0$, process is non-spontaneous and will not occur unless surroundings do work on it.

If $\Delta G = 0$, reaction is at equilibrium and can no longer do work.

3.7 Effect of Temperature on Reaction Spontaneity

Most exothermic reactions are also spontaneous because the ΔH contribution to ΔG is much greater than the entropy contribution ($T\Delta S$), *i.e.*, the negative ΔH helps make ΔG negative. However, in many cases the T can change the importance of the $T\Delta S$ term.

Let's look at the possibilities (and assume ΔH and ΔS are approximately independent of T , which they are if no phase change occurs.)

$$\text{Remember: } \Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

ΔH°	ΔS°	$-T\Delta S^\circ$	ΔG°	Conclusion
-	+	-	-	$\Delta G^\circ < 0$ at all T rxn spontaneous at all T
+	-	+	+	$\Delta G^\circ > 0$ at all T rxn non-spontaneous at all T
-	-	+	+ or -	$\Delta G < 0$ at low T \therefore spontaneous at low T $\Delta G > 0$ at high T \therefore non-spontaneous at high T
+	+	-	+ or -	$\Delta G > 0$ at low T \therefore non-spontaneous at low T $\Delta G < 0$ at high T \therefore spontaneous at high T

Note: We can drive a non-spontaneous reaction by combining it with a sufficiently spontaneous one.

3.8 Free Energy and Equilibrium

Let's now be more general for all rxns, not just ~100% ones.

The magnitude of ΔG° of a reaction controls the magnitude of K

Consider reaction $A \rightarrow B$ $Q = [B]/[A]$

$A \rightarrow B$ spontaneous direction if $\Delta G < 0$

$B \rightarrow A$ is the non-spontaneous direction

$Q < K$ is the spontaneous direction for left-to-right, where Q = mass-action expression.

How are the two rules related?

$Q/K < 1$, spontaneous, $\Delta G < 0$

$Q/K > 1$, non-spontaneous, $\Delta G > 0$

$Q/K = 1$, equilibrium, $\Delta G = 0$

} for rxn. left \rightarrow right
i.e., $A \rightarrow B$

How are Q/K and ΔG mathematically related?

$$\Delta G = \Delta G^\circ + RT \ln Q$$

When Q becomes K , $\Delta G = 0$

$\therefore \Delta G^\circ = -RT \ln K$ **** Extremely important relationship between ΔG° and K ****

Note: Small change in ΔG can give big change in K .

Since most reactions do not begin with reactants in standard conditions, we can calculate ΔG for any conditions using

Example Compute the standard free energy of the reaction 27°C for the combustion of

methane using the given data: $CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(l)$

Species	CH_4	O_2	CO_2	H_2O
$\Delta H_f^\circ / (kJ mol^{-1})$	-74.8		-393.5	-285.8
$S^\circ / (JK mol^{-1})$	186	205	214	70

Solution:

$$\Delta H^\circ = \Delta H_f^\circ(CO_2) + 2\Delta H_f^\circ(H_2O) - \Delta H_f^\circ(CH_4)$$

$$= 393.5 + 2 \times (-285.8) - (-74.8) = -890 kJ mol^{-1}$$

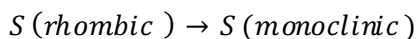
$$\Delta S^\circ = S^\circ(CO_2) + 2S^\circ(H_2O) - \Delta H_f^\circ(CH_4)$$

$$= 393.5 + 2 \times 70 - 186 - 2 \times 205 = 242 J/K/mol$$

$$\Delta G^\circ = \Delta H^\circ - T \Delta S^\circ$$

$$= -890 - 300 \times (-242 \times 10^{-3}) = -890 + 72.6 = -817.4 kJ mol^{-1}$$

Example Sulphur exists in more than one solid form. The stable form at room temperature is rhombic sulphur. But above room temperature the following reaction occurs.



If $\Delta H = 276.144 J$ at 298 K and 1 atm and $\Delta G = 75.312 J$

- (a) Calculate ΔS at 298 K
- (b) Assume that ΔH and ΔS do not vary significantly with temperature, calculate T_{eq} the temperature at which rhombic and monoclinic sulphur exist in equilibrium with each other.

Solution:

(a) Since $\Delta G = \Delta H - T\Delta S$

$$\Rightarrow \Delta S = \frac{\Delta H - \Delta G}{T} = \frac{276.144 - 75.312}{298} = 0.674 \text{ J K}^{-1}$$

(b) Under equilibrium condition $\Delta G = 0$

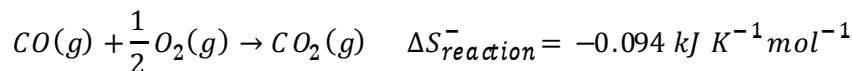
$$\Rightarrow \Delta H - T_{eq}\Delta S = 0$$

$$\Rightarrow T_{eq} = \frac{\Delta H}{\Delta S} = \frac{276.144}{0.674} = 409.7 \text{ K}$$

Example Show that the reaction $CO(g) + (1/2)O_2(g) \rightarrow CO_2(g)$ at 300 K, is spontaneous and exothermic, when the standard entropy change is $-0.094 \text{ kJ mol}^{-1}\text{K}^{-1}$. the standard Gibbs free formation for CO_2 and CO are -394.4 and $-137.2 \text{ kJ mol}^{-1}$, respectively.

Solution:

For the given reaction, we have



The free energy of the reaction is:

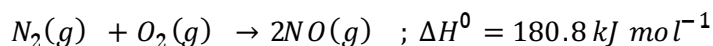
$$\begin{aligned} \Delta G_{reaction}^- &= \Delta G_{r,CO_2}^- - \Delta G_{r,CO}^- \\ &= (-394.4 + 137.2) \text{ kJ mol}^{-1} \\ &= -257.2 \text{ kJ mol}^{-1} \end{aligned}$$

Since $\Delta G_{reaction}^-$ is negative, the reaction is spontaneous. The enthalpy change of the reaction is:

$$\begin{aligned} \Delta H_{reaction}^- &= \Delta G_{reaction}^- + T \Delta S_{reaction}^- \\ &= [-257.2 + (300)(-0.094) \text{ kJ mol}^{-1}] = -285.4 \text{ kJ mol}^{-1} \end{aligned}$$

Since $\Delta H_{reaction}^-$ is negative, the reaction is exothermic.

Example Assume ΔH^0 and ΔS^0 to be independent of temperature, at what temperature will the reaction given below become spontaneous?



$$S^{\circ}/JK^{-1}mol^{-1} \quad 19.14 \quad 204.9 \quad 210.5$$

Solution:

$$\Delta S^{\circ} = 2S^{\circ}(NO) - S^{\circ}(N_2) - S^{\circ}(O_2)$$

$$= 2 \times 210.5 - 191.4 - 204.9$$

$$= 24.7 JK mol^{-1}$$

$$\text{Using: } \Delta G^{\circ} = 180.8 - (T \times 24.7 \times 10^{-3}) kJ mol^{-1}$$

For spontaneously, $\Delta G^{\circ} < 0$ and this occurs when

$$T \Delta S^{\circ} > \Delta H^{\circ}$$

$$\Rightarrow T > \frac{\Delta H^{\circ}}{\Delta S^{\circ}}$$

$$\Rightarrow T > \frac{180.8 \times 10^3}{24.7} = 7320 K$$

The reaction becomes spontaneous above a temperature of 7320 K.

Solved Examples

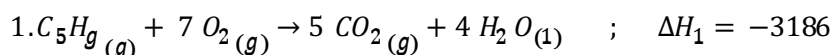
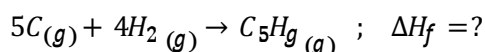
Example Calculate the resonance energy of isoprene (C_5H_8) from the data given.

Heats of combustion of isoprene, carbon and water are $-3186, 395.5$ & $-285.83 kJ/mol$ respectively. Bond energies of $C=C, C-C, C-H$ & $H-H$ bonds are $615, 348, 413, 435.8 kJ/mol$ respectively. Heat of sublimation of graphite is $718.3 kJ/mol$.

Solution:

Resonance energy = ΔH_f (from heat of combustion) - ΔH_f (from bond energies)

Calculate ΔH_f of isoprene from its heat of combustion.



Now operating $5(2) + 4(3) - 1$ to get the equation of heat of formation

From Hess's law we have

$$\Delta H_f = 5 \Delta H_2 + 4 \Delta H_3 - \Delta H_1$$

$$\Rightarrow \Delta H_f = 5(-393.5) + 4(285.83) - 3186 \Rightarrow \Delta H_f = 75.18 kJ$$

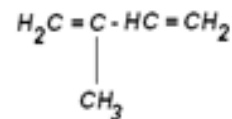
Now calculate heat of formation using the bond energies and structure of isoprene.

1. Bond breaking: (ΔH_1)

$$5[C(s) \rightarrow C(g) ; +718.3]$$

$$4[H_2(g) \rightarrow 2H ; +435.8] \Rightarrow \Delta H_1 = 5 \times 718.3 + 4 \times 435.8$$

$$= +5334.7 \text{ kJ}$$



1. Bond breaking: (ΔH_2)

$$5[C + H \rightarrow C - H ; -413]$$

$$2[C + C \rightarrow C - C ; -348]$$

$$2[C + C \rightarrow C = C ; -615] \Rightarrow \Delta H_2 = -(8 \times 413 + 2 \times 348 + 2 \times 615) =$$

$$-5230 \text{ kJ}$$

From Hess's law: $\Delta H_f = \Delta H_1 + \Delta H_2$

$$\Delta H_f = 5334.7 + (-5230) = 104.7 \text{ kJ}$$

$$\Rightarrow \text{Resonance energy} = 75.18 - 104.7 = -29.52 \text{ kJ}$$

Example Two moles of a perfect gas undergo the following processes:

- A reversible isobaric expansion from (1.0 atm, 20.0 L) to (1.0 atm, 40.0 L);
 - A reversible isochoric change of state from (1.0 atm, 40.0 L) to (0.5 atm, 40.0 L);
 - A reversible isothermal compression from (0.5 atm, 40.0 L) to (1.0 atm, 20.0 L)
- Sketch with labels each of the processes on the same p-V diagram.
 - Calculate the total work (W) and the total heat change (q) involved in the above processes.
 - What will be the values of ΔU , ΔH and ΔS for the overall process?

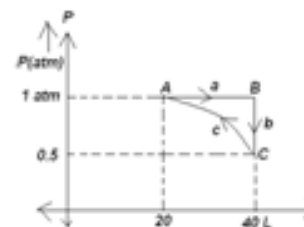
Solution:

(i) The p-V diagram of the given processes a, b and c is shown in figure.

(a) Reversible isobaric expansion (1.0 atm, 20) \rightarrow (1.0 atm, 40)

(b) Reversible isochoric expansion (1.0 atm, 40) \rightarrow (0.5 atm, 40)

(c) Reversible isothermal compression (0.5 atm, 40) \rightarrow (1.0 atm, 20)



(ii) Work involved in the given processes is as follows:

$$\text{Process a } W_1 = -P(\Delta V) = -(1 \text{ atm})(40\text{L} - 20\text{L}) = -20 \text{ atm} \cdot \text{L}$$

$$= -20 \times 101.325 \text{ J} = -2026.5 \text{ J}$$

Process b $W_2 = 0$, since the process occurs at constant volume

$$\begin{aligned} \text{Process c } W_3 &= -nRT \ln \frac{V_2}{V_1} = -P_1 V_1 \ln \frac{V_2}{V_1} \\ &= -(1.0 \text{ atm})(20 \text{ L}) \ln (20 \text{ L}/40 \text{ L}) = 13.86 \text{ atm-L} \\ &= 13.86 \times 101325 \text{ J} = 1404.4 \text{ J} \end{aligned}$$

$$\begin{aligned} \text{The total work done is } W &= W_1 + W_2 + W_3 = -2056.5 \text{ J} + 0 + 1404.4 \text{ J} \\ &= -622.1 \text{ J} \end{aligned}$$

Since the given process constitutes a cyclic process, $\Delta U = 0$, and from the first law of thermodynamics, we get:

$$q = -W = 622.1 \text{ J}$$

(iii) Since the overall process is a cyclic process,

$$\Delta U = 0 \quad \Delta H = 0 \quad \text{and} \quad \Delta S = 0$$

Example Water is brought to boil under a pressure of 1.0 atm. When an electric current of 0.50 A from a 12.0 V supply is passed for 300 s through a resistance in thermal contact with it, it is found that 0.789 g of water is vaporized. Calculate the molar internal energy and enthalpy changes at boiling point (373.15 K).

Solution:

Since the vaporization occurs at constant pressure, the enthalpy change is equal to the work done on the heater (which enters the water as heat):

$$\begin{aligned} \Delta H &= 0.50 \text{ A} \times 12 \text{ V} \times 300 \text{ s} \\ &= 1800 \text{ J} = +1.8 \text{ kJ} \end{aligned}$$

$$\therefore \text{Molar enthalpy of vaporization} = \Delta H_m = \frac{\Delta H}{n_{H_2O}} = \frac{1.8 \text{ kJ}}{\left(\frac{0.789}{18}\right)} = 40.6 \text{ kJ mol}^{-1}$$

Also $\Delta H_m = \Delta E_m + P\Delta V$ ($\Delta E_m = \text{molar internal energy change}$)

$$= \Delta E_m + \Delta n RT \quad (\Delta n = 1)$$

$$\Rightarrow \Delta E_m = \Delta H_m - RT$$

$$= 40.6 - 8.314 \times 10^{-3} \times 373.15$$

$$= 37.5 \text{ kJ mol}^{-1}$$

Example Determine whether or not it is possible for sodium to reduce aluminum oxide to aluminum at 298 K also calculate equilibrium constant.

$$\Delta G^\circ Al_2O_3(s) = -1582 \text{ kJ/mol};$$

$$\Delta G^\circ Na_2O(s) = -377 \text{ kJ/mol};$$

Solution

The reaction is: $Al_2O_3(s) + 6Na(s) \rightarrow 3Na_2O(s) + 2Al(s)$

$$\begin{aligned}\Delta G^0 &= \Delta G_r (Na_2O) - \Delta G_r (Al_2O_3) \\ &= 3 \times (-377) = (-1582) \\ &= +451 \text{ KJ mol}^{-1}\end{aligned}$$

Hence the reaction cannot occur, since ΔG^0 is positive.

$$\text{Also, } \Delta G^0 = 2.30 RT \log K$$

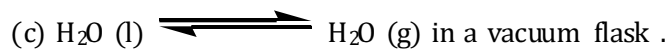
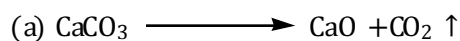
$$\Rightarrow 451 = -2.303 \times 8.314 \times 10^{-3} \times 298 \log K$$

$$\Rightarrow \log K = -79.04$$

$$\Rightarrow K = 9.1 \times 10^{-80}$$

Assignments

1. Identify open, closed and isolated systems out of the following ?



2. Which of the following are state functions and which are not ?

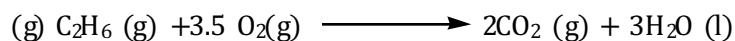
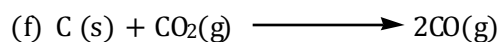
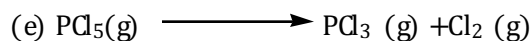
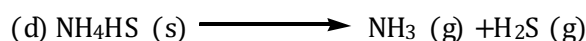
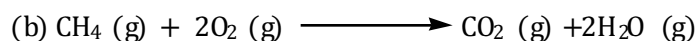
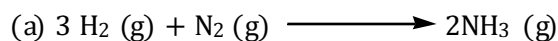
(a) The temperature of an ice cube

(b) The volume of an aerosol can

(c) The amount of work in expansion

3. Calculate the work done when 56 g of Iron reacts with hydrochloric acid in (a) a closed vessel of fixed volume (b) an open beaker at 27 °C.

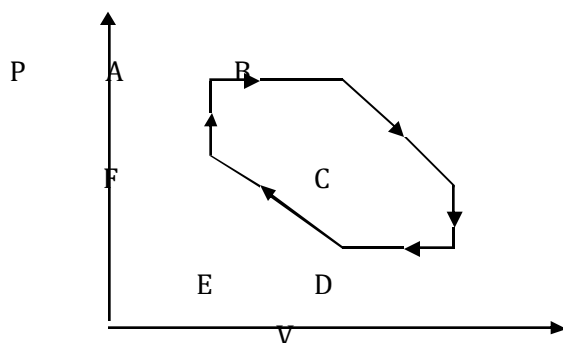
4. Assign the sign of work done (based on SI convention) in the following chemical changes taking place against external atmospheric pressure :



5. In the following cyclic process, A to F specify the type of changes taking place given that

Temperature at A, B and F = T_1

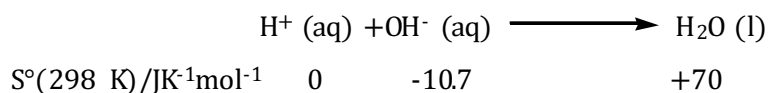
Temperature at C, D and E = $T_2 < T_1$



6. What happens to the internal energy of a system if :
- Work is done on the system
 - Work is done by the system
7. A sample of 4.50 g methane occupies 12.7 L at 310 K.
- Calculate the work done when the gas expands isothermally against a constant external pressure of 200 Torr until its volume has increased by 3.3 L.
 - Calculate the work would be done if the same expansion occurred reversibly.
8. When 1 mol of ice melts at 273 K and a constant pressure of 1 atm, 1440 cal of heat are absorbed by the system. The molar volume of ice and water are 0.0196 and 0.0180 L, respectively. Calculate ΔH and ΔE .
9. What is ΔE° when 1 mol of liquid water vaporizes at 100 °C? the heat of vaporization, ΔH°_{vap} , of water at 100 °C is 40.66 kJ mol⁻¹.
10. The enthalpy change for the reaction of 50.00 ml of ethylene with 50.00 ml of H₂ at 1.5 atm pressure is $\Delta H = -0.31$ kJ. What is the value of ΔE ?
11. Which of the following processes are spontaneous and which are non-spontaneous?
- Diffusion of perfume molecules from one side of a room to the other.
 - Heat flow from a cold object to a hot object.
 - Decomposition of rust (Fe₂O₃.H₂O) to iron metal, oxygen and water.
 - Decomposition of solid CaCO₃.
12. Predict the sign of ΔS in the system for each of the following processes:
- CO₂(s) \longrightarrow CO₂(g), sublimation of dry ice
 - CaSO₄ (s) \longrightarrow CaO (s) + SO₃(g)
 - N₂(g) + 3H₂(g) \longrightarrow 2NH₃(g)
 - I₂(s) \longrightarrow I₂(aq), dissolution of I₂ in water
13. Which state in each of the following pairs has the higher energy per mol of substance?
- H₂ at 25°C in a volume of 10 L or H₂ at 25°C in a volume of 50 L.
 - O₂ at 25°C and 1 atm or O₂ at 25°C and 10 atm
 - H₂ at 25°C and 1 atm or H₂ at 100°C and 1 atm
 - CO₂ at STP or CO₂ at 100°C and 0.1 atm
14. One mol of NaCl (s) on melting absorbed 30.5 kJ of heat and its entropy is increased by 288 J K⁻¹. What is the melting point of sodium chloride?

15. Calculate the entropy change when one mole of water at 373 K is converted into steam. Latent heat of vaporization of water (ΔH_v) is $40.7 \times 10^3 \text{ J mol}^{-1}$.

16. Calculate the standard entropy change for the following reaction :

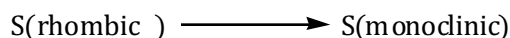


17. Determine whether or not it is possible for sodium to reduce aluminium oxide to aluminium at 298 K.

$$\Delta G_f^\circ(298 \text{ K}) / \text{kJ mol}^{-1} \text{ Al}_2\text{O}_3(\text{s}) = -1582$$

$$\text{Na}_2\text{O} (\text{s}) = -377, \text{element} = 0$$

18. Sulphur exists in more than one solid form. The stable form at room temperature is rhombic sulphur. But above room temperature the following reaction occurs.

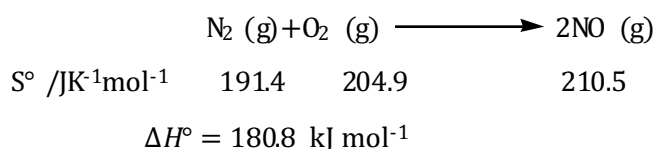


$$\text{If } \Delta H = 276.144 \text{ J at } 298 \text{ K and } 1 \text{ atm and } \Delta G = 75.312 \text{ J}$$

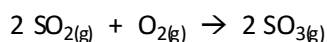
(a) Calculate ΔS at 298 K

(b) Assume that ΔH and ΔS do not vary significantly with temperature, calculate T_{eq} , the temperature at which rhombic and monoclinic sulphur exist in equilibrium with each other.

19. Assume ΔH° and ΔS° to be independent of temperature, at what temperature will the reaction given below become spontaneous ?



20. Calculate the entropy change at 25°C, in J/K for:



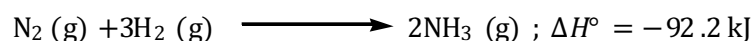
Given the following data:

$$\text{SO}_2(\text{g}) \quad 248.1 \text{ J/K.mol}$$

$$\text{O}_2(\text{g}) \quad 205.3 \text{ J/K.mol}$$

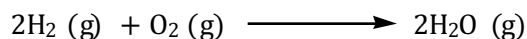
$$\text{SO}_3(\text{g}) \quad 256.6 \text{ J/K.mol}$$

21. For the reaction



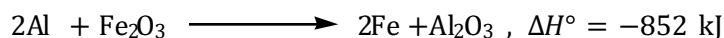
What is the value of ΔE , if the reaction is carried out at constant pressure of 40.0 atm and the volume change is -1.12 L ? (Assume, 1 L-atm = 101.27 J)

22. The reaction between H_2 and O_2 to yield water vapour has $\Delta H^\circ = -484 \text{ kJ}$



How much PV work is done and what is the value of ΔE for the reaction of 0.50 mol of H_2 with 0.25 mol of O_2 at atmospheric pressure if the volume change is -5.6 L ?

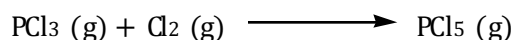
23. How much heat (in kJ) is evolved when 2.7 g of aluminium reacts with a stoichiometric amount of Fe_2O_3 ?



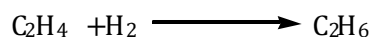
24. Write the equations for which the enthalpy change is the standard heat of formation of

- (a) $HCl(g)$
- (b) $N_2O(g)$
- (c) $B_2O_3(s)$
- (d) $CaCO_3(s)$
- (e) Glycine $NH_2CH_2COOH(s)$

25. ΔH_f° (standard heat of formation) of PCl_5 and PCl_3 are respectively x_1 and x_2 . What is ΔH° of the reaction



26. Standard heat of combustion of C_2H_4 , H_2 and C_2H_6 are $-x_1$, $-x_2$ and $-x_3$ cal at 298 K and at 1 atm. What is enthalpy change of the reaction in the given state?



27. If ΔH_f° of $C_2H_4(g) = 12.4 \text{ kcal mol}^{-1}$

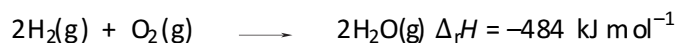
$$CO_2(g) = -94.0 \text{ kcal mol}^{-1}$$

$$H_2O(l) = -68.0 \text{ kcal mol}^{-1}$$

Calculate heat of combustion of $C_2H_4(g)$.

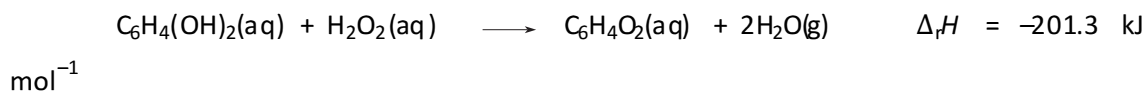
28. The enthalpy of formation of $H_2O(l)$ is $-285.77 \text{ kJ mol}^{-1}$ and enthalpy of neutralization of a strong acid and strong base is $-56.07 \text{ kJ mol}^{-1}$. What is the enthalpy of formation of OH^- ion?

29. Given the following enthalpy data:



Calculate the bond dissociation energy for the O-H bond in a water molecule.

30. The bombardier beetle has a defence mechanism where it squirts out an explosive discharge. The reaction involved is:



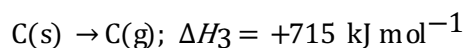
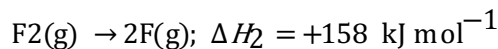
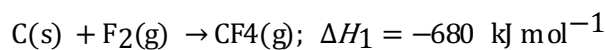
hydroquinone

quinone

A particular beetle squirts out 1.6×10^{-5} mol of hydroquinone and the total volume is equivalent to 8 mg of water. $\Delta H = m \times c \times \Delta t$ where m is the mass of substance c is the specific heat and t is the temperature. For water $c = 4.18 \text{ J g}^{-1} \text{ }^\circ\text{C}^{-1}$.

Calculate the temperature rise if all the energy generated from the reaction is transferred to 8 mg (0.008 g) of water.

31. Given the following data: calculate the average bond enthalpy (in kJ mol^{-1}) for the C—F bond.



32. For the process: $\text{CH}_6(\text{l}) \rightarrow \text{C}_6\text{H}_6(\text{s})$ the standard entropy and enthalpy changes are:

$$\Delta H^\ominus = -9.83 \text{ kJ mol}^{-1} \text{ and } \Delta S^\ominus = -35.2 \text{ J K mol}^{-1}.$$

Predict and explain the effect of an increase in temperature on the spontaneity of the process.

33. For the process $\text{C}_6\text{H}_6(\text{l}) \rightarrow \text{C}_6\text{H}_6(\text{s})$

$\Delta H^\ominus = -9.83 \text{ kJ mol}^{-1}$ and $\Delta S^\ominus = -35.2 \text{ J K}^{-1} \text{ mol}^{-1}$. Calculate the temperature (in $^\circ\text{C}$) at which $\Delta G = 0$ for the above process and explain the significance of this temperature.

34. The standard enthalpy change of formation of $\text{Al}_2\text{O}_3(\text{s})$ is $-1669 \text{ kJ mol}^{-1}$ and the standard enthalpy change of formation of $\text{Fe}_2\text{O}_3(\text{s})$ is -822 kJ mol^{-1} .

(i) Use these values to calculate ΔH^\ominus for the following reaction. $\text{Fe}_2\text{O}_3(\text{s}) + 2\text{Al}(\text{s}) \rightarrow 2\text{Fe}(\text{s}) + \text{Al}_2\text{O}_3(\text{s})$

State whether the reaction is exothermic or endothermic.

(ii) Estimate, without doing a calculation, the magnitude of the entropy

change for this reaction. Explain your answer.

35. Explain in terms of ΔG^\ominus , why a reaction for which both ΔH^\ominus and ΔS^\ominus values are positive can sometimes be spontaneous and sometimes not.

Answers

- 1) Open, Closed, Isolated, Open 2) State functions : (a) ,(b) 3) 0, - 600 cal
7) - 87.99 J, - 167.5 J 8) 1440 cal, 1440.039 cal 9) 36.73 kJ mol⁻¹
10) -0.3024 kJ 12) +,+,-,+ 14) 1059 K 15) 109.11 J K⁻¹ mol⁻¹
16) 80.70 J K⁻¹ mol⁻¹ 17) + 451 kJ mol⁻¹ 18) 0.674 J K⁻¹, 409.7 K 19) 7320 K
20) -188.3 J/K 21) -87.66 kJ 22) -120.43 kJ 23) -42.6 kJ
25) $x_1 - x_2$ 26) $-x_1 - x_2 + x_3$ 27) -336.4 k cal 28) -229.70 kJ
31) -1711 kJ 33) 279 K 34) -847 kJ