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THERMODYNAMICS

PHYSICAL CHEMISTRY

JEE/NEET-2020

IIT-JEE Syllabus

First law of thermodynamics; Internal energy, work and heat, pressure-volume work; Enthalpy, Hess's law; Heat of reaction, fusion and vapourization; Second law of thermodynamics; Entropy; Free energy; Criterion of spontaneity.

TERMS & DEFINITIONS

System and Surroundings

Types of Systems

a)	Real system	In experimental work, the system is called Real.
b)	Ideal system	In pencil and paper work, the system treated is called ideal. An ideal system is always considered to simplify the thermodynamic problems.
c)	Isolated system	A system is said to be isolated when it can neither exchange energy nor matter with its surroundings.
d)	Closed system	A system is said to be closed when it permits passage of energy but not mass, across the boundary.
e)	Open system	A system which can exchange both energy and matter with its surroundings.

State of System (State Variables)

The state variables are generally (T), Pressure (P) Volume (V) and number of moles (n). Besides these there are two more variables. Work (W) and heat (q), which are not state properties.

State Function & Path Function

A property which depends only on the initial & final state of the system but not on the path by which the initial state is converted to final state is called a state function. e.g. pressure, volume, temperature, ΔU, ΔH, ΔS & ΔG.

A quantity which depends on the path or route by which the system reaches from initial state to final state is called path function. e.g. work & heat.

Properties of System

Extensive Property	**Intensive Property**
Volume	Molar volume
No. of moles	Density
Mass	Refractive index
Free Energy	Surface tension
Entropy	Viscosity
Enthalpy	Free energy per mole, specific heat
Heat capacity	Pressure, Temperature, Boiling Point, Freezing Point

Thermodynamic processes

The operation by which a system changes from one state to another state is called a process.

1. **Isothermal process:** The process is termed isothermal if temperature remains constant i.e. for an isothermal process $\Delta T = 0$ and $\Delta E = 0$.
2. **Adiabatic process:** A process is carried out under such condition that no exchange of heat takes place between the system and surroundings i.e. dq = 0.
3. **Isobaric process:** The process is known as isobaric in which the pressure remains constant throughout the change i.e. $\Delta P = 0$.
4. **Isochoric process:** The process is termed as isochoric in which volume remains constant throughout the change i.e. $\Delta V = 0$.
5. **Cyclic process:** When a system undergoes a number of different states by different processes and finally returns to its initial state, it is said to have completed a cycle and the process is called a cyclic process. i.e. $\Delta E = 0$ and also $\Delta H = 0$.

6. **Reversible process:** The process which occurs infinitesimally slowly i.e. opposing force is infinitesimally smaller than driving force and infinitesimal increase in the opposing force can reverse the process.

7. **Irreversible process:** The process goes from initial to final state in a single step or finite number of steps in finite time and cannot be reversed exactly by small changes in P, V, T etc.

THERMODYNAMIC VARIABLES

Internal energy (U or E)

*I*ntrinsic or internal energy (E).

$$E = E_T + E_R + E_V + E_B + E_E \ldots\ldots\ldots$$

Where E_T =Translational energy, E_R =Rotational energy, E_V =Vibrational energy, E_B = Bonding energy and E_E = Electronic energy.

Internal energy of a system is a state function and its absolute value can not be calculated but its change can be determined. When the system undergoes a change in its state, the internal energy change is given by

$$\Delta E = E_2 - E_1$$

Where E_1 = Internal energy in the initial state and E_2 = Internal energy in the final state.

In a chemical reaction, $\Delta E = E_P - E_R$

Where E_P = Internal energy of products and E_R = Internal energy of reactants.

Enthalpy (H)

$$H = E + PV$$

Every substance has a definite value of enthalpy in a particular state. It is also a state function like internal energy. The change in enthalpy accompanying a process can be determined as

$\Delta H = H_2 – H_1$

or $\Delta H = (E_2 + P_2V_2) – (E_1 + P_1V_1) = (E_2 – E_1) + (P_2V_2 – P_1V_1)$

or $\Delta H = \Delta E + \Delta PV$

If P is maintained constant

$\Delta H = \Delta E + P\Delta V$

Hence the change in enthalpy of the system ΔH may be defined as the amount of heat absorbed at constant pressure.

Heat (Q orq)

Heat may be defined as the quantity of energy which flows between a system and its surroundings on account of temperature difference. Heat always flows from high temperature to low temperature.

Sign Convention:

According to IUPAC system.

(i) Heat flowing into the system, q = + ve.

(ii) Heat flowing out of the system, q = - ve

Work (w)

In thermodynamics, work is generally defined as the force multiplied by the distance. If the displacement of body under the force F is ds, the work done will be,

$\delta W = Fds$

a) Work appears only at the boundary of the system

b) Work appears only during a change in state

c) Work is manifested by an effect in the surroundings

d) Work is an algebraic quantity. It is positive if the work has been done by the surroundings. It is negative if the work has been done by the system.

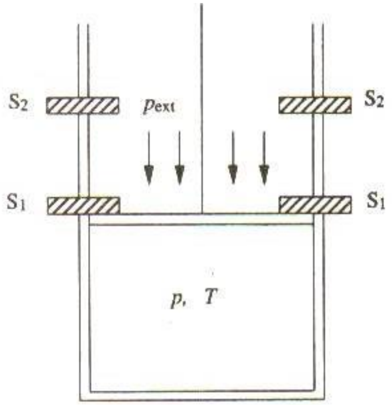
e) In SI system of units, work is expressed in Joule or Kilojoule 1J = 1 Nm.

Types of work

1. Gravitational work = (mg) × h, where m = mass of body, g = acceleration due to gravity,
   h = height moved.

2. Electrical work = charge × potential = q × V
3. Mechanical work = $P_{ext} (V_2 - V_1) = P_{ext} \Delta V$ where P_{ext} = external pressure, ΔV= increase or decrease in volume.

WORK INVOLVED IN EXPANSION AND COMPRESSION PROCESSES



Process of expansion of a gas

force F acting downwards is F = mg and the pressure acting downwards $p_{ext} = \frac{F}{A} = \frac{mg}{A}$ where A is the area of cross section of the piston.

Mathematical Expression of Work

By definition, the work involved is given by:

$w = -$(External force) (Distance through which piston moves)

or $w = -\left(\frac{\text{Force}}{\text{Area of crosssection of piston}}\right)$ (Area of cross section of piston)

$\times$(Distance through which piston moves) or $w = -p_{ext}(\Delta V)$ (ΔV = area × distance)

where ΔV is the change in volume of the system. If the piston moves by an infinitesimal amount, the work involved is given by

$$dw = -p_{ext}\,dV$$

First law of thermodynamics

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Mathematical Formulation of the First Law

Heat absorbed by the system = change in internal energy + work done by the system
= change in internal energy - work done on the system

$\therefore q = \Delta E - w$

$\therefore q + w = \Delta E$ …..(1)

Differential form of the First Law

For an infinitesimal process, above equation takes the form

$$\delta q + \delta w = dE \quad \ldots 2$$

a) Change in internal energy is independent of the path taken. So in mathematical terms, an exact differential is always denoted by a notation d, e.g. dE in equation (2).

b) q and w are not state functions because changes in their magnitude is dependent on the path by which the change is accomplished. Mathematically q & w are not exact differentials and we always write the inexact – differential by δq, δw etc.

c) For a cyclic process, the change in the internal energy of the system is zero because the system is brought back to the original condition.

$$\oint dE = 0$$

or $\oint \delta q = -\oint \delta w$ i.e. the total work obtained is equal to the net heat supplied.

d) In an isolated system, there is no heat exchange with the surrounding i.e. $\delta q = 0$

$$\delta w = dE$$

The sign convention: According to latest S.I. convention, w is taken as negative if work is done by the system whereas it is taken as positive if work is done on the system. When heat is given by the system to surrounding it is given as negative sign. When heat is absorbed by the system from the surrounding then positive sign is given.

4THREMODYNAMIC PROCESSES

4.1 Heat Capacity

***It is defined as the quantity of heat required to raise the temperature of the system by one degree*.**

i.e. $C = \frac{dq}{dT}$ $C = \frac{q}{T_2 - T_1}$

where C = Heat capacity, dq = Amount of heat absorbed by the system

and dT = Rise in temperature.

Its unit is J K^{-1} or J /°C.

Specific heat

***The amount of heat required to raise the temperature of 1 gm of a substance by 1 degree is called specific heat*.**

. $\mathbf{q = m \times C_s \times \Delta T}$

The heat capacity of a system, especially in a gaseous system determined at constant volume is different from that at constant pressure.

At constant volume, $q_V = \Delta E$.   (As w = 0 at constant volume)

So, heat capacity at constant volume per mole,

$$C_V = \left(\frac{dE}{dT}\right)_V$$

At constant pressure, $q_P = \Delta H$.

So, heat capacity at constant pressure per mole,

$$C_P = \left(\frac{dH}{dT}\right)_P$$

Where C_P & C_V are molar heat capacities at constant pressure & constant volume respectively.

THE RELATIONSHIP BETWEEN C_p AND C_v FOR AN IDEAL GAS

At constant volume, the heat capacity, C is denoted by C_v and at constant pressure, this is denoted by C_p. Let us find the relationship between the two.

We can write equation for heat, q

at constant volume as $q_V = C_V \Delta T = \Delta U$

at constant pressure as $q_P = C_P \Delta T = \Delta H$

The difference between C_P and C_V can be derived for an ideal gas as :

For a mole of an ideal gas, $\Delta H = \Delta U + \Delta(pV)$

$$= \Delta U + \Delta(RT)$$

$$= \Delta U + R\Delta T$$

$$\therefore \quad \Delta H = \Delta U + R\Delta T$$

On putting the values of ΔH and ΔU, we have

$$C_P \Delta T = C_V \Delta T + R\Delta T$$

$$\Rightarrow C_P = C_V + R \Rightarrow \quad C_P - C_V = R$$

Poisson’s ratio (γ)

$$\gamma = C_P / C_V$$

for mono atomic gases, $C_V = \frac{3}{2}R,\ C_P = \frac{5}{2}R,\ \&\ \gamma = 1.66$

for diatomic gases $C_V = \frac{5}{2}R,\ C_P = \frac{7}{2}R,\ \&\ \gamma = 1.4$

for Tri atomic gases $C_V = \frac{6}{2}R,\ C_P = \frac{8}{2}R,\ \&\ \gamma = 1.33$

Thermodynamic changes in isothermal Process

Expressions for q, w, ΔU and ΔH

Temperature remains constant throughout the process of expansion. Since for an ideal gas, the internal energy (ΔU), depends only on temperature, the internal energy of the gas remains constant.

i.e. $\Delta U = 0$

From 1st law of thermodynamics,

$\Delta U = q + w$; For isothermal process, $\Delta U = 0$, hence

$q = -w$

The enthalpy change of the system is also zero as

$$\begin{aligned}\Delta H &= \Delta(U + pV) = \Delta U + \Delta(pV)\\ &= \Delta U + \Delta(nRT) = \Delta U + nR(\Delta T)\\ &= 0 + 0 = 0\end{aligned}$$

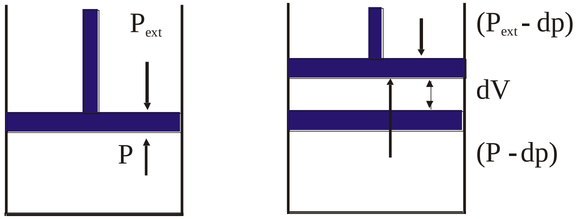
In the case of isothermal expansion, work is done by the system at the cost of heat absorbed. The magnitude of ‘q’ or ‘V’ depends on the manner in which the process of expansion is carried out i.e. reversibly or irreversibly.

(a) Work-done in Reversible isothermal expansion

Let us consider a non-insulated cylinder fitted with a weightless and frictionless piston containing an ideal gas. Let P be the pressure of the gas which equals external pressure, P_{ext}

$$P_{ext} = P$$

An infinitesimal expansion in volume, dV, results from an infinitesimal decrease in the external pressure, say dP. Consequently, the pressure of the gas inside the cylinder falls to (P_{ext} - dP) i.e. it equals again to the external pressure and the piston come to rest again.



work done by the gas in each step of expansion is

$$dw = -(P_{ext} - dp)\ dV = -P_{ext}\ dV = -PdV$$

Since temperature remains constant in an isothermal process, we have

$$w = -nRT\int_{V_1}^{V_2} \frac{dV}{V} = -nRT \ln \frac{V_2}{V_1}$$

In terms of pressure, we have

$$w = -nRT \ln \frac{p_1}{p_2}$$

Hence, for an isothermal reversible expansion or compression, we have

$$q = -w = nRT \ln \frac{V_2}{V_1} = nRT \ln \frac{p_1}{p_2}$$

$$\Delta U = \Delta H = 0$$

Example 1: One dm^3 of an ideal gas at a pressure of 1.0133 Mpa expands reversibly and isothermally from its volume to 10 dm^3. How much of heat is absorbed and how much of work is done in expansion?

Solution: For an ideal gas undergoing reversible volume change, we have

$$q = -w = nRT \ln \frac{V_2}{V_1}$$

The temperature in the above expression can be replaced in terms of p_1 and V_1 by using the ideal gas equation. Thus

$$q = (p_1V_1) \ln \frac{V_2}{V_1}$$

Substituting the values of p_1, V_1 and V_2, we have

$$q = (1.0133 \text{ MPa}) (1 \text{ dm}^3) \times 2.303 \times \log \left(\frac{10\,\text{dm}^3}{1\,\text{dm}^3}\right)$$

$$= 2.3336 \text{ MPa dm}^3 = 2.3336 \text{ kJ}$$

(b) Work done in irreversible isothermal expansion

Two types of irreversible change in volume may be distinguished, namely, expansion against a zero pressure (free expansion) and expansion or compression against a constant pressure (intermediate expansion or compression). The changes in q, w, ΔU and ΔH for these processes are given below.

Free expansion

Here

$$p_{ext} = 0$$

Therefore $w = \int dw = -\int p_{ext}\, dV = 0$

Thus, $q = -w = 0$

$$\Delta U = \Delta H = 0$$

Intermediate expansion or compression

Here, the work is done against a constant external pressure.

Therefore $$w = -\int_{V_1}^{V_2} p_{ext} dV = -p_{ext}(V_2 - V_1)$$

Hence, in the present case, we have

$$q = -w = p_{ext}(V_2 - V_1)$$

$$\Delta U = \Delta H = 0$$

It may be mentioned here that the magnitude of work involved in an intermediate expansion process will be less than that involved in the reversible expansion. Consequently, less heat will be absorbed in the case of intermediate expansion. On the other hand, the work involved in the intermediate compression process is larger than that involved in the reversible compression. Consequently, more heat will be released in the case of intermediate compression.

Example 2: (a)Five moles of an ideal gas at 293 K are expanded isothermally from an initial pressureof 0.4053 MPa to a final pressure of 0.1013 MPa against a constant external pressure of 0.1013 MPa. Calculate q, w, ΔU and ΔH.

(b)Calculate the corresponding values of q, w, ΔU and ΔH if the above process is carried outreversibly.

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

$$w = -p_{ext}(V_2 - V_1) = -p_{ext}\left(\frac{nRT}{p_2} - \frac{nRT}{p_1}\right) = -nRT\ p_{ext}\left(\frac{1}{p_2} - \frac{1}{p_1}\right)$$

Substituting the values, we get

$$w = -(5.0\text{mol})\,(8.314\text{JK}^{-1}\,\text{mol}^{-1})\ (293\ \text{K})\ (0.101\,3\ \text{MPa})$$

$$\times\left(\frac{1}{0.1013\text{MPa}} - \frac{1}{0.4053\text{MPa}}\right)$$

= – 9135.77 J □ – 9.136 kJ

Since temperature is constant

$$\Delta U = 0,\ \Delta H = 0 \text{ and } q = -w$$

(b) For an isothermal reversible expansion, we have

$$w = -nRT\ \ln\frac{V_2}{V_1} = -nRT\ \ln\frac{p_1}{p_2}$$

Substituting the values, we get

$$w = -(5.0\text{mol})(8.314\text{JK}^{-1}\text{mol}^{-1})(293\text{K}) \times 2.303 \times \log\left(\frac{0.405\,3\,\text{MPa}}{0.101\,3\,\text{MPa}}\right)$$

$$= -16\,889\ \text{J} = -16.889\text{kJ}$$

Example 3: 70 gms of nitrogen gas was initially at 50 atm and 25°C

a) It was allowed to expand isothermally against a constant external pressure of one atmosphere. Calculate, ΔU, ΔQ and ΔW assuming the gas to behave ideally.

b) Also find out the maximum work that would be obtained if the gas expanded reversibly and isothermally to one atmosphere.

Solution: a) Amount of gas $n = \frac{70}{28} = 2.5$ moles

Initial pressure; $P_1 = 50$ atm

Final pressure = 1 atm

Since the gas is ideal, $\Delta U = 0$, as the temperature is constant.

The work obtained $\Delta w = P_2 (V_2 - V_1)$

$$\Rightarrow P_2\left[\frac{nRT}{P_2} - \frac{nRT}{P_1}\right] = \frac{nRTP_2(P_1 - P_2)}{P_1 P_2}$$

$$= \frac{2.5 \times 2 \times 298 \times 1(50-1)}{50 \times 1}$$

= 1.5 Kcal

b) The maximum work for its isothermal reversible expansion.

$$\Delta W = nRT \ln \frac{P_1}{P_2}$$

$$= 2.303 \times 2.5 \times 2 \times 298 \log \frac{50}{1} = 5.8 \text{ Kcal}$$

4.3 Thermodynamic changes in adiabatic process

In adiabatic expansion or compression process heat is neither allowed to enter nor leave the system. Therefore

$$q = 0 \qquad (1)$$

So, according to the first law of thermodynamics, $\Delta U = q + w$, we have

$$\Delta U = w \qquad (2)$$

If there is an expansion, w will be negative and, therefore, ΔU will be negative, i.e., there will occur a decrease in the internal energy of the system and hence its temperature will fall. This amounts to the fact that the work is done by the system at the expense of internal energy.

If there is a compression, w will be positive and, therefore, ΔU will also be positive, i.e., there will occur an increase in the internal energy, and hence its temperature will rise. Here, the work is done by the surroundings on the system, which is stored as the internal energy.

Expression for q, w, ΔU and ΔH

We have seen above that

$$q = 0 \text{ and } w = \Delta U$$

$$\Delta U = U_2 - U_1 = nC_{V,m}(T_2 - T_1)$$

Thus, we have

$$w = \Delta U = nC_{V,m}(T_2 - T_1)$$

The change in enthalpy is given by

or $\Delta H = nC_{p,m}(T_2 - T_1)$

We have

$$w = \int dw = -\int p_{ext} dV = -\int p_{int} dV$$

Relationship between T and V

$$\left.\begin{aligned} & T\,V^{R/C_{V,m}} = \text{constant} \\ \text{or} \quad & T^{C_{V,m}/R}\,V = \text{constant} \\ \text{or} \quad & T\,V^{\gamma-1} = \text{constant} \end{aligned}\right\}$$

(where $\gamma = C_{p,m}/C_{V,m}$ & $R = C_{p,m} - C_{V,m}$)

Example 4: 20 g of N_2 at 300 K is compressed reversibly and adiabatically from 20 dm^3 to 10 dm^3. Calculate the final temperature, q, w, ΔU and ΔH.

Solution: Amount of N_2 = $\frac{(20\,g)}{(28\,g\,mol^{-1})} = 0.714 mol$

T_1 = 300 K ; V_1 = 20 dm^3 ; V_2 = 10 dm^3

For an adiabatic reversible process

$$T_2 V_2^{R/C_{V,m}} = T_1 V_1^{R/C_{V,m}}$$

Thus $T_2 = T_1 \left(\frac{V_1}{V_2}\right)^{R/C_{V,m}} = (300\ K)\left(\frac{20\,dm^3}{10\,dm^3}\right)^{2/5}$ = (300 K) (1.32) = 396 K

Hence $\Delta U = w = nC_{V,m}(T_2 - T_1) = (0.714\,mol)\left(\frac{5}{2} \times 8.314\,J\,K^{-1} mol^{-1}\right)(96 K)$

= 1 424.69 J

$$\Delta H = nC_{p.m}(T_2 - T_1) = (0.714\,mol)\left(\frac{7}{2} \times 8.314\,J\,K^{-1}\,mol^{-1}\right)(96 K)$$

= 1 994.56 J

Relationship between T and p

Replacing V in Eq. (7) by RT/p, we get

$$T^{C_{V,m}}\left(\frac{RT}{p}\right)^R = \text{constant}$$

or $T^{C_{p,m}} p^{-R}$ = constant

The alternate forms of this expression are

$$\left.\begin{aligned} T\,p^{-R/C_{p,m}} &= \text{constant} \\ T^{-C_{p,m}/R}\;p &= \text{constant} \\ Tp^{(1-\gamma)/\gamma} &= \text{constant} \\ T^{\gamma/(1-\gamma)}\;p &= \text{constant} \end{aligned}\right\}$$

Relationship between p and V

or $p^{C_{V,m}}V^{C_{p,m}} = \text{constant}$

The alternate form of this expression is

$PV^{\gamma} = \text{constant}$ where $\gamma = (C_{p,m}/C_{V,m})$

Example 5: A sample of a gas initially at 27°C is compressed from 40 litres to 4 litres adiabatically and reversibly. Calculate the final temperature ($C_v = 5$ cal/mole)

Solution: Assuming ideal behaviour

$C_p = C_v + 2 = 7$ cal / mole

$\therefore \gamma = C_p/C_v = 7/5$

If T be the final temperature thus

$$\frac{T}{300} = \left(\frac{40}{4}\right)^{\gamma-1}$$

$T = 300 \times (10)^{7/5-1} = 753.6°K$

(a)Irreversible Expansion or Compression Process

Here again, we consider two cases, namely, free expansion and intermediate expansion or compression processes.

Free expansion

In a free expansion, we have $p_{ext} = 0$

Thus $dw = -p_{ext} dV = 0$

Now according Eq. (2), we have dU = 0

Since, for an ideal gas, *U = f(T)*, it follows that the temperature of the gas after expansion remains unchanged.

Now dH = dU + d(pV) = dU + d(nRT) = dU + nR dT

= 0 + 0 = 0

For a finite change, we will have

$$w = 0,\ \Delta U = 0, \qquad \Delta T = 0, \qquad \Delta H = 0$$

Comparing these changes of properties with those of the isothermal free expansion, we find that the adiabatic irreversible free expansion of an ideal gas is identical with the isothermal free expansion.

Calculation of temperature

In some expansion or compression processes, the values of p_{opp}, p_1, p_2 and T_1 are provided. In such a case, first of all we calculate the temperature of the gas after the expansion or compression.

$$nC_{V,m}(T_2 - T_1) = -p_{ext}(V_2 - V_1) = p_{ext}(V_1 - V_2)$$

Replacing V_2 and V_1 in terms of T and p, we get

$$nC_{V,m}(T_2 - T_1) = p_{ext}\left(\frac{nRT_1}{p_1} - \frac{nRT_2}{p_2}\right) \qquad (18)$$

For a special case, where $p_{ext} = p_2$ (the pressure of the gas after expansion), we get

$$C_{V,m}(T_2 - T_1) = p_2\left(\frac{RT_1}{p_1} - \frac{RT_2}{p_2}\right) \qquad (19)$$

Rearranging this, we get

$$T_2 = T_1\left(\frac{C_{V,m} + R\,p_2/p_1}{C_{p,m}}\right) \qquad (20)$$

After knowing T_2 from Eq. (20) (or from Eq. 18 if p_{ext} is not equal to p_2), we can calculate ΔU and ΔH from Eqs. (15) and (16) respectively.

Example 6: 2.0 mol of an ideal diatomic gas at 300 K and 0.507 MPa are expanded adiabatically to a final pressure of 0.203 MPa against a constant pressure of 0.101 MPa. Calculate the final temperature, $q, w, \Delta U$ and ΔH

Solution: For an adiabatic process q = 0

$$w = -p_{ext}(V_2 - V_1) = -p_{ext}\left(\frac{nRT_2}{p^2} - \frac{nRT_1}{p_1}\right) \qquad \Delta U = w$$

i.e. $$nC_{V,m}(T_2 - T_1) = p_{ext}\, nR\left(\frac{T_1}{p_1} - \frac{T_2}{p_2}\right)$$

$C_{V,m}$ for a diatomic molecule $= \frac{5}{2}R$

Substituting the expression of $C_{V,m}$ in the previous expression, we get

$$n\left(\frac{5}{2}R\right)(T_2 - T_1) = p_{ext}\, nR\left(\frac{T_1}{p_1} - \frac{T_2}{p_2}\right)$$

Substituting the values, we get

$$\frac{5}{2}(T_2 - 300\,K) = (0.101 MPa)\left(\frac{300\,K}{0.507\,MPa} - \frac{T_2}{0.203 MPa}\right)$$

Solving for T_2, we get, $T_2 = 270\,K$

Thus $\Delta U = nC_{V,m}(T_2 - T_1) = (2.0\,mol)\left(\frac{5}{2} \times 8.314\,JK^{-1}mol^{-1}\right) \times (270\,K - 300\,K)$

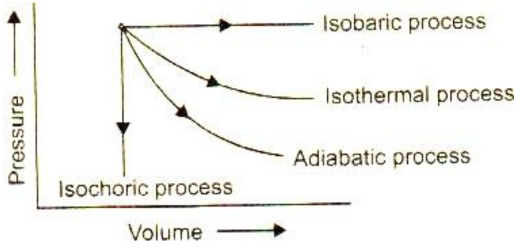
$$= -1\ 247.1 J$$

$$\Delta H = \Delta U + nR(\Delta T) = -1\,247.1 J + (2.0 mol)(8.314 JK^{-1}mol^{-1})(-30K)$$

$$= -1745.9\ J$$

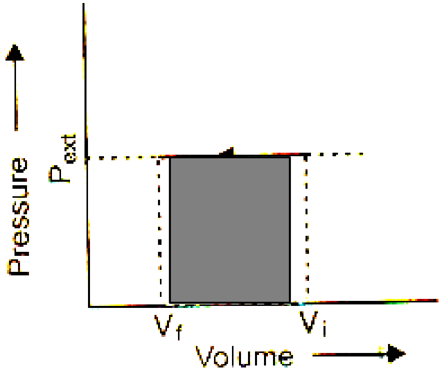
Graphical representation of thermodynamic processes

Graphically, different processes can be represented as



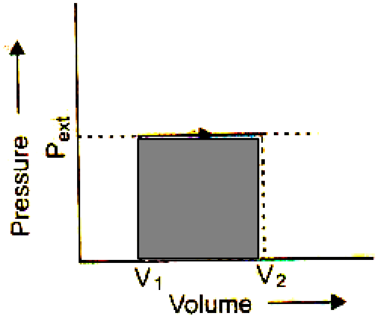
WORK AS AREA UNDER GRAPH

Let a gas compressed from V_i to V_f by an external pressure of P_{ext} . The work done can be calculated by the shaded area as shown in fig. Work is +ve since $V_i > V_f$

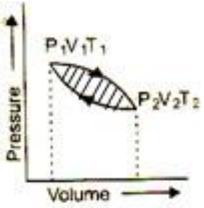


As $w = -P_{ext}\Delta V$ = Area under the curve and x-axis

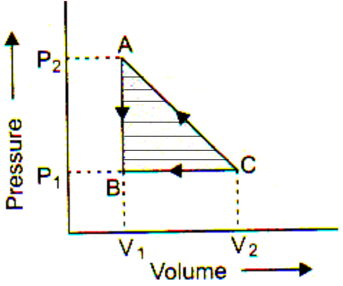
Let a gas is expanded from V_i to V_f against an external pressure of P_{ext} . The work done can be calculated by the shaded area as shown in fig. Work is -ve since $V_i < V_f$



Work in a cyclic process is given by area enclosed by the cycle.



Shaded area gives the net work done by the gas



***Example* 1:**

When a poly atomic gas undergoes an adiabatic process, its temperature and volume are related by the equation TV^n = constant, the value of n will be

(a) 1.33 (b)0.33 (c)2.33 (d)1

Solution:

For adiabatic process

$TV^{\gamma-1}$ = constantfor poly atomic gas $\gamma = \frac{4}{3} = 1.33$

n = 1.33 – 1 = 0.33 ∴ **(b)**

***Example* 2:**

The difference between the heats of reaction at constant pressure and a constant volume for the reaction $2C_6H_6(l) + 15O_2(g) \downarrow \rightarrow 12CO_2(g) + 6H_2O(l)$ at 25°C in kJ is

(a) – 7.43 (b) + 3.72 (c) – 3.72 (d) + 7.43

Solution:

$\Delta H = \Delta E + \Delta n_g RT$. Here $\Delta n_g = 12 - 15 = -3$. Thus, $\Delta H - \Delta E = -3 \times 8.314 \times 298 = -7.43$ kJ.

$\therefore$ **(a)**

***Example* 3:**

A mono atomic gas X and a diatomic gas Y, both initially at the same temperature and pressure are compressed adiabatically from a volume V to V/2, which gas will be at higher temperature

(a) X (b)Y (c)both the same (d)can’t say

Solution:

$$T_1V_1^{\gamma-1} = T_2V_2^{\gamma-1}$$

$$\therefore \quad \frac{T_2}{T_1} = \left(\frac{V_1}{V_2}\right)^{\gamma-1} = 2^{\gamma-1}$$

Since γ is more for the gas X, the temperature will also be more for it.

$\therefore$ **(a)**

THERMOCHEMISTRY

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

Δn_g = change in moles for gaseous species

.

Heat of reaction

$\Delta H = \sum H_P - \sum H_R$.

$H_2(g) + ½\, O_2(g) \downarrow \rightarrow H_2O(g)$; $\Delta H = -57.8$ kcal
$H_2(g) + ½\, O_2(g) \downarrow \rightarrow H_2O(l)$; $\Delta H = -68.32$ kcal

Difference in the value of ΔH is observed because heat is evolved when steam condenses.

$C(diamond) + O_2(g) \downarrow \rightarrow CO_2(g)$; $\Delta H = -94.3$ kcal
$C(amorphous) + O_2(g) \downarrow \rightarrow CO_2(g)$; $\Delta H = -97.6$ kcal

The difference between the two values is equal to the heat absorbed when 12 g of diamond is converted into 12 g of amorphous carbon. This is called heat of transition.

$C(diamond) \downarrow \rightarrow C(amorphous)$; $\Delta H = 3.3$ kcal.

(III) TEMPERATURE

Relation between ΔH or ΔE and temperature are given by Kirchoff's equation.

$$(\Delta H_2 - \Delta H_1) = \Delta C_P\ (T_2 - T_1)$$

$$(\Delta E_2 - \Delta E_1) = \Delta C_V\ (T_2 - T_1)$$

$$\frac{\Delta H_{T_2} - \Delta H_{T_1}}{(T_2 - T_1)} = \Delta C_P$$

$$\frac{\Delta E_{T_2} - \Delta E_{T_1}}{(T_2 - T_1)} = \Delta C_V$$

Example 7:Consider a reaction,

$$H_2O(g) \downarrow \rightarrow H_2(g) + \tfrac{1}{2} O_2(g) \; ; \Delta H^\circ = 241.750 \text{ J at } 291.15 \text{ K.}$$

What would be ΔH° at 298.15 K? Over the small temperature range, the effectively constant C_P values per mole are

$$C_P(H_2O) = 33.56, \quad C_P(H_2) = 28.83 \; ; C_P(O_2) = 29.12 \text{ JK}^{-1} \text{ mol}^{-1}.$$

Solution: (a) $\dfrac{\Delta H^\circ_{298.15} - \Delta H^\circ_{291.15}}{298.15 - 291.15} = \Delta C_P$

Now, $\Delta C_P = C_P(H_2) + \tfrac{1}{2} C_P(O_2) - C_P(H_2O) = 28.83 + \dfrac{29.12}{2} - 33.56 = 9.83 \text{ J K}^{-1}.$

$\therefore \Delta H^\circ_{298} = $ **241.820J**

Example 8: **For Ag, $\bar{C}_p$(JK^{-1} mol^{-1}) is given by 23.43 + 0.00628 T. 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,

$$\Delta H = \int_{T_1}^{T_2} C_p\,dT = \int_{T_1}^{T_2} (23.43 + 0.00628T)\,dT$$

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

Since, T_1 = 273.15 + 25 = 298.15 K and T_2 = 273.15 + 961 = 1234.15 K.

$(T_2 - T_1)$ = 936 K

$\Delta H = 23.43(936) + \frac{1}{2}(0.00628)\,[(1234.15)^2 - (298.15)^2] = 21930 + 4500$

= 26430 J/mol.

For 3 mol, ΔH = 3(26430) J = **79290 J**

5.2 Law of Thermochemistry

1. Lavoisier and Laplace Law: According to this “enthalpy of decomposition of a compound is numerically equal to enthalpy of formation of that compound with opposite sign. e.g.

$$C(s) + O_2(g) \downarrow \ \downarrow \rightarrow CO_2(g) \ ; \ \Delta H = -94.3 \text{ kcal}$$

$$CO_2(g) \downarrow \ \downarrow \rightarrow C(g) + O_2(g) \ ; \Delta H = +\ 94.3 \text{ kcal}$$

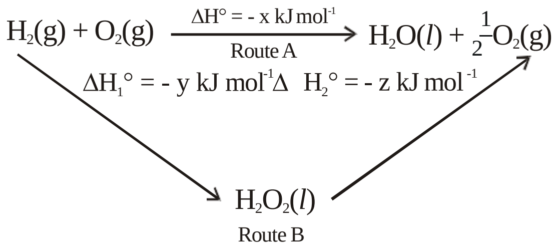
In general

$$A + B \rightarrow C + D \qquad \Delta H$$

$$C + D \rightarrow A + B \qquad -\Delta H$$

2. Hess’s Law of Constant Heat Summation:

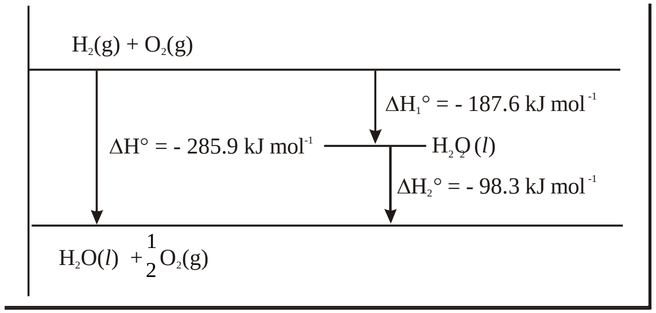
For a chemical equation that can be written as the sum of two or more steps, the enthalpy change for the overall equation is equal to the sum of the enthalpy changes for the individual steps.



For the above example

$$\Delta H° = \Delta H_1° + \Delta H_2°$$

An energy level diagram for the above reaction cycle is shown in figure



Applications :

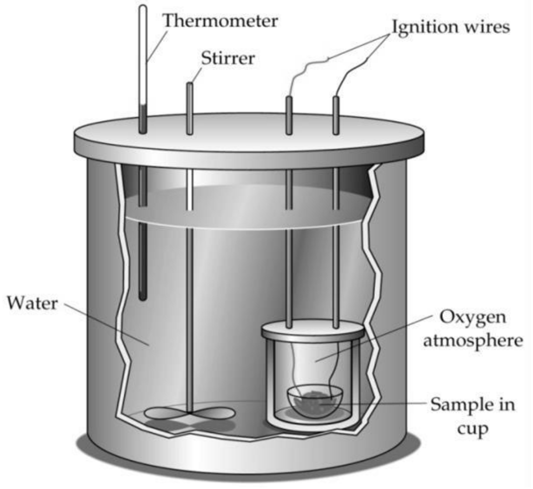
1. In the determination of several heats of reactions like heat of formation, heat of transition, heat of combustion etc.
2. In the determination of lattice energy of crystals, electron affinities of elements, enthalpy of dissociation of acids etc using Born-Haber cycle.

Calorimetry

. Measurements are made under two different conditions :

(i) at constant volume, q_V

(ii) at constant pressure, q_p

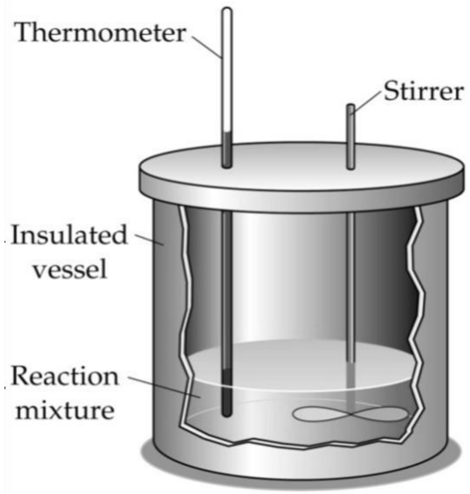


Calculation of q_V (Bomb Calorimeter) :

Since the reaction in a bomb calorimeter proceeds at constant volume, the heat of combustion measured is ΔE.

$$\Delta E = \left(\frac{(W + m)(T_2 - T_1) \times s}{W_1} \times M \right) \text{kcal}$$

where M is the molar mass of the substance and w_1 is the mass of the substance taken, specific heat. ΔH can be calculated from the relation, $\Delta H = \Delta E + \Delta n_g RT$



5.4 *Heat of formation*

It is enthalpy change of a reaction by which a compound is formed from its constituent elements, the reactants and products all being in a given, standard state (i.e. at 298 K and 1 atm pressure).

For example,

$$C_{(S)} + O_{2_{(g)}} \rightarrow CO_{2_{(g)}} \qquad \Delta H_f$$

$$H_{2(g)} + \frac{1}{2}O_{2(g)} \rightarrow H_2O_{(l)} \qquad \Delta H_f$$

$$\frac{1}{2}N_{2(g)} + \frac{1}{2}O_{2(g)} \rightarrow NO_{(g)} \qquad \Delta H_f$$

$$H_{2(g)} + \frac{1}{8}S_{8(s)} + 2O_{2(g)} \rightarrow H_2SO_{4(l)} \qquad \Delta H_f$$

STANDARD ENTHALPY OF FORMATION (H°_f)

It is enthalpy change of a reaction by which a compound is formed from its constituent elements, the reactants and products all being in a given, standard state (i.e. at 298 K and 1 atm pressure). For example,

$$S(s) + O_2(g) \downarrow \rightarrow SO_2(g) \;;\; \Delta H^\circ_f = -296.9 \text{ kJ}$$

$$2Al(s) + \frac{3}{2}O_2(g) \downarrow \rightarrow Al_2O_3(s) \;;\; \Delta H^\circ_f = -1669.8 \text{ kJ}$$

Let us consider a reaction, $C(s) + O_2(g) \downarrow \rightarrow CO_2(g) \;;\; \Delta H^\circ_f = -393.5 \text{ kJ}$

$$\Delta H^\circ_f = H^\circ_P - H^\circ_R = -393.5 \text{ Kj}$$

Enthalpies of free elements in their standard states are assumed to be zero.

so, $\Delta H^\circ_f = \Delta H^\circ_P = -393.5\,kJ$

$$\Delta H^\circ \text{ of a reaction} = \begin{bmatrix}\text{Sum of the standard heats}\\ \text{of formation of products}\end{bmatrix} - \begin{bmatrix}\text{Sum of the standard heats}\\ \text{of formation of reactants}\end{bmatrix}$$

i.e. $\Delta H^\circ = \sum \Delta H^\circ_f(\text{Products}) - \sum \Delta H^\circ_f(\text{reac tants})$

Heat of Combustion

It is the amount of heat evolved when one mole of a compound is completely burned in excess of oxygen

$$CH_4(g) + 2O_2(g) \downarrow \rightarrow CO_2(g) + 2H_2O(l) \quad ; \Delta H^\circ = -890.36\,kJ/mol$$

Enthalpy of Neutralisation

Enthalpy change associated with complete neutralisation of 1g equivalent of an acid with 1g equivalent of a base in dilute solution.

$$H^+ + OH^- = H_2O \qquad \Delta H = -13.68\ kcal\ geq^{-1}.$$

However, if weak acids or bases are involved, part of it is used up in their dissociation (called enthalpy of dissociation, q).

ΔH_{weak} neutralization = -13.68 + q .

Hence, ΔH_{weak} neutralization is mostly lesser than ΔH_{strong} neutralization

Enthalpies of phase transition

(i) ENTHALPY OF FUSION

$H_2O(s) \downarrow \rightarrow H_2O(l)$; ΔH_{fusion}

(ii) ENTHALPY OF VAPOURISATION

$H_2O(l) \downarrow \rightarrow H_2O(g)$; ΔH_{vap}

(iii)ENTHALPY OF SUBLIMATION

$I_2(s) \downarrow \rightarrow I_2(g)$; $\Delta H_{sublimation}$

$\Delta H_{sublimation} = \Delta H_{fusion} + \Delta H_{vapourization}$

(IV) HEAT OF ATOMISATION

$C(s) \downarrow \rightarrow C(g)$; $\Delta H = 171.7$ kcal/mol

$H_2(g) \downarrow \rightarrow 2H(g)$; $\Delta H = 104$ kcal

In this case, heat of atomization of hydrogen is 52 kcal/mol.

Enthalpy or Heat of solution

$H_2SO_4(l)$ + aqueous $\downarrow \rightarrow$ $H_2SO_4(aq)$; $\Delta H = -20.2$ kcal

$KCl(s)$ + aqueous $\downarrow \rightarrow$ $KCl(aq)$; $\Delta H = 4.4$ kcal

Heat ofdilution

$HCl(g) + 10H_2O \downarrow \rightarrow HCl.10H_2O$; $\Delta H_1 = -69.01$ kJ/mol

$HCl(g) + 25H_2O \downarrow \rightarrow HCl.25H_2O$; $\Delta H_2 = -72.03$ kJ/mol

$HCl(g) + 40H_2O \downarrow \rightarrow HCl.40H_2O$; $\Delta H_3 = -72.79$ kJ/mol

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$HCl(g) + \infty H_2O \downarrow \rightarrow HCl.\infty H_2O$; $\Delta H_\infty = -74.85$ kJ/mol.

If we subtract first equation from the second in the above set, we get

$HCl.10H_2O + 15H_2O \downarrow \rightarrow HCl.25H_2O$; $\Delta H = (\Delta H_2 - \Delta H_1) = -3.02$ kJ/mol

.

Bond energy

The amount of energy required to break one mole of a particular type of bond between the atoms in the gaseous state i.e. to separate the atoms in the gaseous state under one atmospheric pressure and the specified temperature is called bond dissociation energy.

e.g. $H\text{–}H(g) \downarrow \rightarrow 2H(g)$; $\Delta H = 433 \text{ kJ mol}^{-1}$.

$H\text{–}I(g) \downarrow \rightarrow H(g) + I(g)$; $\Delta H = 299 \text{ kJ mol}^{-1}$.

. ***This average bond dissociation energy required to break each bond in a compound is called bond energy which is also the heat of formation of the bond from gaseous atoms constituting the bond with reverse sign***.

$H_2O(g) \downarrow \rightarrow H(g) + O\text{–}H(g)$; $\Delta H = 497.8 \text{ kJ mol}^{-1}$

$O\text{–}H(g) \downarrow \rightarrow H(g) + O(g)$; $\Delta H = 428.5 \text{ kJ mol}^{-1}$.

$$\therefore \text{ B.E. of O–H bond} = \frac{497.8 + 428.5}{2} = 463.15 \text{ kJ mol}^{-1}.$$

APPLICATIONS OF BOND ENERGIES

(i) DETERMINATION OF HEAT OF REACTIONS

$\Delta H_{\text{reaction}}$ = Sum of bond energies of reactants – Sum of bond energies of products.

(ii) DETERMINATION OF RESONANCE ENERGY

Resonance Energy =(Experimental or actual heat of formation) – (Calculated heat of formation).

Example 13:For the reactions given below, predict the sign of ΔS as positive or negative?

(a)$2NO(g) + O_2(g) \downarrow \rightarrow 2NO_2(g)$

(b)$Ni(s) + 4CO(g) \downarrow \rightarrow Ni(CO)_4(g)$

(c)$2Ca(s) + O_2(g) \downarrow \rightarrow 2CaO(s)$

(d)$H_2(g) + S(s) \downarrow \rightarrow H_2S(g)$

Solution: (a) Three gas molecules give rise to two gas molecules. Hence, disorderness decreases i.e., $\Delta S < 0$ (negative).

(b) Four gas molecules are converted into a single gas molecule and hence, the disorderness decreases i.e., ΔS is < 0 (negative).

(c) Three reacting units, of which two are solid and one gas are changed to two solid units. Disorderness decreases i.e. $\Delta S < 0$ (negative).

(d) Two reacting units, one of which is a solid, forms a gaseous molecule. Since a heteronuclear gas results, disorderness increases &ΔS is positive ($\Delta S > 0$).

Example 14: 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 and 80 cal/ gmrespectively.

Solution: Entrophy change during condensation of steam

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

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

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

Entrophy change during freezing of water at 0°C

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

So total entropy change = –26.06 – 5.62 – 5.27 = –36.95 cal/°C

Hence difference in entropy between steam and ice = 36.95 cal/°C

Example** 4:

Heat of neutralization of oxalic acid is –53.35 kJ mol^{-1} using NaOH. Hence ΔH of $H_2C_2O_4 \rightleftharpoons C_2O_4^{2-} + 2H^+$ is

(a) 5.88 kJ (b)–5.88 kJ (c)–13.7 kcal (d)7.9 kJ

Solution:

By the definition of heat of neutralization, we have

$\frac{1}{2} H_2C_2O_4 + NaOH \downarrow \rightarrow \frac{1}{2} Na_2C_2O_4 + H_2O$; $\Delta H = -53.35$ kJ

or $\frac{1}{2} H_2C_2O_4 + OH^- \downarrow \rightarrow \frac{1}{2} C_2O_4^{2-} + H_2O$;$\Delta H = -53.35$ kJ …(i)

$H^+ + OH^- \downarrow \rightarrow H_2O$ $\Delta H = -57.3$ kJ…(ii)

Subtracting equation (ii) from (i) we get

$\frac{1}{2} H_2C_2O_4 \downarrow \rightarrow \frac{1}{2} C_2O_4^{2-} + H^+$ $\Delta H = 3.95$ kJ

$\therefore$ $H_2C_2O_4 \downarrow \rightarrow \frac{1}{2} C_2O_4^{2-} + H^+$ $\Delta H = 7.9$ kJ $\therefore$ **(d)**

***Example* 5:**

The standard heat of formation values of SF_6(g), S(g) and F(g) are: –1100, 275 and 80 kJ mol^{-1} respectively. Then the average S – F bond energy in SF_6

(a) 301 kJ mol^{-1} (b)320 kJ mol^{-1} (c)309 kJ mol^{-1} (d)280 kJ mol^{-1}

Solution:

$S(s) + 3F_2(g) \downarrow \rightarrow SF_6(g)$; $\Delta H_f = -1100$ kJ mol^{-1}

$S(s) \downarrow \rightarrow S(g)$; $\Delta H = +275$ kJ mol^{-1}

$\frac{1}{2} F_2(g) \downarrow \rightarrow F(g)$; $\Delta H = 80$ kJ mol^{-1}

Therefore heat of formation = Bond energy of reactants– Bond energy of products

$-1100 = [275 + 6 \times 80] - [6 \times S - F]$

Thus bond energy of S – F = 309 kJ mol^{-1}

***Example* 6:**

At a particular temperature $H^+(aq) + OH^-(aq) \downarrow \rightarrow \quad H_2O(l)$; $\Delta H = -57.1$ kJ

The approximate heat evolved when 400 ml of 0.2 M H_2SO_4 is mixed with 600 ml of 0.1 M KOH solution will be

(a)3.426 kJ (b)13.7 kJ (c)5.2 kJ (d)55 kJ

Solution:

Number of equivalent of H_2SO_4 taken = $\frac{0.2 \times 2 \times 400}{1000} = 0.16$

Number of equivalent of KOH added = $\frac{600 \times 0.1}{1000} = 0.06$

Number of equivalents of acid and bases which neutralized each other = 0.06

$\therefore$ Heat evolved = 0.06×57.1 kJ = 3.426 kJ**(a)**

***Example* 7:**

A sample of oxygen gas expands its volume from 3 litre to 5 litre against a constant pressure of 3 atm. If the work done during expansion be used to heat 10 mole of water initially present at 290 K, its final temperature will be

(Specific heat capacity of water = 4.18 J K^{-1} g^{-1})

(a) 292.0 K (b)290.8 K (c)298.0 K (d)293.7 K

Solution:

Work done in expansion

$= P \times \Delta V$

$= 3 \times (5 - 3) = 6$ lit-atm

we have 1 litre atm = 101.3 J

work done = 6×1.013 J = 607.8 J

Let ΔT be the change in temperature of water.

$\therefore P\Delta V = m \times s \times \Delta T$

$607.8 = 180 \times 4.184 \times \Delta T$

$\Delta T = 0.81$ K

$T_f = T_1 + \Delta T = 290.8$K

$\therefore$ **(b)**

***Example* 8:**

The molar heat capacity of water in equilibrium with ice at constant pressure is

(a)zero **(b)infinity (∞)**

(c)40.45 kJ $K^{-1}mol^{-1}$ **(d)75.48 J $K^{-1}mol^{-1}$**

Solution:

We know that heat capacity at constant pressure is given by

$$C_P = \left(\frac{\Delta H}{\Delta T}\right)_P$$

Since the phase transformation i.e., ice $\rightleftharpoons$ water, takes place at a fixed temperature so $\Delta T = 0$.

$$\therefore\ C_P = \frac{\Delta H}{0} = \infty$$

$\therefore$ **(b)**

Example 9:

One mole of ice is converted into water at 273 K. The entropies of $H_2O(s)$ and $H_2O(l)$ are 38.20 and 60.01 J mole^{-1} K^{-1} respectively. The enthalpy change for the conversion is

(a)59.54 J mol^{-1} (b)5954 J mole^{-1} (c)594.5 J mole^{-1} (d)320.6 J mole^{-1}

Solution:

$\Delta G = \Delta H - T\Delta S$. At equilibrium $\Delta G = 0$, so $\Delta H = T\Delta S$. $\Delta H = 273 \times (60.01 - 38.20) = 5954.13$ J mole^{-1}.

$\therefore$ **(b)**

Example 10:

The ΔH_f° for $CO_2(g)$, $CO(g)$ and $H_2O(g)$ are –393.5, –110.5 and –241.8 kJ. mole^{-1} respectively. The standard enthalpy change in kJ for the reaction.

$CO_2(g) + H_2(g) \downarrow \rightarrow CO(g) + H_2O(g)$ is

(a)+ 524.1 (b)+ 41.2 (c)– 262.5 (d)– 41.2

Solution:

(a)$C(s) + O_2(g) \downarrow \rightarrow CO_2(g)$;ΔH = –393.5kJ mole^{-1}

(b)$C(s) + \frac{1}{2} O_2(g) \downarrow \rightarrow CO(g)$; ΔH = – 110.5 kJ mole^{-1}

(c) $H_2(g) + \frac{1}{2} O_2(g) \downarrow \rightarrow H_2O(g)$; ΔH = –241.8 kJ mole^{-1}

For getting $CO_2(g) + H_2(g) \downarrow \rightarrow CO(g) + H_2O(g)$, add (b) and (c) and subtract (a). Thus –110.5 –241.8 + 393.5 = 395.5 – 352.3 = 41.2 kJ mole^{-1}.

$\therefore$ **(b)**

Example 9: ***The enthalpy of neutralisation of ammonium hydroxide by hydrochloric acid is 51.46 kJ mol^{-1}. Calculate the enthalpy of ionisation of ammonium hydroxide.***

Solution: i) $NH_4OH\ (aq) + H^+\ (aq) \downarrow\rightarrow NH_4^+\ (aq) + H_2O\ (l);\ \Delta H° = -51.46$ kJ/ mol

ii) $H^+(aq) + OH^-\ (aq)\downarrow \rightarrow\ H_2O(l);\qquad \Delta H° = -\ 57.32$ kJ mol^{-1}

iii) $NH_4OH\ (aq) \downarrow\rightarrow NH_4^+\ (aq) + OH^-\ (aq);\ \ \Delta H^0 = \Delta H^0$ ionisation

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

$NH_4OH\ (aq) + H^+\ (aq)\ NH^+_4\downarrow\rightarrow NH^+_4\ (aq) + H_2O(l)$

or $\Delta\ H^0 = -57.32 + \Delta H°_{\text{ionisation}}$

From equation (i), we have, $\Delta H^0 = -51.46$ kJ mol^{-1}

Hence $(-57.32 + \Delta H^0_{\text{ionisation}})$kJ mol^{-1} = –51.46 kJ mol^{-1}

or $\Delta H^0_{\text{Ionisation}} = +\ 5.86$ kJ mol^{-1}.

Example 10: ***If E_{C-C} is 344 kJ mole^{-1} and E_{C-H} is 415 kJ mole^{-1}, calculate the heat of formation of propane. The heats of atomization of carbon and hydrogen are 716 kJ mole^{-1} and 433 kJ mole^{-1} respectively.***

Solution: The heat of formation is the sum of the heats of atomization and bond energies. For propane, the heats of atomization are

$3C_{(s)} = 3C_{(g0}$; $\Delta H = 3 \times 716 = 2148$ kJ

$4H_{2,(g)} = 8H_{(g)}$; $\Delta H = 4\times 433 = 1732$ kJ

The bond energies are

$2E_{C-C} = 2 \times -344 = -688$ kJ

$8E_{C-H} = 8 \times -415 = -3320$ kJ

Adding,

$3C + 4H_2 = C_3H_8$; $\Delta H_f = 2148 + 1732 - 688 - 3320 =$ **-128 kJ mole^{-1}**

Example 11:150 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 neutralisation of nitric acid with sodium hydroxide.

Solution: Total mass of solution = 150 + 150 = 300 gm

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

$\therefore$ Heat of neutralisation = $\frac{Q}{150} \times 1000 \times \frac{1}{0.5} = \frac{1026}{150} \times 1000 \times \frac{1}{0.5} = 13.68$ kcal.

Since, the enthalpy of neutralisation is always –ve, so, heat of neutralisation = **– 13.68 kcal**.

Example 12: A sample of 0.16 g CH_4 was subjected to combustion at 27°C in a bomb calorimeter. The temperature of the calorimeter system (including water) was found to rise by 0.5°C. Calculate the heat of combustion of methane at (i) constant volume and (ii) constant pressure. The thermal capacity of calorimeter system is 17.7 kJ K^{-1} and R = 8.314 $JK^{-1}mol^{-1}$.

Solution: Heat of combustion at constant volume, ΔE

$$= \text{Heat capacity of calorimeter} \times \text{Rise in temperature} \times \frac{\text{Molar mass of compound}}{\text{Mass of compound}}$$

$$= 17.7 \times 0.5 \times \frac{16}{0.16} = 885$$

i.e., ΔE = **– 885 kJ mol^{-1}**

$$CH_4(g) + 2O_2(g) \downarrow\downarrow\rightarrow CO_2(g) + 2H_2O(l)$$

$\Delta n_g = 1 - 3 = -2$, T = 300 K, $R = 8.314 \times 10^{-3}$ kJ K^{-1} mol^{-1}

$\Delta H = \Delta E + \Delta n_g RT = -885 + (-2) \times 8.314 \times 10^{-3} \times 300$

$= -885 - 4.988 =$ **– 889.988 kJ mol^{-1}**

SECOND LAW OF THERMODYNAMICS

Limitations of 1st law:

1. First law gives definite relationship between the heat absorbed and the work done by the system in a given process, but it does not tell about the direction of flow of heat

2. According to first law energy of an isolated system remains constant during a specified change of state. But it does not tell whether that specified change including a chemical reaction can occur spontaneously i.e. whether it is feasible.

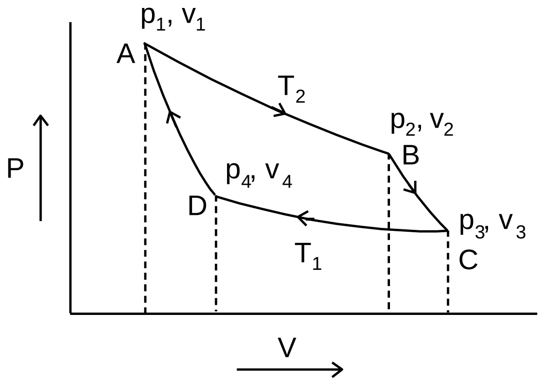
3. First law states that energy of one form can be converted to an equivalent amount of energy of another form but it does not tell that heat cannot be completely converted into an equivalent amount of work without producing some change elsewhere.

Advantage of Second Law :

1. Second law helps us to determine the direction in which energy can be transferred
2. It helps us to predict whether a given process or a chemical reaction can occur spontaneously.
3. It helps us to know the equilibrium conditions of a chemical reaction.
4. It helps us to calculate the maximum fraction of heat that can be converted to work in a given process.

Carnot cycle

It is a reversible cycle which demonstrates maximum convertibility of heat into work. The system consists of one mole of ideal gas which is subjected to a series of four successive operations.



Path AB : Isothermal expansion :

The gas is allowed to expand reversibly and isothermally at a higher temperature T_2. The gas absorb q_2 amount of heat and perform a work $-w_1$.

$$q_2 = -w_1 = RT_2 \ln \frac{V_2}{V_1}$$

Path BC : Adiabatic expansion :

The gas is allowed to expand adiabatically from volume V_2 to V_3. Here heat absorbed q = 0. As a result of this expansion temperature falls to T_1. Work done by the system, $-W_2 = C_V (T_1 - T_2)$

Path CD : Isothermal compression :

The gas is subjected to isothermal compression at constant temperature T_1. Heat given out by the gas is $-q_1$ and work done on the gas is W_3

$$-q_1 = W_3 = RT \ln \frac{V_4}{V_3}$$

Path DA : Adiabatic compression :

The gas is now subjected to adiabatic compression and restored to original volume V_1. As a result of this compression the temperature increases from T_1 to original T_2. Here heat given out by gas is zero and the work done on gas $W_4 = C_V(T_2 - T_1)$

$$\text{Network done } (-W) = RT_2 \ln \frac{V_2}{V_1} + C_V(T_1 - T_2) + RT_1 \ln \frac{V_4}{V_3} + C_V(T_2 - T_1)$$

$$= RT_2 \ln \frac{V_2}{V_1} + RT_1 \ln \frac{V_4}{V_3}$$

$$= R(T_2 - T_1) \ln \frac{V_2}{V_1} \qquad \left[\because \frac{V_2}{V_1} = \frac{V_3}{V_4}\right]$$

$$\text{Net heat absorbed} = q_2 - q_1$$

$$= RT_2 \ln \frac{V_2}{V_1} + R\,T_1 \ln \frac{V_4}{V_3} = R(T_2 - T_1) \ln \frac{V_2}{V_1}$$

$\therefore$ net work done = net heat absorbed

$$-\frac{W}{q_2} = \frac{T_2 - T_1}{T_2}$$

Since, $\frac{T_2 - T_1}{T_2} < 1$, $-W < q_2$

i.e. work done by the system is lesser than heat absorbed.

So, only a part of the heat absorbed by the system at higher temperature T_2 is converted to work, the rest of the heat q_1 is given out to the surroundings when the system is at lower temperature T_1.

Second law of thermodynamics

It is impossible to use a cyclic process to extract heat from a reservoir and to convert into work without transforming at the same time a certain amount of heat from a hotter to a colder part of the body or It is impossible to convert heat into work without compensation.

Efficiency of heat engine:

The fraction of heat absorbed by an engine which it can convert into work gives its efficiency.

$$\eta = \frac{-W}{q_2} = \frac{T_2 - T_1}{T_2}$$

$\because \frac{T_2 - T_1}{T_2} < 1$ efficiency of heat engine is always less than 1.

In a cyclic process net heat absorbed by the system ($q_2 - q_1$) is equal to net work done (-w)

$$-W = q_2 - q_1$$

$$\frac{q_2 - q_1}{q_2} = \frac{T_2 - T_1}{T_2}$$

$$1 - \frac{q_1}{q_2} = 1 - \frac{T_1}{T_2}$$

$$\frac{q_2}{T_2} = \frac{q_1}{T_1}$$

Definition of Entropy

If any process is carried out reversibly, so that dq_{rev} is the heat absorbed by the system the process at constant temperature(T), then the entropy change (dS) is given by

$$ds = \frac{dq_{rev}}{T}$$

For finite changes, $\Delta S = \frac{q_{rev}}{T}$

The total entropy change (ΔS_{total}) for the system and surroundings of a spontaneous process is given by

$$\Delta S_{total} = \Delta S_{system} + \Delta S_{surr} > 0$$

When a system is in equilibrium, the entropy is maximum, and the change in entropy, $\Delta S = 0$.

We can say that entropy for a spontaneous process increases till it reaches maximum and at equilibrium the change in entropy is zero. Since entropy is a state property, we can claculate the change in entropy of a reversible process by

$$\Delta S_{sys} = \frac{q_{sys,rev}}{T}$$

Units of entropy :

CGS : cal k^{-1} or entropy unit (e.u)

1 e.u = 1 cal k^{-1}

SI : J k^{-1}

ΔS in Reversible and Irreversible Process :

In a thermodynamically reversible process

$$\Delta S_{\text{Total}} = \Delta S_{\text{System}} + \Delta S_{\text{Surroundings}} = 0$$

In a thermodynamically irreversible process (spontaneous)

$$\Delta S_{\text{Total}} = \Delta S_{\text{System}} + \Delta S_{\text{Surroundings}} > 0$$

Meaning of Entropy :

(i) Entropy is the degree of disorder or randomness of a system.

(ii) Change in entropy is the capacity for spontaneous change in a system.

SPONTANCITY AND ENTROPY

Spontaneous Process :

In any system, a spontaneous process is one which occurs on its own without the help of external energy. The natural changes that occur around us result from such processes.

Statement of the IInd Law :

Second law of thermodynamics is concerned with the direction and spontaneity of processes.

Clausius stated the law as ‘The transference of heat from a cold to a hot body cannot be achieved without the performance of work’.

‘Any process occurring on its own is thermodynamically irreversible’.

The basic concept of the second law of thermodynamics is that all spontaneous processes are unidirectional and thermodynamically irreversible.

ENTROPY(S)

To decide whether a chemical reaction can take place or not, the first factor that has to be considered is whether there is enough energy available. If the reaction is exothermic, there is no reason why it should not take place spontaneously but if the reaction is endothermic then it would not. But in nature, we come across numerous examples of endothermic reactions, which are spontaneous (for example, evaporation of water). From this, we conclude that energy alone is not the deciding factor. This is where the concept of entropy becomes important.

We find that both for reversible and irreversible expansion for an ideal gas, under isothermal conditions, $\Delta U = 0$, but ΔS_{total} i.e., $\Delta S_{sys} + \Delta S_{surr}$ is not zero for irreversible process. Thus, ΔU does not discriminate between reversible and irreversible process, whereas ΔS does.

Entropy change in ideal gases :

1. T & V as Variables :

$$\Delta S = nC_V \ln \frac{T_2}{T_1} + nR \ln \frac{V_2}{V_1}$$

$$= 2.303\ nC_V \log \frac{T_2}{T_1} + 2.303\, nR \log \frac{V_2}{V_1}$$

2. T & P as Variables:

$$\Delta S = nC_P \ln \frac{T_2}{T_1} + nR \ln \frac{P_1}{P_2}$$

$$\Delta S = 2.303\ nC_P \log \frac{T_2}{T_1} + 2.303\ nR \log \frac{P_1}{P_2}$$

3. Isothermal process:

$$\Delta S_T = nR \ln \frac{P_1}{P_2} = 2.303\, nR \log \frac{P_1}{P_2}$$

$$\Delta S_T = nR \ln \frac{V_2}{V_1} = 2.303\, nR \log \frac{V_1}{V_2}$$

4. Isobaric process

$$\Delta S_P = nC_P \ln \frac{T_2}{T_1} = 2.303\, nC_p \log \frac{T_2}{T_1}$$

5. Isochoric process

$$\Delta S_V = nC_V \ln \frac{T_2}{T_1} = 2.303\, nC_V \log \frac{T_2}{T_1}$$

6. Adiabatic process:

$$\Delta S = 0$$

STANDARD ENTROPY:

The absolute entropy of a pure substance at 1 bar pressure is called standard entropy.

The absolute entropy of an element is zero only at zero Kelvin.

For a chemical reaction

$$\Delta S^o = \Delta S^o \text{ (compound) } - \sum S^o \text{ (reactants)}$$

STANDARD ENTROPY OF FORMATION:

It is the entropy change observed when one mole of substance is formed in its standard state from its elements in their reference states at 25°C and 1 bar or 1 atm pressure.

$$\Delta S^o_f = \Delta S^o \text{ (compound) } - \sum S^o \text{ (elements)}$$

Gibbs free energy (Δ G)

According to II law in any spontaneous process there is always an increase in entropy of universe i.e. $\Delta S_{\text{Total}} > 0$. This increase is taken into account the entropy changes in both systems and surroundings.

$$\Delta S_{\text{Total}} = \Delta S_{\text{System}} + \Delta S_{\text{Surroundings}}$$

$$\Delta S_{\text{Total}} = \Delta S_{\text{System}} \frac{-\Delta H_{system}}{T} \qquad \left[\Delta H_{Surroundings} = -\Delta H_{System}\right]$$

$$T\Delta S_{\text{Total}} = -\left(\Delta H_{system} - T\Delta S_{system}\right)$$

For a spontaneous process, T ΔS Total should be positive, $\therefore \Delta H_{system} - T\ \Delta S_{system}$ should be negative. At this point it is convenient to introduce another thermodynamic state function called Gibbs free energy (G), which is defined as G = H – TS and the change in free energy $\Delta G = \Delta H - T\Delta S$ .For a spontaneous process, ΔG should be –ve

ΔH	ΔS	ΔG
-ve	+ve	-ve at all T i.e. spontaneous all temperatures
+ve	+ve	-ve at high T i.e. spontaneous at high T
-ve	-ve	-ve at low T i.e. spontaneous at low T
+ve	-ve	+ve at all T i.e. not spontaneous at all tens

ΔG represent the maximum energy released in a process occurring at constant temperature and pressure i.e. free or available to perform a useful work other than the work of expansion.

ΔG is a driving force in a chemical change that can be harnessed to perform useful work.

ΔG for an ideal gas in Isothermal change

$$\Delta G = nRT \ln \frac{P_2}{P_1} = 2.303\, nRT \log \frac{P_2}{P_1}$$

$$\Delta G = nRT \ln \frac{V_1}{V_2} = 2.303\, nRT \log \frac{V_2}{V_1}$$

Gibbs – Helmholtz equation :

$$\Delta G = \Delta H + T\left[\frac{\partial(\Delta G)}{\partial T}\right]_P$$

ΔG in chemical reactions

$$a\,A_{(g)} + b_{(g)} \rightleftharpoons c\,C_{(g)} + d\,D_{(g)}$$

$$\Delta G = \Delta G^o + RT \ln \frac{P_C^c \times P_D^d}{P_A^a \times P_B^b}$$

$\because$ $\Delta G^o \rightarrow$ standard free energy

at equilibrium, $\Delta G = 0$

$$\Delta G^o = -RT \ln Kp = -2.303 RT \log Kp.$$

$$\Delta G = RT \ln Q_P - RT \ln Kp$$

1. BASIC DEFINATIONS

1. For isochoric process, the change in
(A) Volume is zero (B) Pressure is zero
(C) Internal energy is zero (D) None

2. Molar heat capacity of water in equilibrium with the ice at constant pressure is :
(A) zero (B) infinity (C) $40.45\ k^{-1}\ mol^{-1}$ (D) None

3. 1^{ST} LAW OF THERMODYNAMICS, Simple calculations of w, Q, & ΔE

4. Work done in reversible isothermal process by an ideal gas is given by
(A) $2.303\ nRT \log \frac{V_2}{V_1}$ (B) $\frac{nR}{(\gamma - 1)}(T_2 - T_1)$
(C) $2.303\ nRT \log \frac{V_1}{V_2}$ (D) None

4. Work done in reversible adiabatic process by an ideal gas is given by
(A) $2.303\ RT \log \frac{V_1}{V_2}$ (B) None
(C) $2.303\ RT \log \frac{V_2}{V_1}$ (D) $\frac{nR}{(\gamma - 1)}(T_2 - T_1)$

5. The work done during the process when 1 mole of gas is allowed to expand freely into vacum is
(A) 0 (B) Positive (C) Negative (D) Either of these

6. A gas expands against a constant external pressure of 2.00 atm, increasing its volume by 3.40 L. Simultaneously, the system absorbs 400 J of heat from its surroundings. What is ΔE, in joules, for this gas ?

(A) – 689 (B) – 289 (C) + 400 (D) + 289

7. When a certain mass of an ideal gas is adiabatically compressed so that its volume is reduced to 1/32 times, its absolute temperature is increased 4 times. The number of atoms in a molecule (atomicity) of the gas is
(A) 3 (B) 4 (C) 2 (D) 1

8. 10 litres of a monoatomic ideal gas at 0°C and 10 atm pressure is suddenly released to 1 atm pressure and the gas expands adiabatically against this constant pressure. The final temperature and volume of the gas respectively are.
(A) T = 174.9 K, V = 64.04 litres (B) T = 153 K, V = 57 litres
(C) T = 165.4 K, V = 78.8 litres (D) T = 161.2 K, V = 68.3 litres

9. Which of the following is true regarding reversible adiabatic expansion of an ideal gas?
(A)Plot of T vs V is a straight line with slope equal o γ.
(B)Plot of ln T vs ln V is a straight line with slop equal to γ.
(C)Plot of ln T vs ln V is a straight line with slope equal to $-\gamma$.
(D)Plot of ln T vs ln V is a straight line with slope $(1-\gamma)$

10. During the adiabatic expansion of an ideal gas against atmospheric pressure, the internal energy will
(A) increase (B) decrease (C) stay the same (D)Impossible to say

11. A system undergoes a 2-step process. In step 1, 15 J of work is done on the system as its internal energy increases by a total of 30 J. In step 2, at constant volume, the system decreases its internal energy by 20 J. Which statement is true about these changes?
(A) The system loses 5J of internal energy as a result of the net heat flow in steps 1 & 2.
(B) 20 J of work is done on the surroundings in step 2.
(C) $q = +45$ J in step 1
(D) $q = +20$ J in step 2

12. If 50 calorie are added to a system and system does work of 30 calorie on surroundings, the change in internal energy of system is
(A) 20 cal (B) 50 cal (C) 40 cal (D) 30 cal

3. CALCULATION OF ΔH , W, Q, & ΔE IN DIFFERENT PROCESSCS

13. Consider a classroom that is roughly 5 m × 10m × 3m. Initially t = 20°C and P = 1 atm. There are 50 people in an insulated class loosing energy to the room at the average rate of 150 watt per person. How long can they remain in class if the body temperature is 37°C and person feels uncomfortable above this temperature. Molar heat capacity of air = (7/2) R.
(A) 4.34 minutes (B) 5.73 minutes
(C) 6.86 minutes (D)7.79 minutes

14. The increase in internal energy of 1 kg of water at 100°C when it is converted into steam at the same temperature and at 1 atm (100 k Pa) will be [The density of water and steam are 1000 kg/m^3 & 0.6 kg/m^3 respectively. The latent heat of vapourisation of water is 2.25×10^6 J/kg.]
(A) 2.08×10^6 J (B) 4×10^7 J (C) 3.27×10^8 J (D) 5×10^9 J

15. The internal energy of a monoatomic ideal gas is 1.5 nRT. 1 mole of helium is kept in a cylinder of cross section 8.5 cm^2. The cylinder is closed by a light frictionless piston. The gas is heated slowly in a process during which a total of 42 J heat is given to the gas. If the temperature rises through 2°C, the distance moved by the piston is [Atmospheric pressure being 100 k Pa.]
(A) 10 cm (B) 20 cm (C) 25 cm (D) 30 cm

16. A piston is cleverly designed so that it extracts the maximum amount of work out of a chemical reaction, by matching $P_{external}$ to the P_{internal} at all times. This 8 cm diameter piston initially holds back 1 mol of gas occupying 1 L, and comes

to rest after being pushed out a further 2 L at 25°C. After exactly half of the work has been done, the piston has travelled out a total of

(A) 10.0 cm (B) 11.2 cm (C) 14.5 cm (D) 20.0 cm

17. A biochemical reaction triggers the expansion of 2.5 mol of an ideal gas reversibly, coming to rest at an equalized pressure of 58 kPa at 37°C. If the initial volume was 55.5 litres, then the work that was done by the system in this process was approximately

(A) 4466 J (B) −4466 J (C) −3600 J (D) 3600 J

18. One mole of ideal gas goes through the following transformations:
Step I: Isochoric cooling to 1/3 of the initial temperature
Step II: Adiabatic compression to its initial pressure
Step III: Isobaric expansion back to the initial state

If the initial temperature and pressure are 600 K and 3.00 atm and if the ideal gas is monoatomic ($C_v = 3/2R$), what is the work for the third step (going from state 3 to state1)?

Given :- $(16.4)^{5/3} = 105.86$ & $(35.3)^{3/5} = 8.48$

(A) −23.8 L. atm (B) −9.11 L. atm (C) 92.7 L. atm (D) 9.11 L. atm

19. For a fixed amount of perfect gas, which of these statements must be true?
(A) *E* and *H* each depend only on *T*.
(B) C_P is constant.
(C)P dV = *n*RdT for every infinitesimal process.
(D) Both (a) and (c) are true.

4. 2^{ND} LAW OF THERMODYNAMICS, BASICS OF ENTROPY, ENTROPY CALCULATION FOR DIFFERENT PROCESSES

20. Entropy change of vaporisation at constant pressure is given by

(A)$\Delta S_{(v)} = \frac{\Delta H_v}{T}$ (B) $\Delta S_{(v)} = \frac{\Delta E_v}{T}$ (C) $\Delta S_{(v)} = \frac{\Delta H_v}{\Delta T}$ (D) None

21. 1 mole of an ideal gas at 25°C is subjected to expand reversibly ten times of its initial volume. The change in entropy of gas is

(A)19.15 $JK^{-1}\ mol^{-1}$ (B) 16.15 $KJ^{-1}\ mol^{-}$

(C) 22.,15 $JK^{-1}\ mol^{-1}$ (D) None

22. The entropy change during an isothermal expansion of an ideal gas from V_1 to V_2 at temperature T is given by

(A) $\Delta S = 0$ (B) $\Delta S = 2.303\ nR\ \log_{10}(V_2/V_1)$

(C) $\Delta S = 2.303\ RT\ \log_{10}(V_2/V_1)$ (D) $\Delta S = 2.303\ R\ \log_{10}(V_2/V_1)$

23. Select the correct alternate for the endothermic change -

(A) $\Delta H > 0, \Delta S_{(system)} < 0$ (B) $\Delta H > 0, \Delta S_{(system)} > 0$

(C) $\Delta H < 0, \Delta S_{(surrounding)} < 0$ (D) $\Delta H > 0, \Delta S_{(surrounding)} > 0$

24. Select the correct option for the exothermic process

(A) $\Delta H < 0, \Delta S_{(surrounding)} > 0$ (B) $\Delta H < 0, \Delta S_{(system)} < 0$

(C) both (A) and (B) (D) none of these

25. For the gas - phase decomposition, $PCl_5\ (g) \downarrow \downarrow \rightarrow PCl_3\ (g) + Cl_2\ (g)$:

(A) $\Delta H < 0, \Delta S < 0$ (B) $\Delta H > 0, \Delta S > 0$

(C) $\Delta H > 0, \Delta S < 0$ (D) $\Delta H < 0, \Delta S > 0$

26. When one mole of an ideal gas is compressed to half its initial volume and simultaneously heated to twice its initial temperature, the change in entropy (ΔS) is -

(A) $C_V \ln 2$ (B) $C_P \ln 2$ (C) $R \ln 2$ (D) $(C_V - R) \ln 2$

27. The statement " If an object A is in thermal equilibrium with an object B, and B is in thermal equilibrium with an object C, then C is also in thermal equilibrium with A" is an example of which of the following laws?
(A) The Zeroth Law of Thermodynamics
(B) The First Law of Thermodynamics
(C) The Second Law of Thermodynamics
(D) The Thrid Law of Thermodynamics

28. A certain process releases 64.0 kJ of heat, which is transferred to the surroundings at a constant pressure and a constant temperature of 300 K. For this process ΔS_{surr} is
(A) 64.0 kJ (B) −64.0 kJ (C) −213 J/K (D) 213 J/K

5. 2ND LAW OF THERMODYNAMICS, G, G° & SPONTANEITY

29. The entropy change for the reaction given below is
$2H_2(g) + O_2(g) \downarrow \rightarrow 2H_2O(l)$
is … at 300 K. Standard entropies of $H_2(g)$. $O_2(g)$ and $H_2O(l)$ are 126.6, 201.20 and 68.0 $JK^{-1}\,mol^{-1}$ respectively.
(A) $-318.4\ JK^{-1}\,mol^{-1}$ (B) $318.4 \times JK^{-1}\,mol^{-1}$
(C) $31.84 \times JK^{-1}\,mol^{-1}$ (D) None

30. At equilibrium condition, the value of Gibbs free energy change, ΔG is
(A) Equal to zero (B) Greater than one
(C) Less than one (D) Equal to one

31. For spontaneous reaction the value of change of Gibbs free energy, ΔG is
(A) Negative (B) Positive
(C) Greater than one (D) One

32. For the reaction at 298 K $CaCO_3$ (s) ↓ ↓ → CaO(s) + CO_2 (g)

$\Delta H^\circ = 178.3$ kJ, $\Delta S^\circ = 160\ Jk^{-1}$

Select correct statement :

(A) the reaction is spontaneous at this temperature (298 K)

(B) if temperature is decreases forward reaction is fevoured

(C) the reaction is spontaneous in forward direction only at temperature above1000K

(D) the reaction is spontaneous in forward direction only at temperature above1114K

33. $F_2C = CF– CF = CF_2$ ↓ ↓ → Product

For this reaction, $\Delta H = – 49.0$ kJ/mole; $\Delta S = –40.2$ J/K. Upto what temperature is the forward reaction spontaneous?

(A) 1492^0C (B) 1219^0C (C) 946^0C (D) 1080^0C

34. ΔG° for the reaction 2NO (g) + O_2 (g) ↓ ↓ → N_2O_4 (g) at 298K and 1 atm pressure, will be[given that the enthalpy of formation of NO (g) is 90.5 kJ mol^{-1}. The enthalpy of formation of N_2O_4 (g) is 9.7kJ mol^{-1}. The standard entropy of NO (g) is 210 J k^{-1} mol^{-1}, O_2 (g) is 205 JK^{-1} $mole^{-1}$, N_2O_4 (g) is 304 JK^{-1} mol^{-1}.]

(A) – 52.92 KJ (B) – 75.64 KJ (C) – 64.24 KJ (D) – 83.27 KJ

35. The equilibrium constant for the reaction, A ↓ ↓ → B was measured over a range of temperature and can be represented by the equation, ln K_p = 4.814 – (2059/T)

Then ΔG°, ΔH°, ΔS° for the reaction at 298 K will be

(A) $\Delta G^\circ = 6.25$ kJ, $\Delta H^\circ = 18.29$ kJ, $\Delta S^\circ = 45\ Jk^{-1}mole^{-1}$

(B) ΔG° = 7.323 kJ, $\Delta H^\circ = 19.37$ kJ, $\Delta S^\circ = 48\ Jk^{-1}\ mole^{-1}$

(X) ΔG° = 8.729 kJ, $\Delta H^\circ = 20.22$ kJ, $\Delta S^\circ = 51.23\ Jk^{-1}\ mole^{-1}$

(D) $\Delta G^\circ = 5.185$ kJ, $\Delta H^\circ = 17.11$ kJ, $\Delta S^\circ = 40$ Jk^{-1} $mole^{-1}$

36. At 25°C, which of the following substances has the highest molar entropy?
(A) Al(s) (B) $C_6H_6(l)$ (C) $C_2H_6(g)$ (D) $CH_4(g)$

37. What is the minimum temperature at which the process below will be spontaneous, given that $\Delta H^{o}_{r\times n} = +85$ kJ and $\Delta S^{o}_{r\times n} = 198$ J/K for the reaction $N_2F_4(g) \downarrow\downarrow\rightarrow NF_2(g)$
(A) T = 144 K (B) T = 298 K (C) T = 429.3 K (D) T = 2330 K

38. Which of the following is true of this reaction?
$2N_2O_5(g)$ □□□ $4NO_2(g) + O_2(g)$, $\Delta H^o = 110$ kJ
(A) Both ΔH^o and ΔS^o favour the reaction's spontaneity
(B) Both ΔH^o and ΔS^o oppose the reaction's spontaneity.
(C) ΔH^o favours the reaction, but ΔS^o opposes it.
(D) ΔH^o opposes the reaction, but ΔS^o favours it.

39. Use the following data to calculate ΔS^o for the reaction:

$$2NH_3(g) \downarrow\downarrow\rightarrow N_2(g) + 3H_2(g)$$

Compound	S° (J/mol-K)
$H_2(g)$	−98.74
$N_2(g)$	−114.99
$NH_3(g)$	−304.99

(A) −198.8 J/K (B) −91.26 J/K (C) −106.22 J/K (D) 198.8 J/K

40. At what temperature will the following process would not be spontaneous?

$$A(g) \downarrow\downarrow\rightarrow A(l) \quad \Delta H = -20\ kJ \quad \Delta S = -50\ J/K$$

(A) > 200 K (B) > 300 K (C) > 350K (D) > 400 K

41. The temperature at which the reaction,

$Ag_2O(s) \downarrow\rightarrow 2Ag(s) + 1/2O_2(g)$

Is at equilibrium is …; Given $\Delta H = 30.5\ kJ\ mol^{-1}$ and $\Delta S = 0.066\ kJ\ K^{-1}\ mol^{-1}$

(A) 462.12 K (B) 362.12 K (C) 262.12 K (D) 562.12 K

42. If S^0 for H_2, Cl_2 and HCl are 0.13, 0.22 and 0.19 kJ $K^{-1}\ mol^{-1}$ respectively. The total change in standard entropy for the reaction $H_2 + Cl_2 \downarrow\rightarrow 2HCl$ is

(A) 30 $JK^{-1}mol^{-1}$ (B) 40 $JK^{-1}mol^{-1}$ (C) 60 $JK^{-1}mol^{-1}$ (D) 20 $JK^{-1}mol^{-1}$

43. In which case, a reaction is possible at any temperature?

(A) $\Delta H < 0, \Delta S > 0$ (B) $\Delta H < 0, \Delta S < 0$(C) $\Delta H > 0, \Delta S > 0$(D) None

44. Which of the following has impossibilities of reaction at any temperature?

(A) $\Delta H > 0, \Delta S < 0$ (B) $\Delta H > 0, \Delta S > 0$(C) $\Delta H < 0, \Delta S < 0$(D) None

6 . THERMOCHEMISTRY :- □$H°_{formation}$, □$H°_{combustion}$, Kirchoff's Equation, Hesse's Law

45. When solute remains in equilibrium with given solvent then

(A) $\Delta H_{hydration}$ = Lattice energy (B) $\Delta H_{hydration}$< Lattice energy

(C) $\Delta H_{hydration}$> Lattice energy (D) None

46. Which of the following is the heat of combustioin?

(A) $C(graphite) + 1/2\ O_2(g) \downarrow\downarrow\rightarrow CO(g) + x\ cal$

(B) $C(diamond) + O_2(g) \downarrow\downarrow\rightarrow CO_2(g) + y\ cal$

(C) $C(diamond) + 1/2\ O_2(g) \downarrow\downarrow\rightarrow\ CO(g) + z$ cal
(D) None

47. Heat of reaction at constant p or constant v varies with temperature as given by *Kirchoff's* equation is/are
(A) $\Delta H_2 = \Delta H_1 + \Delta C_P(T_2 - T_1)$ (B) $\Delta E_2 = \Delta E_1 + \Delta C_P(T_2 - T_1)$
(C) $H_2 = H_1 + \Delta C_p(T_2 - T_1)$ (D) $\Delta E_2 = \Delta E_1 + C_p(T_2 - T_1)$

48. For the combustion reaction at 298K $H_2(g) + 1/2\ O_2(g) \downarrow\downarrow\rightarrow\ H_2O(l)$
Which of the following alternative(s) is/are correct?
(A) $\Delta H = \Delta E$
(B) $\Delta H > \Delta E$
(X) $\Delta H < \Delta E$
(Δ) ΔH & ΔE has no relation with each there

49. Given $N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$; $\Delta H^0 = -22$ kcal. The standard enthalpy of formation of NH_3 gas is
(A) –11 kcal/mol (B) 11 kcal/mol (C)–22kcal/mol (D)22kcal/mol

50. Heat of combustion of CH_4, C_2H_4, C_2H_6 are –890, –1411 and –1560 kJ/mol respectively. Which of the given hydrocarbons has the lowest calorific fuel value in kJ/g.
(A) CH_4 (B) C_2H_4 (C) C_2H_6 (D)All same

51. ΔH for $CaCO_3(s) \downarrow\rightarrow\ CaO(s) + CO_2(g)$ is 176 kJ mol^{-1} at 1240 K. The ΔE for the reaction is equal to
(A) 160 kJ (B) 165.6 kJ (C) 186.3 kJ (D) 180.0 kJ

52. $C_{diamond} + O_2(g) \downarrow\rightarrow\ CO_2(g)$; $\Delta H = -395$ kJ ..(i)
$C_{graphite} + O_2(g) \downarrow\rightarrow\ CO_2(g)$; $\Delta H = -393.5$ kJ ..(ii)
The ΔH, when diamond is formed from graphite is

(A)–1.5 kJ (B) +1.5 kJ (C) +3.0 kJ (D) –3.0 kJ

53. An athlete is given 100 g of glucose ($C_6H_{12}O_6$) of energy equivalent to 1560 kJ. He utilizes 50 percent of this gained energy in the event. In order to avoid storage of energy in the body, the weight of water he would need to perspire is- (The enthalpy of evaporation of water is 44 kJ/mole.)

(A) 319 gm (B) 422 gm (C) 293 gm (D) 378 gm

54. If $H_2 + 1/2\ O_2 \downarrow\rightarrow H_2O$, $\Delta H = -68.39$ kcal

$K + H_2O \downarrow \rightarrow$ KOH (aq) + $1/2\ H_2$, $\Delta H = -48$ kcal

KOH + water $\downarrow\rightarrow$ KOH (aq), $\Delta H = -14$ kcal

The heat of formation of KOH is

(A) – 68.39 + 48 – 14 (B) – 68.39 – 48 + 14

(C) 68.39 – 48 + 14 (D) + 68.39 + 48 – 14

55. The difference between the heat of reaction at constant pressure and constant volume for the reaction $2C_6H_6(l) + 15O_2(g) \downarrow\rightarrow 12CO_2(g) + 6H_2O\ (l)$ at 25°C in kJ is

(A) – 7.43 (B) 3.72 (C) – 3.72 (D) 7.43

56. For the combustion of n-octane $C_8H_{18}(g) + O_2\ (g) \downarrow\rightarrow CO_2\ (g) + H_2O\ (l)$ at 25°C (ignoring resonance in CO_2), which statement is correct.

(A) $\Delta H = \Delta E - 5.5 \times 8.31 \times 0.298$ in kJ/mol

(B) $\Delta H = \Delta E + 4.5 \times 8.31 \times 0.298$ in kJ/mol

(C) $\Delta H = \Delta E - 4.5 \times 8.31 \times 0.298$ in kJ/mol

(D) $\Delta H = \Delta E - 4.5 + 8.31 \times 0.298$ in kJ/mol

57. In the reaction $CO_2(g) + H_2(g) \downarrow\rightarrow CO(g) + H_2O(g)$; $\Delta H = 2.8$ kJ; ΔH represents

(A) heat of reaction (B) heat of combustion

(C) heat of formation (D) heat of solution

58. The standard heat of combustion of Al is – 837.8 kJ mol^{-1} at 25°C which of the following releases 250 kcal of heat ?
(A) The reaction of 0.624 mol of Al
(B) The formation of 0.624 mol of Al_2O_3
(C) The reaction of 0.312 mol of Al
(D) The formation of 0.150 mol of Al_2O_3

59. If $S + O_2 \downarrow \rightarrow SO_2, \Delta H = -298.2$ kJ $mole^{-1}$
$SO_2 + 1/2\, O_2 \downarrow \rightarrow SO_3\ \Delta H = -98.7$ kJ $mole^{-1}$
$SO_3 + H_2O \downarrow \rightarrow H_2SO_4, \Delta H = -130.2$ kJ $mole^{-1}$
$H_2 + 1/2\, O_2 \downarrow \rightarrow H_2O, \Delta H = -287.3$ kJ $mole^{-1}$
the enthalpy of formation of H_2SO_4 at 298 K will be -
(A) – 814.4 kJ mol|–1 (B) + 814.4 kJ $mole^{-1}$
(C) – 650.3 kJ $mole^{-1}$ (D) – 433.7 kJ $mole^{-1}$

60. When a certain amount of ethylene was combusted, 6226 kJ heat was evolved. If heat of combustion of ethylene is 1411 kJ, the volume of O_2 (at NTP) that entered into the reaction is -
(A) 296.5 ml (B) 296.5 litres (C) 6226 × 22.4 litres (D) 22.4 litres

61. Given the following reactions :
$N_2(g) + 2O_2\,(g) \downarrow\rightarrow 2NO_2\ (g), \Delta H_1 = 16.18$ kcal
$N_2(g) + 2O_2(g) \downarrow\rightarrow N_2O_4\ (g), \Delta H_2 = 2.31$ kcal
Based on the above facts :

(A) NO_2 is more stable than N_2O_4 at low temperature
(B) N_2O_4 is more stable than NO_2 at low temperature
(C) both are equally stable at low temperature
(D) none of the above

62. Given $H_2(g) + Br_2(g) \downarrow \rightarrow$ 2HBr(g), ΔH^0_1 & standard enthalpy of condensation of bromine is ΔH^0_2, standard enthalpy of formation of HBr at 25^0C is

(A) $\frac{\Delta H_1^o}{2}$ (B) $\frac{\Delta H_1^o}{2} + \Delta H_2^o$
(C) $\frac{\Delta H_1^o}{2} - \Delta H_2^o$ (D) $\frac{\Delta H_1^o - \Delta H_2^o}{2}$

63. Trans – 2 – butene is more stable as compared to cis – butene. When a given sample of 2 – butene is heated at constant volume, the concentration of trans – 2 – butene
(A) increases (B) decreases
(C) remains same (D) changes unpredictably

64. In the reaction CS_2 (l) + $3O_2$ (g) $\downarrow \rightarrow CO_2$ (g) + $2SO_2$ (g) $\Delta H = -265$ kcal
The enthalpies of formation of CO_2 and SO_2 are both negative and are in the ratio 4 : 3. The enthalpy of formation of CS_2 is +26kcal/mol. Calculate the enthalpy of formation of SO_2.
(A) – 90 kcal/mol (B) – 52 kcal/mol
(C) – 78 kcal/mol (D)–71.7 kcal/mol

65. When 12.0 g of carbon reacted with oxygen to form CO and CO_2 at 25°C and constant pressure,75.0 kcal of heat was liberated and no carbon remained. The mass of oxygen needed for it will be [Given $\Delta H_f (CO_2) = -94.05$ kcal mole^{-1} and $\Delta H_f (CO) = -26.41$ kcal mole^{-1}.]

(A) 32.33 gm (B) 27.49 gm (C) 49.99 gm (D) 56.62 gm

66. For which of the following equations, will ΔH be equal to ΔE?
(A) $H_2(g) + ½ O_2(g) \downarrow \rightarrow H_2O(l)$ (B) $H_2(g) + I_2(g) \downarrow \rightarrow 2HI(g)$
(C) $2NO_2(g) \downarrow \rightarrow N_2O_4(g)$ (D) $4NO_2(g) + O_2(g) \downarrow \rightarrow 2N_2O_5(g)$

67. The enthalpy of combustion of carbon and carbon monoxide are –390 kJ and –278 Kj respectively. The enthalpy of formation of CO in kJ is
(A) 668 (B) 112 (C) –112 (D) –668

68. Which of the following corresponds to the definition of enthalpy of formation at 298 K?
(A) $C(graphite) + 2H_2(g) + 1/2\ O_2(l) \downarrow \downarrow \rightarrow CH_3OH(g)$
(B) $C(diamond) + 2H_2(g) + 1/2\ O_2(g) \downarrow \downarrow \rightarrow CH_3OH\ (l)$
(C) $2C(graphite) + 4H_2(g) + 4H_2(g) + O_2(g) \downarrow \downarrow \rightarrow 2CH_3OH\ (l)$
(D) $C(graphite) + 2H_2(g) + 1/2\ O_2(g) \downarrow \downarrow \rightarrow CH_3OH(l)$

7. **THEIRMOCHEMISTRY:** ΔH^0neturalization, ΔH^0resonance , Bond Enthapy.

69. The enthalpy of neutralisation of the given reaction
$H_2SO_4 + 2NaOH \downarrow\downarrow\rightarrow Na_2SO_4 + 2H_2O$ + y kcal
is (D)–y/2 kcal
(A) y kcal (B) –y kcal (C) + y/2 kcal

70. The temperature of a 5 ml of strong acid increases by 5°C when 5 ml of a strong base is added to it. If 10 ml of each are mixed, temperature should increase by
(A) 5°C (B)10°C (C) 15°C (D) Cannot be known

71. If $H_2(g) \rightarrow 2H(g)$; ΔH = 104 kcal, then heat of atomisation of hydrogen is

(A) 52 kcal (B) 104 kcal (C) 208 kcal (D)None of thes

72. In which case of mixing of a strong acid and a strong base each of 1 N concentration, temperature increase is highest.
(A) 20 ml acid – 30 ml alkali (B) 10 ml acid – 40 ml alkali
(C) 25 ml acid – 25 alkali (D) 35 ml acid – 15 ml alkali

73. The enthalpy of combustion of $H_2(g)$ at 298 K to give H_2O is – 298 kJ mol^{-1} and bond enthalpies of H – H and O = O are 433 kJ mol^{-1} and 492 kJ mol^{-1} respectively. The bond enthalpies of O – H is: (Given :- ΔH_{vap} of water =42 kJ mol^{-1}
(A) 464 kJ mol^{-1} (B) 488.5 kJ mol^{-1}
(C) 232 kJ mol^{-1} (D) – 232 kJ mol^{-1}

74. The heat of formation $H_2O(l)$ is – 68.0 kcal, the heat of formation of $H_2O(g)$ is likely to be
(A) – 68.0 kcal (B) – 69.4 kcal (C) 80.0 kcal (D) – 58.3 kcal

75. Enthalpy of polymerisation of ethylene, as represented by the reaction,
$nCH_2{=}CH_2\downarrow\rightarrow(-CH_2-CH_2-)_n$ is Δ100 kJ per mole of ethylene. Given bond enthalpy of C=C bond is 600 kJ/mol, enthalpy of CΔ C bond (in kJ mol) will be :
(A) 116.7 (B) 350 (C) 700 (D) indeterminate

76. The enthalpy of neutralisation of a strong acid is –13,700 calories. A certain monobasic weak acid is 14% ionized in a molar solution. If the enthalpy of ionization of the weak acid is + 366 calories/mole, what is the enthalpy of neutralisation of one molar solution of the weak acid?
(A) –13,649 cals (B) –13,385 cals (C) –14,066 cals (D) –13,334 cals

77. The bond enthalpies of H–H, Cl–Cl and H–Cl are 435, 243 and 431 kJ mol^{-1}, respectively. The enthalpy of formation of HCl(g) will be
(A) 92 kJ mol^{-1} (B) – 92 kJ mol^{-1} (C) 247 kJ mol^{-1} (D) 770 kJ mol^{-1}

78. If $H^+ + OH^- \downarrow\rightarrow H_2O$ + 13.7 kcal then the enthalpy change for complete neutralisation of 1 mole of H_2SO_4 by base will be
(A) 13.7 kcal (B) 27.4 kcal (C) 6.85 kcal (D) 3.425 kcal

79. Under the same conditions how many ml of 1 M KOH and 0.5 M H_2SO_4 solutions, respectively when mixed for a total volume of 100 ml produce the highest rise in temperature
(A) 67 : 33 (B) 33 : 67 (C) 40 : 60 (D) 50 : 50

80. ΔH of sublimation of a solid is equal to
(A) $\Delta H_{fusion} + \Delta H_{condensation}$ (B) $\Delta H_{condensation} + \Delta H_{sublimation}$
(C) $\Delta H_{condensation} - \Delta H_{fusion}$ (D) $\Delta H_{vaporisation} + \Delta H_{fusion}$

81. AB, A_2 and B_2 are diatomic molecules. If the bond enthalpies of A_2, AB & B_2 are `in the ratio 1:1:0.5 and enthalpy of formation of AB from A_2 and B_2 –100 kJ/mol^{-1}. What is the bond enthalpy of A_2?
(A) 400 kJ/mol (B) 200 kJ/mol (C) 100 kJ/mol (D)300 kJ/mol

1.	(A)	2.	(B)	3.	(C)	4.	(D)	5.	(A)	6	(B)	7	(C)
8	(A)	9	(D)	10	(B)	11	(A)	12	(A)	13	(C)	14	(A)

15	(B)	16	(C)	17	(B)	18	(A)	19	(D)	20	(A)	21	(A)
22	(B)	23	(B)	24	(C)	25	(B)	26	(D)	27	(A)	28	(D)
29	(A)	30	(A)	31	(A)	32	(D)	33	(C)	34	(B)	35	(D)
36	(C)	37	(C)	38	(D)	39	(D)	40	(D)	41	(A)	42	(A)
43	(A)	44	(A)	45	(A)	46	(D)	47	(A)	48	(C)	49	(A)
50	(B)	51	(B)	52	(B)	53	(A)	54	(B)	55	(A)	56	(A)
57	(A)	58	(B)	59	(A)	60	(B)	61	(B)	62	(D)	63	(B)
64	(D)	65	(B)	66	(B)	67	(C)	68	(D)	69	(D)	70	(A)
71	(A)	72	(C)	73	(B)	74	(D)	75	(B)	76	(B)	77	(B)
78	(B)	79	(D)	80	(D)	81	(A)						

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