Thermodynamics

It involves a study of interrelation of various kinds of energy accompanying physical or chemical changes. Initially it meant for studies accompanying heat changes (thermos = heat, dynamics = flow) and interrelate heat energy with work. Now the term in broader sense involves all kinds of energy changes accompanying the process.

Terminology of Thermodynamics:

**System:** A specified part of universe selected for the study of effect of certain properties such as P, T, etc.

**Surroundings:** The adjacent part of universe outside the real or imaginary boundaries of system.

Types of Systems:

1. **Homogeneous System:** A system is supposed to homogeneous if it is uniform throughout i.e. all the substance present in it have only one phase.
2. **Heterogeneous System:** Not uniform throughout, i.e. it has more than one phase.

Classification of system may also be made as:

1. **Open system:** A system which can exchange matter as well as energy with surroundings e.g. liquid kept in a beaker.
2. **Closed system:** A system which can exchange only energy with surroundings e.g. liquids kept in a beaker.
3. **Isolated system:** Neither exchange of matter nor exchange of energy is possible with surroundings.

**State Functions:** The measurable properties of a system which depend only upon the state of system are known as state variables, e.g., P, V, T composition; energy, etc.

**The cyclic rule:** For 1 mole of an idle gas:

\[
\left( \frac{\partial P}{\partial V} \right)_T \times \left( \frac{\partial V}{\partial P} \right)_V \times \left( \frac{\partial T}{\partial P} \right)_V = -1 \quad \text{or} \quad \left( \frac{\partial P}{\partial V} \right)_V \times \left( \frac{\partial V}{\partial P} \right)_V \times \left( \frac{\partial P}{\partial T} \right)_V = -1
\]
State of system: The state of the system at a time signify for the fact that the variable factors, e.g., \( P, V, T \), etc. (which completely define the state of system) are known.

Properties of system: The thermodynamics properties of a system are divided as:

1. **Intensive properties**: Mass independent properties, e.g., temperature, pressure, viscosity, density, refraction index, surface tension, chemical potential, etc.
2. **Extensive properties**: Mass dependent properties, e.g., mass, volume, energy, heat enthalpy, entropy.

   [Note: An extensive property becomes intensive by specifying a unit amount of matter, e.g., mass and volume are extensive but density \( = \frac{M}{V} \) is intensive property.]

Thermodynamics process: The operations, by which the changes from one state to other are made, are known as thermodynamics process. All thermodynamics properties satisfy

\[
\Delta U = q + w \\
H = U + PV \\
S = \frac{q_{rev}}{T}
\]

1. **Reversible process**: A reversible or quasistatic process is one in which all changes occurring at any part of the process are exactly reversed, when it is carried out in opposite direction. A reversible process involves.
   a. A slow change during investigations.
   b. Driving force in infinitesimally greater than the opposing force and vice versa.
   c. The process may take place in either direction.
   d. Maximum work is obtained.

2. **Irreversible process**: A process whose direction cannot be reversed by small changes in variables is irreversible process. It involves.
   a. A fast change during investigation
   b. Driving force is much different than opposing force.
   c. The unidirectional process.
   d. Network somewhat lesser than maximum work, is obtained.

Heat and Temperature:

1. Heat is a measure of quantity of energy transferred from one body to other as a result of temperature difference between them.
2. Temperature is a measure of intensity of energy, i.e., how much energetic each individual particle is.
Work: Work is expressed as the product of two factors, i.e,
\[ W = (\text{intensity factor}) \times (\text{capacity factor}) \]

Intensity factor is measure of force against which work is done. Capacity factor is the extent for which work is done.

i.e,

A. Mechanical Work = (force) x (displacement) = \( F \times d \)
B. Gravitational work = (gravitational force) x (height) = \( mg \times h \)
C. Electrical work = (pot. Difference) x (quantity of current) = \( E \times Q \)
D. Work of expansion = (pressure) x (change in volume)
E. A (–ve) sign is given for work done by the system.
F. A (+ve) sign is given for work done on the system.

The general expression for all types of \( PV \) work can be written as \( W = -P \Delta V \)

For expansion: \( \Delta V = V_2 - V_1 = +ve \) (\( V_2 > V_1 \)) \( \therefore W = -ve \)

For compression: \( \Delta V = V_2 - V_1 = -ve \) (\( V_2 < V_1 \)) \( \therefore W = +ve \)

Units of work: \( W = \text{dyne cm or erg} \)

\[ = \text{newton m or joule} \]
\[ = \text{calorie} \]

1 cal = 4.184 \times 10^{7} \text{ erg} = 4.184 \text{ J}

It is thus, evident that work, heat and energy have same units.

In P-V diagram as

\( W_{AC} = 0 \), since no area is covered by straight line.

\( W_{AB} = \text{Area covered by square ABEF} \).

\( W_{BC} = \text{Area covered by BCEF} \)

\[ = \text{Area of square CDEF} + \text{Area of triangle BCD} \]

\[ = P_1 \times (V_2 - V_1) + \frac{1}{2} \times \text{Area of square ABCD} \]

\[ = P_1 \times (V_2 - V_1) + \frac{1}{2} \times (P_2 - P_1) \times (V_2 - V_1) \]
Also in a cyclic process \( w = -ve \) if clockwise and \( w = +ve \) if anticlockwise.

**Internal energy:** Each substance is associated with a definite amount of energy involving the energy depending upon the chemical nature of substance and the conditions of \( P, V, T \). It includes many types of energies such as translational, vibrational, rotational, columbic, potential energy, etc. Therefore, exact magnitude of internal energy cannot be determined. Furthermore it is a state function and denoted by \( U \) and is independent of path. In thermodynamics we deal with the change in internal energy of two states.

\[
\Delta U = U_2 - U_1
\]

**Heat enthalpy or heat content:** Enthalpy ‘\( H \)’ is also a state function and independent of path. It is expressed as:

\[
H = U + PV
\]

Like \( U \), in thermodynamics we deal with change in heat enthalpy \( \Delta H \):

\[
\Delta H = H_2 - H_1
\]

**Relation in between \( \Delta H \) and \( \Delta U \):** The two are related by

\[
\Delta H = \Delta U + P \Delta V
\]

at constant volume

\[
\Delta H = \Delta U
\]

**First law of thermodynamics:** According to this law, mass and energy of an isolated system remains constant. The law is expressed mathematically as

\[
dq = dU + (-dW) \quad \ldots \ldots \ldots (1) \text{(For an infinitesimal change)}
\]

Where, \( dq = \text{change in internal energy} \)

\( dU = \text{heat supplied to system} \)

\( -dW = \text{work done by the system} \)

Also, \( q = \Delta U + (-W) \) \ldots \ldots (2)

or \( \Delta U = q + W \) \text{(For finite change)}
Some useful formulae based upon I law:

1. **Isothermal process:** A process in which temperature of the system remains constant throughout the studies.

   \[ \Delta T = 0 \quad \therefore \Delta U = 0 \]

   \[ \therefore \text{By equation (2)} \quad q = -W \]

   i.e. heat given to a system is used in work done by the system.

2. **Adiabatic process:** A process during which no exchange of heat takes place in between system and surroundings.

   \[ \therefore q = 0 \]

   \[ \therefore \text{By equation (2)} \quad + \Delta U = W \]

   \[ -\Delta U = -W \]

   i.e. work is done by the system on the cost of its internal energy.

3. **Cyclic process:** A process in which initial state of system is regained after a series of operations.

   \[ \therefore \Delta U = 0 \]

   \[ \therefore \text{By equation (2)} \quad q = -W \]

4. **Isochoric process:** A process in which volume of the system remains constant throughout the investigations.

   \[ \therefore \Delta V = 0 \]

   \[ \therefore \text{By equation (2)} \quad q_v = \Delta U \]

5. **Isobaric process:** A process in which pressure of the system remains constant throughout the investigation.

   \[ \Delta P = 0 \]

Consider a system showing increase in volume from \( V_1 \) to \( V_2 \) at a constant pressure \( P \), during absorption of heat \( q \). The expansion work to work done by the system is \( W = -P \Delta V \).

Thus by equation (2)

\[ q_p = \Delta U - P \Delta V \]
\[ = U_2 - U_1 - [ -P(V_2 - V_1)] = (U_2 + PV_2) - (U_1 + PV_1) \]
\[ = H_2 - H_1 \]
\[ q_p = \Delta H \]

I.e. heat given to a system under constant \( P \) is used up in increasing heat enthalpy of system.

Work done in isobaric process = \( dU - dq \)

\[ = nC_v \times ddT - nC_p \times dT = -nRdT \]

\[ = nR (T_{final} - T_{initial}) \]
6. **Work done in irreversible isothermal process:** Suppose an ideal gas expands against external pressure $P$ and its volume changes by an amount $dV$ then work done $W$ can be given by

$$ W = -PdV $$

(a) **Free expansion:** $W = 0$, Since $P = 0$

(b) **Expression or compression against external pressure $P$**

For a finite change $V_1$ to $V_2$,

Total work done on the system $W$ is derived by

$$ W = -P (V_2 - V_1) $$

Or

$$ W_{irr} = -P (V_2 - V_1) $$

Also,

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

Also,

If $V_2 > V_1$ then $W_{irr}$ is $-ve$ i.e., expansion work or work done by the system.

If $V_2 < V_1$ then $W_{irr}$ is $+ve$ i.e., compression work or work done on the system.

7. **Work done in isothermal reversible process:** Consider a system under isothermal condition, showing reversible expansion of an ideal gas by a volume $dV$, then

$$ \therefore \Delta U = 0 \therefore d_q = -dW = +PdV \quad (\because dW = -PdV) $$

The total work done during expansion of gas from $V_1$ to $V_2$

$$ W_{rev} - nRT \log_e \frac{v^2}{v^1} = -2.303 \ nRT \ \log_{10} \frac{v^2}{v^1} \quad .............. \quad (5) \quad (\because p \propto \frac{1}{V}) $$

Also,

$$ W_{rev} = -2.303 \ nRT \ \log_{10} \frac{p^1}{p^2} $$

8. **Work done in adiabatic reversible process:** Consider a system under adiabatic conditions, showing reversible expansion of an ideal gas by a volume $dV$, then from 1 law of thermodynamics,

$$ (\because dq = 0 \ ) $$

$$ + dU = dW $$

$$ + dU = nC_v \ dT \quad or \quad C_v \cdot n \cdot dT = dW $$

This equation reveals on further treatment within temperature limits of $T_1$ and $T_2$, reveals

$$ w_{rev} = \frac{nR}{Y - 1} \ [ T_2 - T_1 ] $$
If $T_2 > T_1$ then $W_{\text{rev}} = +\text{ve}$, i.e., work done on the system

If $T_2 < T_1$ then $W_{\text{rev}} = -\text{ve}$, i.e., work done on the system

Where $\gamma$ is Poisson’s ratio $= \frac{C_p}{C_v}$

Also, $\Delta H = nC_p(T_2 - T_1)$

If final temperature is not known:

**Entrance;**

$$w = -nC_vT_1 \left[ 1 - \left( \frac{P_2}{P_1} \right)^{\frac{R}{C_p}} \right]$$

Some important results of adiabatic equations

1. $PV^\gamma = \text{constant}$
2. $T^\gamma P^{1-\gamma} = \text{constant}$
3. $V^{\gamma-1}T = \text{constant}$

9. Work done in adiabatic irreversible expansion or compression:
   - (a) Expansion against vacuum or free expansion: $w = 0$
   - (b) Expansion or compression against external pressure:
     $$w = -P_{\text{ext}} x R \left[ \frac{P_1T_2 - P_2T_1}{P_1P_2} \right]$$

Efficiency $\eta$ of Carnot Cycle:

(a)

$$\eta = \frac{w}{Q_2} = \frac{T_2 - T_1}{T_2} = \frac{Q_2 - Q_1}{Q_2}$$

Where, $Q_2$ is the heat absorbed from the source at $T_2$ and $-Q_1$ is the heat lost to the sink at $T_1$.

**Joule – Thomson Effect:** The phenomenon of change of temperature produced when a gas is made to expand adiabatically from a region of high pressure to a region of extremely low pressure through a small jet is called Joule – Thomson effect.

(a) The temperature below which a gas becomes cooler on expansion is known as the inversion temperature $T_i$. Above this temperature gas shows heating effect.

$$T_i = \frac{2a}{Rb}$$

Where, $a$ and $b$ called van der Waal’s constant.
(b) Joule – Thomson effect is zero for an ideal gas in which van der Waal’s forces of attraction are negligible and there is no expenditure of energy in overcoming these forces of attraction.

Joule – Thomson coefficient \( \mu_\pi \) is given by

\[
\mu_\pi = \left( \frac{\delta T}{\delta p} \right)_T = - \left( \frac{\delta H}{\delta p} \right)_T / C_p
\]

\( \mu_\pi = 0 \) for an ideal gas, \( \mu_\pi = -ve \) for heating effect;

\( \mu_\pi = +ve \) for cooling effect

**Entropy:** Entropy (S) is a state function and is a measure of degree of disorder of randomness of system. More is the disorder in system, higher is its entropy. It is normally expressed in terms of change in entropy.

1. For a reaction entropy change (\( \Delta S \)) is given by

\[
(\Delta S = \Sigma S_{\text{products}} - \Sigma S_{\text{reactants}})
\]

2. \( \Delta S = \frac{q_{rev}}{T} = \frac{W_{rev}}{T} = \frac{n r t \log e \frac{V_2}{V_1}}{T} = n R \log e \frac{V_2}{V_1} \)

3. At constant \( P \), \( q_{rev} = \Delta H_{rev} \)

\[
\Delta S = \frac{\Delta H_{rev}}{T}
\]

i.e, entropy change of fusion: \( \Delta S_f = \frac{\Delta H_{rev}}{T} \) where \( T \) is freezing point

And entropy change of vaporization: \( \Delta S_v = \frac{\Delta H_v}{T} \) where \( T \) is boiling point

4. Entropy of one mole of a substance in pure state at one atmosphere and 25 \(^\circ\)C is termed as standard entropy, \( S^\circ \).

For a reaction in standard state, \( A \rightarrow B \)

\[
\Delta S^\circ = S^\circ_B - S^\circ_A
\]

5. Entropy, \( S \), is related to thermodynamics probability, \( W \) by the relation:

\[
S = k \log e W \text{ or } s = 2.303 K \log_{10} W
\]

Where, \( k \) is Boltzmann’s constant.
6. At absolute zero temperature, as solid is supposed to have highly ordered state, i.e., \( W = 1 \) and hence \( S = 0 \), i.e., \( \lim_{T \to 0} S = 0 \); This is zeroth law of thermodynamics.

Free energy F or G: Free energy (F or G) is also a state function and is a measure of maximum work done. It is expressed as

\[
G = H - TS
\]

\[
\Delta G = \Delta H - T\Delta S
\]

Standard free energy change (\( \Delta G^\circ \))

1. \( \Delta G^\circ = -2.303 \, RT \, \log_{10} K \)
2. At equilibrium \( \Delta G = 0 \)
3. The decrease in free energy (\( -\Delta G \)) is given as:

\[
-\Delta G = W_{net} = 2.303 \, nRT \, \log_{10} \frac{V_2}{V_1}
\]

4. \( \Delta G_f^\circ \) for free elemental state = 0
5. \( \Delta G_f^\circ = \Delta G_{\text{products}}^\circ - \Delta G_{\text{reactants}}^\circ \)

Conditions for spontaneity of reaction: For a spontaneous change \( \Delta G = -\text{ve} \).

Thus following results can also be evaluated for spontaneously process.

<table>
<thead>
<tr>
<th>( \Delta H )</th>
<th>( \Delta S )</th>
<th>( \Delta H - T\Delta S )</th>
<th>Nature</th>
</tr>
</thead>
<tbody>
<tr>
<td>Negative</td>
<td>Positive</td>
<td>( \therefore \Delta G = -\text{ve} )</td>
<td>Spontaneous</td>
</tr>
<tr>
<td>Positive</td>
<td>Negative</td>
<td>( \therefore \Delta G = +\text{ve} )</td>
<td>Non - Spontaneous</td>
</tr>
<tr>
<td>Positive</td>
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<td>Spontaneous</td>
</tr>
<tr>
<td>Negative</td>
<td>Negative</td>
<td>If ( \therefore \Delta H &gt; T\Delta S ) i.e., ( T ) is low ( \Delta G = +\text{ve} )</td>
<td>Spontaneous</td>
</tr>
<tr>
<td></td>
<td></td>
<td>If ( \therefore \Delta H &lt; T\Delta S ) i.e., ( T ) is high</td>
<td>Non - Spontaneous</td>
</tr>
</tbody>
</table>

Gibb’s Helmholtz equations: It interrelates \( \Delta G \) and \( \Delta H \) at constant pressure:

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

or

\[
\frac{\Delta G - \Delta H}{T} = \left[ \frac{\partial (\Delta G)}{\partial T} \right]_p
\]

or

\[
-\Delta S = \left[ \frac{\partial (\Delta G)}{\partial T} \right]_p
\]
Thus temperature coefficient of the emf of a cell is

\[ \left( \frac{\partial E_{\text{cell}}}{\partial T} \right)_p \frac{\Delta S}{nF} \]

**Temperature dependence of vapour state or the Clapeyron – Clausius equation.**

*Variation of the vapour pressure for the liquid = gas equilibrium is given by Capeyron – Clausis equation.*

\[
\log P = -\frac{\Delta H_v}{2.303R} \left( \frac{1}{T} \right) + K
\]

If vapour \( P_1 \) and \( P_2 \) at temperatures \( T_1 \) and \( T_2 \) are known then by equation;

\[
\log P = -\frac{\Delta H_v}{2.303R} \left( \frac{1}{T} \right) + K
\]

\[
\log \frac{P_2}{P_1} = \frac{\Delta H_v}{2.303R} \left[ \frac{T_2 - T}{T_1 T_2} \right]
\]
PRACTISE QUESTIONS

1. A system is provided 50 J of heat and work done on the system is 110 J. What is the change in internal energy?  
   \[ \text{Ans: } 60 \text{ J} \]

2. The work done by a system is 8 J, when 40 J heat is supplied to it. Calculate the increase in internal energy of system.  
   \[ \text{Ans: } 32 \text{ J} \]

3. A gas occupies 2 litres at STP. It is provided 300 J heat so that its volume becomes 2.5 litres at 1 atm. Calculate change in its internal energy.  
   \[ \text{Ans: } 249.37 \text{ J} \]

4. A certain electric motor produced 15kJ of energy each second as mechanical work and lost 2kJ as heat to the surroundings. What is the change in the internal energy of the motor and its power supply each second?  
   \[ \text{Ans: } -17 \text{ kJ} \]

5. An insulated container is divided into two equal portions. One portion contains an ideal gas at pressure P and temperature T. The other portion is a perfect vacuum. If a hole is opened between two portions, calculate:
   
   (a) The change in internal energy
   
   (b) The change in temperature of gas

6. Two litres of N\(_2\) at 0°C and 5 atm pressure are expanded isothermally against a constant external pressure of 1 atm until the pressure of gas reaches 1 atm, assuming gas to be ideal, calculate work of expansion.  
   \[ \text{Ans: } 810.10 \text{ J} \]

7. 2.8 g of N\(_2\) gas at 300 K and 20 atm was allowed to expand isothermally against a constant external pressure of 1 atm. Calculate \(\Delta U\), \(q\) and \(W\) for the gas.  
   \[ \text{Ans: } q = 236.95 \text{ J}, \ W = -236.95 \text{ J} \]

8. Calculate the work done in open vessel at 300 K, when 92 g Na reacts with water, assume ideal gas nature.  
   \[ \text{Ans: } -4988.4 \text{ J} \]

9. The internal energy change in the conversation of 1.0 mole of the calcite for of CaCO\(_3\) to the aragonite for is +0.21 kJ. Calculate the enthalpy change when the pressure is 1.0 bar; given that the densities of the solids are 2.71 g cm\(^{-3}\) and 2.93 g cm\(^{-3}\) respectively.  
   \[ \text{Ans: } 209.72 \text{ J} \]
10. Calculate the work done when a system raises a column of water of radius 5.0 mm through 10 cm. [Ans: \(-3.85 \times 10^{-3} \text{ J}\)]

11. Calculate the work done when 50 g of iron reacts with hydrochloric acid in (1) a closed vessel of fixed volume (2) an open beaker at 25°C.

12. A gas present in a cylinder fitted with a frictionless piston expands against a constant pressure of 1 atm from a volume of 2 litres to a volume of 6 litres. In doing so, it absorbs 800 J heat from surroundings. Determine increase in internal energy of process. [Ans: 394.95 J]

13. Work done in expansion of an ideal gas from 4 litres to 6 litres against a constant external pressure of 2.5 atm was used to heat up 1 mole of water at 293 K. if specific heat of water is 4.184 J g⁻¹ K⁻¹, what is the final temperature of water? [Ans: 299.723 K]

14. A gas expands from 3 dm³ to 5 dm³ against a constant pressure of 3 atm. The work done during expansion is used to heat 10 mole of water of temperature 290 K. Calculate final temperature of water. Specific heat of water = 4.184 J g⁻¹ K⁻¹. [Ans: 290.81 K]

15. Calculate the maximum work done in expanding 16 g of oxygen at 300K and occupying a volume of 5 dm³ isothermally until the volume becomes 25dm³. [Ans: 2.01 x 10³ J]

16. Calculate q, W, ΔU and ΔH for the isothermal reversible expansion of one mole of an ideal gas from an initial pressure of 1.0 bar to a final pressure of 0.1 bar at a constant temperature of 273 K. [Ans: W = -5772.2 J, q = 5227.2 J, ΔH = 0]

17. What work is to be done on 2 mole of a perfect gas at 27 °C if it is compressed reversibly and isothermally from a pressure of 1.01 x 10⁵ Nm⁻² to 5.05 x 10⁻⁶ Nm⁻²? Also calculate the free energy change.

18. 1 mole of an ideal gas undergoes reversible isothermal expansion from an initial volume \(V_1\) to a final volume 10\(V_1\) and does 10kJ of work. The initial pressure was 1 x 10⁷ Pa.

(a) Calculate \(V_1\). [Ans: \(V = 4.34 \times 10^{-4} \text{ m}^3\)]

(b) If there were 2 mole of gas, what must its temperature have been? [Ans: \(T = 261.13K\)]
19. 10 g of argon gas is compressed isothermally and reversibly at a temperature of 27°C from 10L to 5L. Calculate $q$, $W$, $\Delta U$ and $\Delta H$ for this process. $R = 2.0 \text{ cal K}^{-1} \text{mol}^{-1}$, 
$\log_{10} 2 = 0.30$. Atomic weight of Ar = 40.

20. At 27°C one mole of an ideal gas is compressed isothermally and reversibly from a pressure of 2 atm to 10 atm. Calculate $\Delta U$ and $q$. 
[Ans: $q = -965.84 \text{ cal}$]

21. One mole of an ideal gas is heated at constant pressure from 0°C to 100°C.
(a) Calculate work done. 
[Ans: -198.7 cal]
(b) If the gas were expanded isothermally and reversibly at 0°C from 1 atm to some other pressure $P_f$, what must be the final pressure if the maximum work is equal to the work involved in (a)? 
[Ans: 0.694 atm]

22. Water is boiled under a pressure of 1.0 atm. When an electric current of 0.50A from a 12V 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)

23. In an insulated container 1 mole of a liquid molar volume 100 mL at 1 bar. Liquid is steeply taken to 100 bar, when volume of liquid decreases by 1 mL. Find $\Delta H$ and $\Delta U$ for the process. 
[Ans: 9900 bar mL]

24. Calculate the standard internal energy change for the reaction;
$\text{OF}_2 (g) + \text{H}_2\text{O}(g) \rightarrow \text{O}_2(g) + 2\text{HF} (g)$ at 298 K. The standard enthalpies of formation of $\text{OF}_2 (g), \text{H}_2\text{O}(g), \text{HF} (g)$ are +20, +250 and -270kJ mol$^{-1}$. 
[Ans: -312.4775 kJ]

25. In an insulated container 1 mole of an ideal gas is reversibly expanded at 600 K to 300 K. Calculate the work done by gas if:
(a) Gas is monoatomic 
[Ans: $-3.779 \times 10^3 \text{ kJ}$]
(b) Gas is diatomic 
[Ans: $-6.236 \times 10^3 \text{ kJ}$]

26. 0.40 mole of a monoatomic gas fills a 1 dm$^3$ container to a pressure 1.013 x 10$^6$ Pa. It is expanded reversibly to a pressure 1.013 x 10$^6$ Pa. It is expanded reversibly and adiabatically until a pressure of 1.013 x 10$^5$ Pa is reached. Calculate:
(a) What is final volume of gas? 
[Ans: 3.98 dm$^3$]
(b) Initial and final temperature of gas. 
[Ans: $T_1 = 404.6 K$, $T_2 = 121.28 K$]
(c) Work done by gas during expansion. 
[Ans: $-923.7 J$]
27. 14 g oxygen at 0°C and 10 atm is subjected to reversible adiabatic expansion to a pressure of 1 atm. Calculate the work done in:

(a) Litre-atm  
   [Ans: -11.82 litre – atm]

(b) Calories  
   [Ans: -286.0 Cal]

28. 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 in this process. C_v,m for argon is 12.48 JK⁻¹ mol⁻¹.  
   [Ans: -114.51 J]

29. Two moles of an ideal monoatomic gas (C_v = 12.55 JK⁻¹ mol⁻¹) expands irreversibly and adiabatically from an initial pressure of 1.013 x 10⁶ Pa against a constant external pressure of 1.013 x 10⁵ Pa until the temperature drops from the initial value of 325 K to a final value of 275 K. Calculate the work done by the gas and its final volume.  
   [Ans: -1255 J, 17.72 dm³]

30. An ideal monoatomic gas (C_v = 1.5 R) initially at 298 K and 1.013 x 10⁶ Pa pressure expands adiabatically until it is in equilibrium with a constant external pressure of 1.013 x 10⁵ Pa. Calculate the final temperature of gas.  
   [Ans: T₂ = 190.7 K]

31. A given volume of N₂ gas (C_v = 5/2 R) at 373 K and 1.013 x 10⁵ Pa pressure is adiabatically compressed against a definite value of pressure in order to raise its temperature to 673 K. Calculate the minimum value of this definite pressure.  
   [Ans: 3.865 x 10⁸ Pa]

32. Calculate the equilibrium constant for the reaction given below at 400 K if ΔH° = 77.2 kJ mol⁻¹ and ΔS° = 122 JK⁻¹ mol⁻¹. PCl₅(g) → PCl₃ (g) + Cl₂ (g).  
   [Ans: K_c = 1.958 x 10⁻⁴]

33. The standard enthalpy and entropy changes for the reaction in equilibrium for the forward direction are given below:

\[
CO (g) + H₂O ⇌ CO₂(g) + H₂(g)
\]

\[
\Delta H°_{300K} = -41.16 \text{ kJ mol}^{-1}
\]

\[
\Delta S°_{300K} = -4.24 \times 10^{-2} \text{ kJ mol}^{-1}
\]

\[
\Delta H°_{1200K} = -32.93 \text{ kJ mol}^{-1}
\]

\[
\Delta S°_{1200K} = -2.96 \times 10^{-2} \text{ kJ mol}^{-1}
\]
Calculate $K_p$ at each temperature and predict the direction at 300 K and 1200 K, when $P_{CO} = P_{CO2} = P_{H2} = P_{H2O} = 1$ at the initial state.

34. An athlete in a gymnasium room lifts a 50kg mass through a vertical distance of 2.0m; $g = 9.8 \text{ m s}^{-2}$. The mass is allowed to fall through 2.0m distance while coupled to an electrical generator. The electrical generator produces an equal amount of electrical work. This electrical work is used to produce aluminum by Hall’s process involving the change,

$$Al_2O_3 \text{ (molten)} + 3C \text{ (s)} \rightarrow 2Al(1) + 3CO \text{ (g)}$$

The reaction required standard Gibbs energy change equal to 593 kJ. How many times must the athlete lift the 50 kg mass and to drop and couple with generator to produce sufficient Gibbs energy to produce 27 g Al?

35. A gas present in a cylinder fitted with a frictionless piston expands against a constant pressure of 1 atm from a volume of 2 litres to a volume of 6 litres. In doing so, it absorbs 800 J heat from surroundings. Determine increase in internal energy of process.

36. Determine the value of $\Delta H$ and $\Delta U$ for the reversible isothermal evaporation of 90.0 g of water at 100°C. Assume that water vapour behaves as an ideal gas and heat of evaporation of water is 540 cal g$^{-1}$. ($R = 2$ cal mol$^{-1}$ K$^{-1}$)