Physics I

Thermodynamics

Thermodynamics is that branch of physics which deals with heat in motion.

Zeroth law of Thermodynamics: When two bodies are separately in thermal equilibrium with a third then they are also in thermal equilibrium with each other.

First law of Thermodynamics: 1ˢᵗ form: A definite amount of work is needed to a definite amount of heat and vice versa. If W be the amount of work done, then the heat H will be produced if

$$W = JH \qquad\qquad J = 4.186 \text{ J/cal}$$

Second form: In all transformations the amount of heat supplied to a system must be balanced by sum of the gain in thermal energy of the system due to the rise in temperature and the external work done.

$$dQ = dU + \frac{dW}{J}$$

$dQ \rightarrow$ Heat supplied

$dU \rightarrow$ change in internal energy

$\frac{dW}{J} \rightarrow$ heat $\approx$ workdone

Reversible Process: A process which can be retraced in the opposite direction is called Reversible Process.

Example: Change in volume reverse as the substance freeze.

Irreversible Process: A process which cannot be retraced in the opposite direction is called Irreversible Process.

Example: All nature process are Irreversible Process.

Efficiency of Heat Engine:

Heat engine is a device for converting heat into mechanical energy. The ratio of total work done, and heat absorbed in a cycle by a heat engine is the efficiency of that heat engine. If W amount of work obtainable from a heat engine expensing Q amount of heat in one cycle, then its efficiency η is given by

$$\eta = \frac{W}{Q}$$

The Carnot cycle:

A cycle in which the working substance starting from a given conditions temperature, pressure and volume is made to undergo two successive expansions and then two successive compressions at the end of which the working substance is brought back to its initial conditions is called Carnot's cycle.

Efficiency of Carnot engine:

$$\eta = \frac{Work\ done}{Heat\ drawn\ from\ the\ source}$$

$$= \frac{Heat\ converted\ into\ work}{Heat\ drawn\ from\ the\ source}$$

$$= \frac{Q_1 - Q_2}{Q_1}$$

$$= 1 - \frac{Q_2}{Q_1}$$

$\therefore$ $\quad\quad$ $$\eta = 1 - \frac{Q_2}{Q_1} = 1 - \frac{T_2}{T_1}$$

$$=> \frac{Q_2}{Q_1} = \frac{T_2}{T_1}$$

Example 20.1: Find the efficiency of a Carnot engine working between the steam point and the ice point.

Solution: We know,

$$\eta = 1 - \frac{T_2}{T_1} \quad\quad\quad\quad\quad\quad T_1 = (273 + 100)$$

$$= 1 - \frac{273}{373} \quad\quad\quad\quad\quad\quad\quad = 373\ K$$

$$= \frac{100}{373} \quad\quad\quad\quad\quad\quad\quad\quad T_2 = (273 + 0) = 273\ K$$

$$= 0.2681$$

% of efficiency $= 0.2681 \times 100 = 26.81\%$

Example 20.5: A Carnot Engine whose temperature of the source is 400 K takes 200 calories of heat at this temperature and rejects 150 cal of heat in the sink.

  i. What is the temperature of the sink?
 ii. Calculate the η efficiency of the engine.

Solution: We know,

$$\frac{Q_1}{T_1} = \frac{Q_2}{T_2}$$

$$=> T_2 = \frac{Q_2}{Q_1} \times T_1$$

$$=> T_2 = \frac{150}{200} \times 400`$$

$$\therefore T_2 = 300 \ K$$

$Q_1 = 200 \ cal$

$Q_2 = 150 \ cal$

$T_1 = 400 \ K$

$T_2 = ?$

Efficiency,

$$\eta = 1 - \frac{T_2}{T_1}$$

$$=> \eta = 1 - \frac{300}{400}$$

$$\therefore \ \eta = 0.25$$

% of efficiency, $.25 \times 100 = 25\%$

2nd law of Thermodynamics: Kelvin-Planck's statement of 2nd law of thermodynamics:

It is impossible to construct an engine which operating in a cycle will produce no other effect than the extraction of heat from a reservoir and the performance of an equivalent amount of work.

Carnot's Theorem:

  i.   All reversible engines working between the same temperature limits have the same efficiency.
 ii.   Working between the same initial and final temperatures no engine can be more efficient that a reversible one.

Example 20.13: A Carnot engine is operated between two reservoirs at temperature 400 K and 300 K.

i. If the engine receives 1200 cal from the reservoir at 400 K in each cycle. How many calories does it reject to the reservoir at 300 K?

Solution: We know,

$$\frac{Q_1}{T_1} = \frac{Q_2}{T_2}$$ $Q_1 = 1200 \ cal$

$$=> Q_2 = \frac{Q_1}{T_1} \times T_2$$ $T_1 = 400 \ K$

$$=> Q_2 = \frac{1200}{400} \times 300$$ $T_2 = 300 \ K$

$$\therefore \ Q_2 = 900 \ cal$$

ii. If the engine operated in reverse as a refrigerator and receives 1200 cal from the reservoir at 300 K, How many calories does it deliver to the reservoir at 400 K?

Solution: We know,

$$\frac{Q_1}{T_1} = \frac{Q_2}{T_2}$$ $T_1 = 400 \ K$

$$=> Q_1 = \frac{Q_2}{T_2} \times T_1$$ $T_2 = 300 \ K$

$$=> Q_1 = \frac{1200}{300} \times 400$$ $Q_2 = 1200 \ cal$

$$\therefore \ Q_1 = 1600 \ cal$$ $Q_1 =?$

Adiabatic Process: the thermodynamic process in which no heat can go out from the system nor can inter into the system from outside is known as adiabatic process.

Isothermal Process: the thermodynamic process in which the temperature of the system remain constant is called isothermal Process.

Isobaric Process: the thermodynamic process in which the pressure of the system remains constant is called isobaric process.

Isochoric Process: the thermodynamic process in which the volume of the closed system remains constant.

Thermodynamic function

Internal energy: The internal energy is defined as function of entropy and volume can be written as

$$U = U(S,V)$$

Or, $dU = \left(\frac{\partial U}{\partial s}\right)_V ds + \left(\frac{\partial U}{\partial v}\right)_S dV$

Implies, $\left(\frac{\partial U}{\partial s}\right)_V = T$ & $\left(\frac{\partial U}{\partial v}\right)_S = -P$

Helmholtz free energy function: The Helmholtz Free energy function is defined as

$$F = U - TS$$

Where U is the internal energy, T is the temperature and S is the entropy. It is used in the equation of state of auto-encoder.

Gibbs free energy function: The Gibbs Free energy function is defined as

$$G = U - TS + PV$$

The state of minimum G is the state of stable equilibrium at a definite set of temperature and pressure.

The Gibbs free energy function is used to determine the voltage of electrochemical cell and the equilibrium constant for a reversible process.

Enthalpy: The Enthalpy is defined as total heat function can be written as

$H = U + PV$

The Enthalpy is a function of entropy and pressure.

$H = H(S, P)$

$or, dH = \left(\frac{\partial H}{\partial S}\right)_P ds + \left(\frac{\partial H}{\partial P}\right)_S dP$

The Enthalpy is the amount of heat energy used or released in a system at a constant pressure.

The Enthalpy can be used in refrigerator and hand warmers. In refrigerator the freon is vaporized. The Enthalpy of vaporization is equivalent to the coldness of our food.

Prove the following two relations (i) $U = \left(\frac{\partial(F/T)}{\partial(1/T)}\right)_V$ **(ii)** $F = \left(\frac{\partial(G/P)}{\partial(1/P)}\right)_T$

Solution

We know

$(i) F = U - TS \ \& \ S = -\left(\frac{\partial F}{\partial T}\right)_V$

Combining the above two equations we have

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

$= -T^2 \left(\frac{\partial(F/T)}{\partial T}\right)_V = \left(\frac{\partial(F/T)}{\partial(1/T)}\right)_V$ since $\partial(1/T) = -1/T^2 \, dT$

$(ii) \ F = G - PV \ \& \ V = -\left(\frac{\partial G}{\partial P}\right)_T$

Combining the above two equations we have

$F = G - P\left(\frac{\partial G}{\partial P}\right)_T$

$= -P^2 \left(\frac{\partial(G/P)}{\partial P}\right)_T = \left(\frac{\partial(G/P)}{\partial(1/P)}\right)_T$ since $\partial(1/P) = -1/P^2 \, dP$

Show that (i) $S = \left(\frac{\partial G}{\partial T}\right)_P$ **(ii)** $V = \left(\frac{\partial G}{\partial P}\right)_T$

Solution:

The Gibbs free energy function can be written as

$$G = U - TS + PV \qquad\qquad\qquad (i)$$

For an infinitesimal reversible process

$$\partial G = \partial U - T\partial S - S\partial T + P\partial V + V\partial P$$

$$= T\partial S - T\partial S - S\partial T + V\partial P$$

$$= -S\partial T + V\partial P \qquad\qquad (ii) \qquad since, T\partial S = \partial U + P\partial V$$

Hence, G is a function of two independent variables T & P.

So we have, $G = G(T, P)$

$$or, dG = \left(\frac{\partial G}{\partial T}\right)_P dT + \left(\frac{\partial G}{\partial P}\right)_T dP \qquad\qquad (iii)$$

Equating the co-efficient of dT & dP, using equation (ii) & (iii)

$$S = -\left(\frac{\partial G}{\partial T}\right)_P \quad \& \quad V = \left(\frac{\partial G}{\partial P}\right)_T \qquad\qquad (Shown)$$

Using Maxwell thermodynamic relation prove that $C_P - C_V = T\left(\frac{\partial P}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P$

Solution

We know $S = S(T, V)$ where T & V are two independent variables.

$$or, dS = \left(\frac{\partial S}{\partial T}\right)_V dT + \left(\frac{\partial S}{\partial V}\right)_T dV$$

$$or, \left(\frac{\partial S}{\partial T}\right)_P = \left(\frac{\partial S}{\partial T}\right)_V + \left(\frac{\partial S}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P$$

Multiplying both sides by T and rearranging we have

$$T\left(\frac{\partial S}{\partial T}\right)_P - T\left(\frac{\partial S}{\partial T}\right)_V = T\left(\frac{\partial S}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P \qquad since, T\partial S = \partial Q \ \& \ T\left(\frac{\partial P}{\partial T}\right)_V = \left(\frac{\partial Q}{\partial V}\right)_T$$

So, $C_P - C_V = T\left(\frac{\partial P}{\partial T}\right)_V \left(\frac{\partial V}{\partial T}\right)_P$ (proved)

- For perfect gas show that $C_P - C_V = R$

Solution

For perfect gas $PV = RT$

$\left(\frac{\partial P}{\partial T}\right)_V = R/V$ & $\left(\frac{\partial V}{\partial T}\right)_P = R/P$

But $C_P - C_V = T\left(\frac{\partial P}{\partial T}\right)_V \left(\frac{\partial V}{\partial T}\right)_P = \frac{TR}{V} \times \frac{R}{P} = \frac{TR^2}{RT}$

Hence, $C_P - C_V = R$ **(Shown)**

Ex.22.5 Compute the slope of vaporization and the sublimation curve of H_2O at $0°C$ and show that they are two different line not two parts of same line. Given that the latent heat of vaporization = 607cal and the latent heat of sublimation = 687cal. Assume that $V_g - V_l \approx V_g - V_S = 21 \times 10^4 CC$.

Solution

From Clapeyron's equation

$$\frac{dP}{dT} = \frac{L}{T(V_f - V_i)}$$

The slope of vaporization at $0°C$

$\left(\frac{dP}{dT}\right)_{T=273} = \frac{607 \times 4.2 \times 10^7}{273 \times 21 \times 10^4}$

$= 4.45 \times 10^2 \text{dyne/sqcm/ } 0°C$

The slope of sublimation at $0°C$

$\left(\frac{dP}{dT}\right)_{T=273} = \frac{687 \times 4.2 \times 10^7}{273 \times 21 \times 10^4}$

$= 5.03 \times 10^2 \text{dyne/sqcm/ } 0°C$

Since there are different slopes so they are two different line not two parts of same line.

Ex.22.4 Using Maxwell thermodynamic relation prove that the ratio of the adiabatic to the isochoric pressure coefficient of expansion is equal to $\gamma/(\gamma-1)$

Solution

We know adiabatic pressure coefficient of expansion is

$$B_S = \frac{1}{P}\left(\frac{\partial P}{\partial T}\right)_S \qquad\qquad \text{(i)}$$

Again, isochoric pressure coefficient of expansion is

$$B_V = \frac{1}{P}\left(\frac{\partial P}{\partial T}\right)_V \qquad\qquad \text{(ii)}$$

Dividing (i) by (ii) we have

$$\frac{B_S}{B_V} = \frac{\frac{1}{P}\left(\frac{\partial P}{\partial T}\right)_S}{\frac{1}{P}\left(\frac{\partial P}{\partial T}\right)_V}$$

$$= \frac{\left(\frac{\partial P}{\partial T}\right)_S}{\left(\frac{\partial P}{\partial T}\right)_V} = \frac{1}{\left(\frac{\partial T}{\partial P}\right)_S\left(\frac{\partial P}{\partial T}\right)_V}$$

But from Maxwell's relation we know $\left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P$

Hence, $\dfrac{B_S}{B_V} = \dfrac{1}{\left(\frac{\partial V}{\partial S}\right)_P\left(\frac{\partial P}{\partial T}\right)_V} = \dfrac{1}{\left(\frac{\partial V}{\partial T}\right)_P\left(\frac{\partial T}{\partial S}\right)_P\left(\frac{\partial P}{\partial T}\right)_V}$

$$= \frac{\left(\frac{\partial S}{\partial T}\right)_P}{\left(\frac{\partial V}{\partial T}\right)_P\left(\frac{\partial P}{\partial T}\right)_V} = \frac{T\left(\frac{\partial S}{\partial T}\right)_P}{T\left(\frac{\partial V}{\partial T}\right)_P\left(\frac{\partial P}{\partial T}\right)_V} = \frac{\left(\frac{\partial Q}{\partial T}\right)_P}{T\left(\frac{\partial V}{\partial T}\right)_P\left(\frac{\partial P}{\partial T}\right)_V}$$

$$= \frac{C_P}{C_P - C_V} = \frac{C_P/C_V}{C_P/C_V - 1} = \frac{\gamma}{\gamma - 1} \qquad\qquad \text{(proved)}$$

Ex.22.3 Show that for a Van der waals gas $C_P - C_V = R\left(P + \frac{a}{V^2}\right)\left(P - \frac{a}{V^2} + \frac{2ab}{V^3}\right)$

Solution

For one mole of Van der Waals gas we know

$$P = \frac{RT}{V-b} - \frac{a}{V^2}$$

Or, $\left(\frac{\partial P}{\partial T}\right)_V = \frac{R}{V-b}$

Rearranging Van der Waal's equation we get,

$$PV + \frac{a}{V} - Pb - \frac{ab}{V^2} = RT$$

Differentiating the above equation with respect to T keeping P fixed

$$P\left(\frac{\partial V}{\partial T}\right)_P - \frac{a}{V^2}\left(\frac{\partial V}{\partial T}\right)_P + \frac{2ab}{V^3}\left(\frac{\partial V}{\partial T}\right)_P = R$$

or, $\left(\frac{\partial V}{\partial T}\right)_P = R\left/\left(P - \frac{a}{V^2} + \frac{2ab}{V^3}\right)\right.$

But from Maxwell thermodynamic relation we know

$$C_P - C_V = T\left(\frac{\partial P}{\partial T}\right)_V\left(\frac{\partial V}{\partial T}\right)_P = T \times \frac{R}{V-b} \times R\left/\left(P - \frac{a}{V^2} + \frac{2ab}{V^3}\right)\right.$$

Since, $\left(P + \frac{a}{V^2}\right) = \frac{TR}{V-b}$

Hence, $C_P - C_V = R\left(P + \frac{a}{V^2}\right)\left/\left(P - \frac{a}{V^2} + \frac{2ab}{V^3}\right)\right.$　　　**(Shown)**