Phase Transformations (Part - 1)

Q. 185. A saturated water vapour is contained in a cylindrical vessel under a weightless piston at a temperature $t = 100^{\circ}$ C. As a result of a slow introduction of the piston a small fraction of the vapour $\Delta m = 0.70$ g gets condensed. What amount of work was performed over the gas? The vapour is assumed to be ideal, the volume of the liquid is to be neglected.

Solution. 185. The condensation takes place at constant pressure and temperature and the work done is $p \Delta V$

Where ΔV is the volume of the condensed vapour in the vapour phase. It is

 $p \Delta V = \frac{\Delta m}{M} RT = 120.6 \text{ J}$

Where M = 18 gm is the molecular weight of water.

Q. 186. A vessel of volume V = 6.0 l contains water together with its saturated vapour under a pressure of 40 atm and at a temperature of 250° C. The specific volume of the vapour is equal to V'_c = 50 l/kg under these conditions. The total mass of the system water-vapour equals m = 5.0 kg. Find the mass and the volume of the vapour.

Solution. 186. The specific volume of water (the liquid) will be written

as $V_{l'}$ Since $V_{v} > > V_{l'}$ most of the weight is due to water. Thus if ml is mass of the

liquid and my that of the vapour then

 $m = m_l + m_v$

$$V = m_l V'_l + m_v V'_v$$
 or $V - mV'_l = m_v (V'_v - V'_l)$

So $m_v = \frac{V - mV_l}{V_v - V_1} = 20 \text{ gm}$ in the present case. Its volume is $m_v V_v = 1.01$

Q. 187. The saturated water vapour is enclosed in a cylinder under a piston and occupies a volume $V_0 = 5.0$ l at the temperature $t = 100^{\circ}$ C. Find the mass of the

liquid phase formed after the volume under the piston decreased isothermally to V = 1.6 l. The saturated vapour is assumed to be ideal.

Solution. 187. The volume of the condensed vapour was originally V_0 - V at

temperature T = 373 K. Its mass will be given by

$$p(V_0 - V) = \frac{m}{M}RT$$
 or $m = \frac{Mp(V_0 - V)}{RT} = 2$ gm where p = atmospheric pressure

Q. 188. A volume occupied by a saturated vapour is reduced isothermally n-fold. Find what fraction ri of the final volume is occupied by the liquid phase if the specific volumes of the saturated vapour and the liquid phase differ by N times (N > n). Solve the same problem under the condition that the final volume of the substance corresponds to the midpoint of a horizontal portion of the isothermal line in the diagram p, V.

Solution. 188. We let V_l = Specific volume of liquid. $V_v = N V_l$ = Specific volume of vapour.

Let V = Original volume of the vapour. Then

$$M\frac{pV}{RT} = m_{l} + m_{v} = \frac{V}{NV_{l}} \text{ or } \frac{V}{n} = (m_{l} + Nm_{v})V'_{l}$$

$$(N-1)m_{l}V'_{l} = V\left(1 - \frac{1}{n}\right) = \frac{V}{n}(n-1) \text{ or } \eta = \frac{m_{l}V'_{l}}{V/n} = \frac{n-1}{N-1}$$
So

In the case when the final volume of the substance corresponds to the midpoint of a horizontal portion of the isothermal line in the p y v diagram, the final volume must

be $(1+N)\frac{V_l}{2}$ per unit mass of the substance. Of this the volume of the liquid is V'₁/2 per unit total mass of the substance.

Thus $\eta = \frac{1}{1+N}$

Q. 189. An amount of water of mass m = 1.00 kg, boiling at standard atmospheric pressure, turns completely into saturated vapour. Assuming the saturated vapour to be an ideal gas find the increment of entropy and internal energy of the system.

Solution. 189. From the first law of thermodynamics

 $\Delta U + A = Q = m q$

Where q is the specific latent heat of vaporization

Now $A = p (V_v - V_i) m = m \frac{RT}{M}$

 $\Delta U = m \left(q - \frac{RT}{M} \right)$ Thus

For water this gives $\approx 2.08 \times 10^6$ Joules.

Q. 190. Water of mass m = 20 g is enclosed in a thermally insulated cylinder at the temperature of 0°C under a weightless piston whose area is S = 410 cm². The outside pressure is equal to standard atmospheric pressure. To what height will the piston rise when the water absorbs Q = 20.0 kJ of heat?

Solution. 190. Some of the heat used in heating water to the boiling temperature $T = 100^{\circ}C = 373$ K The remaining heat $= Q - mc \Delta T$

(c = specific heat of water, ΔT - 100 K) is used to create vapour. If the piston rises to a

height h then the volume of vapour will be \approx sh (neglecting water). Its mass will

be $\frac{p_0 sh}{RT} \times M$ and heat of vaporization will be $\frac{p_0 sh Mq}{RT}$. To this must be added the work

done in creating the saturated vapour $\sim p_0 sh$. Thus

$$Q - m c \Delta T = p_0 S h \left(1 + \frac{q M}{RT} \right) \qquad \text{or} \quad h = \frac{Q - m c \Delta T}{p_0 s \left(1 + \frac{q M}{RT} \right)} = 20 \text{ cm}$$

Q. 191. One gram of saturated water vapour is enclosed in a thermally insulated cylinder under a weightless piston. The outside pressure being standard, m = 1.0 g of water is introduced into the cylinder at a temperature $t_0 = 22^{\circ}$ C. Neglecting the heat capacity of the cylinder and the friction of the piston against the cylinder's walls, find the work performed by the force of the atmospheric pressure during the lowering of the piston.

 $mc (T - T_0)$

Solution. 191. A quantity *q* of saturated vapour must condense to heat the

water to boiling point $T = 373^{\circ}K$

(Here c = specific heat of water, $T_0 = 295$ K = initial water temperature).

The work done in lowering the piston will then be

$$\frac{mc(T-T_0)}{q} \times \frac{RT}{M} = 25 \text{ J},$$

Since work done per unit mass of the condensed vapour is $p V - \frac{RT}{M}$

Q. 192. If an additional pressure Δp of a saturated vapour over a convex spherical surface of a liquid is considerably less than the vapour pressure over a plane surface, then $\Delta p = (\rho_v / \rho_l) 2\alpha / r$, where p_0 and P_1 are the densities of the vapour and the liquid, α is the surface tension, and r is the radius of curvature of the surface. Using this formula, find the diameter of water droplets at which the saturated vapour pressure exceeds the vapour pressure over the plane surface by $\eta = 1.0\%$ at a temperature t = 27° C. The vapour is assumed to be an ideal gas.

Solution. 192. Given
$$\Delta P = \frac{\rho_v}{\rho_l} \frac{2\alpha}{r} = \frac{\rho_v}{\rho_l} \times \frac{4\alpha}{d} = \eta p_{vap} = \eta \frac{\frac{m}{M}RT}{V_{vap}} = \frac{\eta RT}{M} \rho_v$$

$$d = \frac{4\alpha M}{\rho_1 R T \eta}$$

F or water a = 73 dynes/cm, M = 18gm, $p_1 = gm/cc$, T = 300 K, and with $\eta = 0.01$, we get

d = 0·2 μ m

Q. 193. Find the mass of all molecules leaving one square centimetre of water surface per second into a saturated water vapour above it at a temperature $t = 100^{\circ}$ C. It is assumed that $\eta = 3.6\%$ of all water vapour molecules falling on the water surface are retained in the liquid phase.

Solution. 193. In equilibrium the number of "liquid" molecules evaporating must equals the number of "vapour" molecules condensing. By kinetic theory, this number is

$$\eta \times \frac{1}{4} n < v > = \eta \times \frac{1}{4} n \times \sqrt{\frac{8}{\pi} \frac{kT}{m}}$$

Its mass is

$$\mu = m \times \eta \times n \times \sqrt{\frac{kT}{2\pi m}} = \eta n k T \sqrt{\frac{m}{2\pi kt}}$$

$$= \eta p_0 \sqrt{\frac{M}{2 \pi RT}} = 0.35 \text{ g/cm}^2 \cdot \text{s.}$$

Where p_0 is atmospheric pressure and T = 373 K and M = molecular weight of water.

Q. 194. Find the pressure of saturated tungsten vapour at a temperature T = 2000 K if a tungsten filament is known to lose a mass $\mu = 1.2 \cdot 10^{-13}$ g/(s•cm²) from a unit area per unit time when evaporating into high vacuum at this temperature.

Solution. 194. Here we must assume that |i is also the rate at which the tungsten filament loses mass when in an atmosphere of its own vapour at this temperature and that η (of the previous problem) ≈ 1 . Then

$$p = \mu \sqrt{\frac{2 \pi RT}{M}} = 0.9 \text{ n Pa}$$

From the previous problem where p = pressure of the saturated vapour.

Q. 195. By what magnitude would the pressure exerted by water on the walls of the vessel have increased if the intermolecular attraction forces had vanished?

Solution. 195. From the Vander Waals equation

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

Where V = Volume of one gm mole of the substances.

For water V = 18 c.c. per mole = $1*8 \times 10^{-2}$ litre per mole

$$a = 5.47 \text{ atmos} \cdot \frac{\text{litre}^2}{\text{mole}^2}$$

If molecular attraction vanished the equation will be

$$p' = \frac{RT}{V-b}$$

For the same specific volume. Thus

$$\Delta p = \frac{a}{V^2} = \frac{5 \cdot 47}{1 \cdot 8 \times 1 \cdot 8} \times 10^4 \text{ atmos} = 1 \cdot 7 \times 10^4 \text{ atmos}$$

Q. 196. Find the internal pressure p_i of a liquid if its density p and specific latent heat of vaporization q are known. The heat q is assumed to be equal to the work performed against the forces of the internal pressure, and the liquid obeys the Van der Waals equation. Calculate p_i in water.

Solution. 196. The internal pressure being $\frac{a}{V^2}$ the work done in condensation is

$$\int_{V_l}^{V_a} \frac{a}{V^2} dV = \frac{a}{V_l} - \frac{a}{V_g} = \frac{a}{V_l}$$

This by assumption is Mq , M being the molecular weight and V_1 , Vg being the molar volumes of the liquid and gas.

$$p_i = \frac{a}{V_l^2} = \frac{Mq}{V_l} = \rho q$$

Thus

Where p is the density of the liquid. For water $p_i = 3-3 \times 10^{13}$ atm

Q. 197. Demonstrate that Eqs. (2.6a) and (2.6b) are valid for a substance, obeying the Van der Waals equation, in critical state.

Instruction. Make use of the fact that the critical state corresponds to the point of inflection in the isothermal curve p (V).

Solution. 197. The Vander Waal's equation can be written as (for one mole) $p(V) = \frac{RT}{V-b} - \frac{a}{V^2}$

At the critical point $\left(\frac{\partial p}{\partial V}\right)_T$ and $\left(\frac{\partial^2 p}{\partial V^2}\right)_T$ vanish. Thus

$$0 = \frac{RT}{(V-b)^2} + \frac{2a}{V^3} \text{ or } \frac{RT}{(V-b)^2} = \frac{2a}{V^3}$$
$$0 = \frac{2RT}{(V-b)^3} - \frac{6a}{V^4} \text{ or } \frac{RT}{(V-b)^3} = \frac{3a}{V^4}$$

Solving these simultaneously we get on division

$$V - b = \frac{2}{3} V, \quad V = 3 b = V_{MCr}$$

This is the critical molar volume. Putting this back

$$\frac{R}{4b^2} \frac{T_{Cr}}{27b^3} = \frac{2a}{27b^3} \text{ or } T_{Cr} = \frac{8a}{27bR}$$

$$P_{Cr} = \frac{RT_{Cr}}{V_{MCr} - b} - \frac{a}{V_{MCr}^2} = \frac{4a}{27b^2} - \frac{a}{9b^2} = \frac{a}{27b^2}$$
Finally
$$\frac{P_{Cr}V_{MCr}}{RT_{Cr}} = \frac{a/9b}{8a/27b} = \frac{3}{8}$$

From these we see that

Q. 198. Calculate the Van der Waals constants for carbon dioxide if its critical temperature $T_{cr} = 304$ K and critical pressure $p_{cr} = 73$ atm.

Solution. 198.
$$\frac{P_{Cr}}{RT_{Cr}} = \frac{a/27 b^2}{8 a/27 b} = \frac{1}{8 b}$$

Thus

$$b = R \frac{T_{Cr}}{8 p_{Cr}} = \frac{0.082 \times 304}{73 \times 8} = 0.043 \text{ litre/mol}$$

And
$$\frac{(RT_{Cr})^2}{p_{Cr}} = \frac{64a}{27}$$
 or $a = \frac{27}{64}(RT_{Cr})^2/p_{Cr} = 3.59 \frac{\text{atm-litre}^2}{(\text{mol})^2}$

Q. 199. Find the specific volume of benzene (C_6H_6) in critical state if its critical temperature $T_{cr} = 562$ K and critical pressure $p_{cr} = 47$ atm.

Solution. 199. Specific volume is molar volume divided by molecular weight. Thus

$$V'_{Cr} = \frac{V_{MCr}}{M} = \frac{3 RT_{Cr}}{8 M p_{Cr}} = \frac{3 \times .082 \times 562}{8 \times .78 \times 47} \frac{\text{litre}}{g} = 4.71 \frac{\text{cc}}{g}$$

Q. 200. Write the Van der Waals equation via the reduced parameters π , v, and τ , having taken the corresponding critical values for the units of pressure, volume,

and temperature. Using the equation obtained, find how many times the gas temperature exceeds its critical temperature if the gas pressure is 12 times as high as critical pressure, and the volume of gas is equal to half the critical volume.

Solution. 200.

$$\begin{pmatrix} p + \frac{a}{V_M^2} \end{pmatrix} (V_m - b) = RT$$
or
$$\frac{p + \frac{a}{V_m^2}}{P_{Cr}} \times \frac{V_m - b}{V_{MCr}} = \frac{8}{3} \frac{T}{T_{Cr}}$$
or
$$\begin{pmatrix} \pi + \frac{a}{p_{Cr}^2 V_m^2} \end{pmatrix} \times \left(v - \frac{b}{V_{MCr}} \right) = \frac{8}{3} \tau,$$
or
$$\pi = \frac{p}{p_{Cr}}, v = \frac{V_m}{V_{MCr}}, \tau = \frac{T}{T_{Cr}}$$
where

Or
$$\left(\pi + \frac{27 b^2}{V_M^2}\right) \left(\nu - \frac{1}{3}\right) = \frac{8}{3}\tau$$
, or $\left(\pi + \frac{3}{\nu^2}\right) \left(\nu - \frac{1}{3}\right) = \frac{8}{3}\tau$

When

 $\pi = 12$ and $\nu = \frac{1}{2}$, $\tau = \frac{3}{8} \times 24 \times \frac{1}{6} = \frac{3}{2}$

Q. 201. Knowing the Van der Waals constants, find:

(a) the maximum volume which water of mass m = 1.00 kg can occupy in liquid state:

(b) the maximum pressure of the saturated water vapour.

Solution. 201. (a) The critical Volume V_{MCr} is the maximum volume in the liquid phase and the minimum volume in the gaseous. Thus

 $V_{\text{max}} = \frac{1000}{18} \times 3 \times 030$ litre = 5 litre

(b) The critical pressure is the maximum possible pressure in the vapour phase in equilibrium with liquid phase. Thus

$$p_{\text{max}} = \frac{a}{27 b^2} = \frac{5.47}{27 \times .03 \times .03} = 225 \text{ atmosphere}$$

Q. 202. Calculate the temperature and density of carbon dioxide in critical state, assuming the gas to be a Van der Waals one.

Solution. 202.

$$T_{Cr} = \frac{8}{27} \frac{a}{bR} = \frac{8}{27} \times \frac{3.62}{.043 \times .082} = 304 \text{ K}$$

 $\rho_{Cr} = \frac{M}{3b} = \frac{44}{3 \times 43} \, \text{gm/c.c.} = 0.34 \, \text{gm/c.c.}$

Phase Transformations (Part - 2)

Q. 203. What fraction of the volume of a vessel must liquid ether occupy at room temperature in order to pass into critical state when critical temperature is reached? Ether has $T_{cr} = 467$ K, $p_{cr} = 35.5$ atm, M = 74 g/mol.

Solution. 203. The vessel is such that either vapour or liquid of mass m occupies it at critical point. Then its volume will be

$$v_{Cr} = \frac{m}{M} V_{MCr} = \frac{3}{8} \frac{RT_{Cr}}{p_{Cr}} \frac{m}{M}$$

The corresponding volume in liquid phase at room temperature is

$$V = \frac{m}{\rho}$$

where p = density of liquid ether at room temperature. Thus

$$\eta = \frac{V}{V_{Cr}} = \frac{8 M p_{Cr}}{3 R T_{Cr} \rho} \approx 0.254$$

using the given data (and p = 720gm per litre)

Q. 204. Demonstrate that the straight line 1-5 corresponding to the isothermalisobaric phase transition cuts the Van der Waals isotherm so that areas I and II are equal (Fig. 2.5).



Solution. 204. We apply the relation (T = constant)

 $T\oint dS = \oint dU + \oint p \, dV$ to the cycle 1234531. Here $\oint dS = \oint dU = 0$ So $\oint p \, dV = 0$

This implies that the areas I and II are equal.

This reasoning is inapplicable to the cycle 1231, for example. This cycle is irreversible because it involves the irreversible transition from a single phase to a two-phase state at the point 3.



Q. 205. What fraction of water supercooled down to the temperature $t = -20^{\circ}C$ under standard pressure turns into ice when the system passes into the equilibrium state? At what temperature of the supercooled water does it turn into ice completely?

Solution. 205. When a portion of supercool water turns into ice some heat is liberated, which should heat it upto ice point. Neglecting the variation of specific heat of water, the fraction of water turning inot ice is clearly

$$f = \frac{c|t|}{q} = 0.25$$

where c = specific heat of water and q \approx latent heat of fusion of ice, Clearly f = 1 at t = - 80°C

Q. 206. Find the increment of the ice melting temperature in the vicinity of 0° C when the pressure is increased by $\Delta p = 1.00$ atm. The specific volume of ice exceeds that of water by' $\Delta V' = 0.091$ cm³/g.

Solution. 206. From the Claussius-Clapeyron (C-C) equations

$$\frac{dT}{dp} = \frac{T\left(V_2 - V_1\right)}{q_{12}}$$

 q_{12} is the specific latent heat absorbed in $1 \rightarrow 2$ (1 = solid, 2 = liquid)

$$\Delta T = \frac{T\left(\frac{V_w - V_{ice}}{q_{12}}\right)}{q_{12}} \Delta p = -\frac{273 \times \cdot 091}{333} \times 1 \frac{\operatorname{atm} \times \operatorname{cm}^3 \times \mathrm{K}}{\mathrm{joule}}$$

$$1 \frac{\text{atm} \times \text{cm}^3}{\text{Joule}} \approx \frac{10^5 \frac{\text{N}}{\text{m}^2} \times 10^{-6} \text{m}^3}{\text{Joule}} = 10^{-1}, \ \Delta T = -.0075 \text{ K}$$

Q. 207. Find the specific volume of saturated water vapour under standard pressure if a decrease of pressure by Ap = 3.2 kPa is known to decrease the water boiling temperature by $\Delta T = 0.9$ K.

Solution. 207. Here 1 =liquid, 2 =Steam

$$\Delta T = \frac{T \left(V'_s - V'_{uq} \right)}{q_{12}} \Delta P$$

$$V'_s \approx \frac{q_{12}}{T} \frac{\Delta T}{\Delta p} = \frac{2250}{373} \times \frac{0.9}{3.2} \times 10^{-3} \text{ m}^3/\text{g} = 1.7 \text{ m}^3/\text{kg}$$
or

Q. 208. Assuming the saturated water vapour to be ideal, find its pressure at the temperature 101.1 $^\circ C.$

Solution. 208. From C-C equations

$$\frac{dp}{dT} = \frac{q_{12}}{T(V_2 - V_1)} \approx \frac{q_{12}}{TV_2}$$

Assuming the saturated vapour to be ideal gas

$$\frac{1}{V_2} = \frac{mp}{RT}$$
, Thus $\Delta p = \frac{Mq}{RT^2} p \Delta T$

 $p \approx p_0 \left(1 + \frac{Mq}{RT^2} \Delta T\right) \approx 1.04$ atmosphere And

Q. 209. A small amount of water and its saturated vapour are enclosed in a vessel

at a temperature $t = 100^{\circ}$ C. How much (in per cent) will the mass of the saturated vapour increase if the temperature of the system goes up by $\Delta T = 1.5$ K? Assume that the vapour is an ideal gas and the specific volume of water is negligible as compared to that of vapour.

Solution. 209. From C-C equation, neglecting the volume of the liquid

$$\frac{dp}{dT} = \frac{q_{12}}{TV_2} = \frac{Mq}{RT^2}p, (q = q_{12})$$

or $\frac{dp}{p} = \frac{Mq}{RT}\frac{dT}{T}$
 $pV = \frac{m}{M}RT$ or $m = \frac{MpV}{RT}$ for a perfect gas

So $\frac{dm}{m} = \frac{dp}{p} - \frac{dT}{T}$ (V is Const = specific volume)

$$= \left(\frac{Mq}{RT} - 1\right) \frac{dT}{T} = \left(\frac{18 \times 2250}{8 \cdot 3 \times 373} - 1\right) \times \frac{1 \cdot 5}{373} = 4.85 \%$$

Q. 210. Find the pressure of saturated vapour as a function of temperature p(T) if at a temperature T_0 its pressure equals p_0 . Assume that: the specific latent heat of vaporization q is independent of T, the specific volume of liquid is negligible as compared to that of vapour, saturated vapour obeys the equation of state for an ideal gas. Investigate under what conditions these assumptions are permissible.

Solution. 210. From C-C equation

$$\frac{dp}{dT} \sim \frac{q}{TV_2} \sim \frac{Mq}{RT^2}p$$

Integrating In $p = constant - \frac{Mq}{RT}$

$$p = p_0 \exp\left[\frac{Mq}{R}\left(\frac{1}{T_0} - \frac{1}{T}\right)\right]$$
So

This is reasonable for $|T - T_0| \ll T_0$ and far below critical temperature.

Q. 211. An ice which was initially under standard conditions was compressed up to the pressure p = 640 atm. Assuming the lowering of the ice melting temperature to be a linear function of pressure under the given conditions, find what fraction of

the ice melted. The specific volume of water is less than that of ice by $\Delta V' = 0.09$ cm³/g.

Solution. 211. As before (Q.206) the lowering of melting point is given by

$$\Delta T = -\frac{T \Delta V'}{q} p$$

The superheated ice will then melt in part. The fraction that will melt is

$$\eta = \frac{C T \Delta V'}{q^2} p \approx \cdot 03$$

Q. 212. In the vicinity of the triple point the saturated vapour pressure p of carbon dioxide depends on temperature T as log p = a - bIT, where a and b are constants. If p is expressed in atmospheres, then for the sublimation process a = 9.05 and b = 1.80 kK, and for the vaporization process a = 6.78 and b = 1.31 kK. Find:

(a) temperature and pressure at the triple point;

(b) the values of the specific latent heats of sublimation, vaporization, and melting in the vicinity of the triple point.

Solution. 212. (a) The equations of the transition lines are

$$\log p = 9.05 - \frac{1800}{T}$$
: Solid gas
= 6.78 - $\frac{1310}{T}$: Liquid gas

At the triple point they intersect Thus

$$2.27 = \frac{490}{T_{tr}}$$
 or $T_{tr} = \frac{490}{2.27} = 216 \text{ K}$

Corresponding p_{r} is 5.14 atmosphere.

In the formula log $p = a - \frac{b}{T}$, we compare b with the corresponding term in the equation in Q.210. Then

 $\ln p = a \times 2.303 - \frac{2.303 b}{T}$ So, $2.303 = \frac{Mq}{R}$

$$q_{sublimation} = \frac{2 \cdot 303 \times 1800 \times 8 \cdot 31}{44} = 783 \text{ J/gm}$$

or,
$$q_{liquid-gas} = \frac{2 \cdot 303 \times 1310 \times 8 \cdot 31}{44} = 570 \text{ J/gm}$$

Finally q_{solid - liquid} = 213 J/gm on subtraction

Q. 213. Water of mass m = 1.00 kg is heated from the temperature $t_1 = 10^{\circ}C$ up to $t_2 = 100^{\circ}C$ at which it evaporates completely. Find the entropy increment of the system.

Solution. 213.

$$\Delta S = \int_{T_1}^{T_2} mc \, \frac{dT}{T} + \frac{mq}{T_2} = m \left(c \ln \frac{T_2}{T_1} + \frac{q}{T_2} \right)$$
$$= 10^3 \left(4.18 \ln \frac{373}{283} + \frac{2250}{373} \right) = 7.2 \, \text{kJ/K}$$

Q. 214. The ice with the initial temperature $t_1 = 0^{\circ}C$ was first melted, then heated to the temperature $t_2 = 100^{\circ}C$ and evaporated. Find the increment of the system's specific entropy.

Solution. 214.

$$\Delta S = \frac{q_m}{T_1} + c \ln \frac{T_2}{T} + \frac{q_v}{T_2}$$
$$= \frac{333}{273} + 4.18 \ln \frac{373}{283} = 8.56 \text{ J/°K}$$

Q. 215. A piece of copper of mass m = 90 g at a temperature $t_1 = 90^{\circ}C$ was placed in a calorimeter in which ice of mass 50 g was at a temperature $-3^{\circ}C$. Find the entropy increment of the piece of copper by the moment the thermal equilibrium is reached.

Solution. 215. $c = specific heat of copper = \frac{-0.39 \cdot J}{g \cdot K}$ Suppose all ice does not melt, then

heat rejected = $90 \times 0.39 (90 - 0) = 3159 \text{ J}$ heat gained by ice = $50 \times 2.09 \times 3 + x \times 333$

Thus x = 8-5 gm

The hypothesis is correct and final temperature will be T = 273K.

Hence change in entropy of copper piece = $mc \ln \frac{273}{363} = -10 \text{ J/K}.$

Q. 216. A chunk of ice of mass $m_1 = 100$ g at a temperature $t_1 = 0^{\circ}C$ was placed in a calorimeter in which water of mass $m_2 = 100$ g was at a temperature t_2 . Assuming the heat capacity of the calorimeter to be negligible, find the entropy increment of the system by the moment the thermal equilibrium is reached. Consider two cases: (a) $t_2 = 60^{\circ}C$; (b) $t_2 = 94^{\circ}C$.

Solution. 216. (a) Here $t_2 = 60^{\circ}$ C. Suppose the final temperature is t°C. Then

heat lost by water = m_2c (t_2 -1)

heat gained by ice = $m_1qm + m_1c (t - t_1)$, if all ice melts

In this case $m_1 q_m = m_2 x 4.18 (60 - t)y$ for $m_1 = m_2$

So the final temperature will be 0°C and only some ice will melt.

Then $100 \times 4.18 (60) = m'_1 \times 333$

 $m'_1 = 75.3 \text{ gm} =$ amount of ice that will melt

 $\Delta S = 75.3 \times \frac{333}{273} + 100 \times 4.18 \ln \frac{273}{333}$

Finally

$$\Delta S = \frac{m'_1 q_m}{T_1} + m_2 c \ln \frac{T_1}{T_2}$$

= $m_2 c \frac{(T_2 - T_1)}{T_1} - m_2 \ln \frac{T_2}{T_1}$
= $m_2 C \left[\frac{T_2}{T_1} - 1 - \ln \frac{T_2}{T_1} \right] = 8.8 \text{ J/K}$

(b) If $m_2 c t_2 > m_1 q_m$ then all ice will melt as one can check and the final temperature can be obtained like this

$$m_2 c (T_2 - T) = m_1 q_m + m_1 c (T - T_1)$$

(m_2 T_2 + m_1 T_1) c - m_1 q_m = (m_1 + m_2) cT

or
$$T = \frac{m_2 T_2 + m_1 T_1 - \frac{m_1 q_m}{c}}{m_1 + m_2} = 280 \text{ K}$$

$$\Delta S = \frac{m_1 q}{T_1} + c \left(m_1 \ln \frac{T}{T_1} - m_2 \ln \frac{T_2}{T} \right) = 19 \text{ J/K}$$
 and

Q. 217. Molten lead of mass m = 5.0 g at a temperature $t_2 = 327^{\circ}C$ (the melting temperature of lead) was poured into a calorimeter packed with a large amount of ice at a temperature $t_1 = 0^{\circ}C$. Find the entropy increment of the system lead-ice by the moment the thermal equilibrium is reached. The specific latent heat of melting of lead is equal to q = 22.5 J/g and its specific heat capacity is equal to c = 0.125 J/(g • K).

$$\Delta S = -\frac{m q_1}{T_2} - mc \ln \frac{T_2}{T_1} + \frac{M q_{ice}}{T_1}$$

Solution. 217.

$$M q_{ice} = m (q_2 + c (T_2 - T_1))^{-1}$$

$$= mq_2 \left(\frac{1}{T_1} - \frac{1}{T_2}\right) + mc \left(\frac{T_2}{T_1} - 1 - \frac{T_2}{T_1}\right)$$
$$= 0.2245 + 0.2564 = 0.48 \text{ J/K}$$

where

Q. 218. A water vapour filling the space under the piston of a cylinder, is compressed (or expanded) so that it remains saturated all the time, being just on the verge of condensation. Find the molar heat capacity C of the vapour in this process as a function of temperature T, assuming the vapour to be an ideal gas and neglecting the specific volume of water in comparison with that of vapour. Calculate C at a temperature $t = 100^{\circ}C$.

Solution. 218. When heat dQ is given to the vapour its temperature will change by dT, pressure by dp and volume by dV, it being assumed that the vapour remains saturated. Then by C-C equation

$$\frac{dp}{dT} = \frac{q}{TV'} \left(V'_{\text{vapour}} >> V'_{\text{Liq}} \right), \text{ or } dp = \frac{q}{TV'} dT$$

on the other hand, $pV = \frac{RT}{M}$

So
$$pdV' + V' dp = \frac{RdT}{M}$$
,

Hence $pdV' = \left(\frac{R}{M} - \frac{q}{T}\right)dT$

finally dQ = CdT = dU + pdV'

$$= C_V dT + \left(\frac{T}{M} - \frac{q}{T}\right) dT = C_p dT - \frac{q}{T} dT$$

 $(C_p, C_v \text{ refer to unit mass here})$. Thus

$$C = C_p - \frac{q}{T}$$

For water $C_p = \frac{R\gamma}{\gamma - 1} \cdot \frac{1}{M}$ with $\gamma = 1.32$ and M = 18

$$S_O C_p = 1.90 \text{ J/gm K}$$

$$C = -4.13 \text{ J/gm}^{\circ}\text{K} = -74 \text{ J/mole K}$$

Q. 219. One mole of water being in equilibrium with a negligible amount of its saturated vapour at a temperature T_1 was completely converted into saturated vapour at a temperature T_2 . Find the entropy increment of the system. The vapour is assumed to be an ideal gas, the specific volume of the liquid is negligible in comparison with that of the vapour.

Solution. 219. The required entropy change can be calculated along a process in which the water is heated from T_1 to T_2 and then allowed to evaporate. The entropy change for this is

$$\Delta S = C_p \ln \frac{T_2}{T_1} + \frac{qM}{T_2}$$

Where q = specific latent heat of vaporization.