2.6 PHASE TRANSFORMATIONS

2.185 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

$$p\,\Delta V = \frac{\Delta m}{M} RT = 120{\cdot}6\ \mathrm{J}$$

where $M = 18$ gm is the molecular weight of water.

2.186 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 m_l is mass of the liquid and m_v that of the vapour then

$$m = m_l + m_v$$

$$V = m_l V'_l + m_v V'_v \quad \text{or} \quad V - mV'_l = m_v (V'_v - V'_l)$$

So $m_v = \dfrac{V - mV'_l}{V'_v - V'_1} = 20$ gm in the present case. Its volume is $m_v V'_v = 1{\cdot}0$ l

2.187 The volume of the condensed vapour was originally $V_0 - V$ at temperature $T = 373$ K. Its mass will be given by

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

2.188 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

$$M \frac{pV}{RT} = m_l + m_v = \frac{V}{N\,V'_l} \quad \text{or} \quad \frac{V}{n} = (m_l + N m_v)\,V'_l$$

So $$(N-1)\,m_l V'_l = V\left(1 - \frac{1}{n}\right) = \frac{V}{n}(n-1) \quad \text{or} \quad \eta = \frac{m_l V'_l}{V/n} = \frac{n-1}{N-1}$$

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, v diagram, the final volume must be $(1+N)\dfrac{V'_l}{2}$ 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 $$\eta = \frac{1}{1+N}$$

2.189 From the first law of thermodynamics

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

where q is the specific latent heat of vaporization

Now $$A = p\,(V'_v - V'_l)\,m = m\frac{RT}{M}$$

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

For water this gives $\approx 2{\cdot}08 \times 10^6$ Joules.

2.190 Some of the heat used in heating water to the boiling temperature

$$T = 100°\text{C} = 373\text{ K. The remaining heat}$$

$$= Q - m\,c\,\Delta T$$

($c =$ specific heat of water, $\Delta T = 100\,K$) 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 vapourization will be $\frac{p_0\,sh\,Mq}{RT}$. To this must be added the work done in creating the saturated vapour $\approx p_0\,sh$. Thus

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

2.191 A quantity $\frac{mc\,(T - T_0)}{q}$ of saturated vapour must condense to heat the water to boiling point $T = 373°\text{K}$

(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 $p\,V = \frac{RT}{M}$

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

or
$$d = \frac{4\,\alpha\,M}{\rho_1\,RT\,\eta}$$

For water $\alpha = 73$ dynes/cm, $M = 18$gm, $\rho_l =$ gm/cc, $T = 300$ K, and with $\eta \approx 0{\cdot}01$, we get

$$d \approx 0{\cdot}2\,\mu\,\text{m}$$

2.193 In equilibrium the number of "liquid" molecules evaporoting must equals the number of "vapour" molecules condensing. By kinetic theory, this number is

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

Its mass is

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

$$= \eta\,p_0\sqrt{\frac{M}{2\,\pi\,RT}} = 0{\cdot}35\ \text{g/cm}^2\cdot\text{s}.$$

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

2.194 Here we must assume that μ 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

$$p = \mu \sqrt{\frac{2\pi RT}{M}} = 0{\cdot}9 \text{ n Pa}$$

from the previous problem where $p =$ pressure of the saturated vapour.

2.195 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 $= 1{\cdot}8 \times 10^{-2}$ litre per mole

$$a = 5{\cdot}47 \text{ atmos} \cdot \frac{\text{litre}^2}{\text{mole}^2}$$

If molecular attraction vanished the equation will be

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

for the same specific volume. Thus

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

2.196 The internal pressure being $\frac{a}{V^2}$, the work done in condensation is

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

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

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

where ρ is the density of the liquid. For water $p_i \approx 3{\cdot}3 \times 10^{13}$ atm

2.197 The Vandar 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

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

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

Solving these simultaneously we get on division

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

This is the critical molar volume. Putting this back

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

Finally $$p_{Cr}=\frac{RT_{Cr}}{V_{MCr}-b}-\frac{a}{V^2_{MCr}}=\frac{4a}{27b^2}-\frac{a}{9b^2}=\frac{a}{27b^2}$$

From these we see that $$\frac{P_{Cr}V_{MCr}}{RT_{Cr}}=\frac{a/9b}{8a/27b}=\frac{3}{8}$$

2.198 $$\frac{P_{Cr}}{RT_{Cr}}=\frac{a/27b^2}{8a/27b}=\frac{1}{8b}$$

Thus $$b=R\frac{T_{Cr}}{8p_{Cr}}=\frac{0{\cdot}082\times 304}{73\times 8}=0{\cdot}043\text{ litre/mol}$$

and $$\frac{(RT_{Cr})^2}{p_{Cr}}=\frac{64a}{27}\quad\text{or}\quad a=\frac{27}{64}(RT_{Cr})^2/p_{Cr}=3{\cdot}59\,\frac{\text{atm}\cdot\text{litre}^2}{(\text{mol})^2}$$

2.199 Specific volume is molar volume divided by molecular weight. Thus

$$V'_{Cr}=\frac{V_{MCr}}{M}=\frac{3RT_{Cr}}{8Mp_{Cr}}=\frac{3\times{\cdot}082\times 562}{8\times 78\times 47}\frac{\text{litre}}{g}=4{\cdot}71\frac{\text{cc}}{g}$$

2.200 $$\left(p+\frac{a}{V_M^2}\right)(V_m-b)=RT$$

or $$\frac{p+\dfrac{a}{V_m^2}}{P_{Cr}}\times\frac{V_m-b}{V_{MCr}}=\frac{8}{3}\frac{T}{T_{Cr}}$$

or $$\left(\pi+\frac{a}{p_{Cr}V_m^2}\right)\times\left(\nu-\frac{b}{V_{MCr}}\right)=\frac{8}{3}\tau,$$

where $$\pi=\frac{p}{p_{Cr}},\ \nu=\frac{V_m}{V_{MCr}},\ \tau=\frac{T}{T_{Cr}}$$

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

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

2.201 (a) The ciritical Volume V_{MCr} is the maximum volume in the liquid phase and the mirimum volume in the gaseous. Thus

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

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

$$p_{\max} = \frac{a}{27\,b^2} = \frac{5{\cdot}47}{27 \times {\cdot}03 \times {\cdot}03} = 225\text{atmosphere}$$

2.202 $T_{Cr} = \frac{8}{27}\frac{a}{bR} = \frac{8}{27} \times \frac{3{\cdot}62}{{\cdot}043 \times {\cdot}082} = 304\text{ K}$

$$\rho_{Cr} = \frac{M}{3b} = \frac{44}{3 \times 43}\text{gm/c.c.} = 0{\cdot}34\text{ gm/c.c.}$$

2.203 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 ρ = density of liquid ether at room tmeperature. Thus

$$\eta = \frac{V}{V_{Cr}} = \frac{8\,Mp_{Cr}}{3\,RT_{Cr}\,\rho} \approx 0{\cdot}254$$

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

2.204 We apply the relation (T = constant)

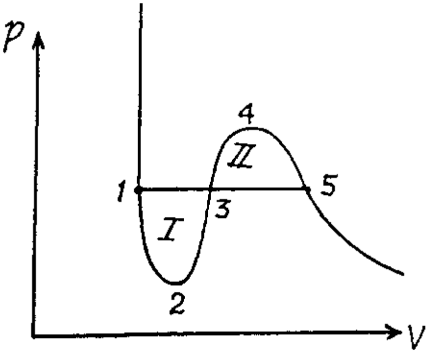
$$T\oint dS = \oint dU + \oint p\,dV$$

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.



2.205 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

$$f = \frac{c\,|t|}{q} = 0{\cdot}25$$

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

2.206 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 → 2 (1 = solid, 2 = liquid)

$$\Delta T=\frac{T\left(V'_w-V'_{ice}\right)}{q_{12}}\,\Delta p=-\frac{273\times\cdot091}{333}\times 1\,\frac{\text{atm}\times\text{cm}^3\times\text{K}}{\text{joule}}$$

$$1\,\frac{\text{atm}\times\text{cm}^3}{\text{Joule}}\approx\frac{10^5\,\frac{\text{N}}{\text{m}^2}\times 10^{-6}\,\text{m}^3}{\text{Joule}}=10^{-1},\ \Delta T=-\cdot0075\ \text{K}$$

2.207 Here 1 = liquid, 2 = Steam

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

or $$V'_s\approx\frac{q_{12}}{T}\frac{\Delta T}{\Delta p}=\frac{2250}{373}\times\frac{0\cdot9}{3\cdot2}\times 10^{-3}\,\text{m}^3/\text{g}=1\cdot7\ \text{m}^3/\text{kg}$$

2.208 From C-C equations

$$\frac{dp}{dT}=\frac{q_{12}}{T\left(V'_2-V'_1\right)}\approx\frac{q_{12}}{TV'_2}$$

Assuming the saturated vapour to be ideal gas

$$\frac{1}{V'_2}=\frac{mp}{RT},\ \text{Thus}\ \ \Delta p=\frac{Mq}{RT^2}p\,\Delta T$$

and $$p\approx p_0\left(1+\frac{Mq}{RT^2}\,\Delta T\right)\approx 1\cdot04\ \ \text{atmosphere}$$

2.209 From C-C equation, neglecting the voolume of the liquid

$$\frac{dp}{dT}\approx\frac{q_{12}}{TV'_2}\approx\frac{Mq}{RT^2}p,\ \ (q=q_{12})$$

or $$\frac{dp}{p}=\frac{Mq}{RT}\frac{dT}{T}$$

Now $$pV=\frac{m}{M}RT\ \ \text{or}\ \ m=\frac{MpV}{RT}\ \text{for a perfect gas}$$

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

$$=\left(\frac{Mq}{RT}-1\right)\frac{dT}{T}=\left(\frac{18\times 2250}{8\cdot3\times 373}-1\right)\times\frac{1\cdot5}{373}\approx 4\cdot85\ \%$$

2.210 From C-C equation

$$\frac{dp}{dT} = \frac{q}{TV'_2} = \frac{Mq}{RT^2}p$$

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

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

This is reasonable for $|T - T_0| << T_0$, and far below critical temperature.

2.211 As before (2.206) 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

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

2.212 (a) The equations of the transition lines are

$$\log p = 9{\cdot}05 - \frac{1800}{T}: \text{ Solid gas}$$

$$= 6{\cdot}78 - \frac{1310}{T}: \text{ Liquid gas}$$

At the triple point they intersect. Thus

$$2{\cdot}27 = \frac{490}{T_{tr}} \text{ or } T_{tr} = \frac{490}{2{\cdot}27} = 216\text{ K}$$

corresponding p_{tr} is 5.14 atmosphere.

In the formula $\log p = a - \frac{b}{T}$, we compare b with the corresponding term in the equation in 2.210. Then

$$\ln p = a \times 2{\cdot}303 - \frac{2{\cdot}303\,b}{T} \quad \text{So, } 2{\cdot}303 = \frac{Mq}{R}$$

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

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

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

2.213 $$\Delta S = \int_{T_1}^{T_2} mc\frac{dT}{T} + \frac{mq}{T_2} = m\left(c\ln\frac{T_2}{T_1} + \frac{q}{T_2}\right)$$

$$= 10^3\left(4{\cdot}18\ln\frac{373}{283} + \frac{2250}{373}\right) = 7{\cdot}2\text{ kJ/K}$$

2.214 $\Delta S = \frac{q_m}{T_1} + c \ln \frac{T_2}{T} + \frac{q_v}{T_2}$

$$= \frac{333}{273} + 4{\cdot}18 \ln \frac{373}{283} = 8{\cdot}56 \text{ J/°K}$$

2.215 c = specific heat of copper = $0{\cdot}39 \frac{\text{J}}{\text{g} \cdot \text{K}}$. Suppose all ice does not melt, then

heat rejected = $90 \times 0{\cdot}39\,(90 - 0) = 3159$ J

heat gained by ice = $50 \times 2{\cdot}09 \times 3 + x \times 333$

Thus $x = 8{\cdot}5$ gm

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

Hence change in entropy of copper piece

$$= mc \ln \frac{273}{363} = -10 \text{ J/K}.$$

2.216 (a) Here $t_2 = 60$°C. Suppose the final temperature is t °C. Then

$$\text{heat lost by water} = m_2\, c\, (t_2 - t)$$

$$\text{heat gained by ice} = m_1\, q_m + m_1\, c\, (t - t_1)\text{, if all ice melts}$$

In this case $m_1\, q_m = m_2 \times 4{\cdot}18\,(60 - t)$, for $m_1 = m_2$

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

Then $100 \times 4{\cdot}18\,(60) = m'_1 \times 333$

$m'_1 = 75{\cdot}3$ gm = amount of ice that will melt

Finally $\Delta S = 75{\cdot}3 \times \frac{333}{273} + 100 \times 4{\cdot}18 \ln \frac{273}{333}$

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

$$= m_2\, c\, \frac{(T_2 - T_1)}{T_1} - m_2 \ln \frac{T_2}{T_1}$$

$$= m_2\, C \left[\frac{T_2}{T_1} - 1 - \ln \frac{T_2}{T_1} \right] = 8{\cdot}8 \text{ J/K}$$

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

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

2.217 $\Delta S = -\dfrac{m\,q_1}{T_2} - mc\ln\dfrac{T_2}{T_1} + \dfrac{M\,q_{ice}}{T_1}$

where $$M\,q_{ice} = m\left(q_2 + c\,(T_2 - T_1)\right)$$

$$= mq_2\left(\frac{1}{T_1} - \frac{1}{T_2}\right) + mc\left(\frac{T_2}{T_1} - 1 - \frac{T_2}{T_1}\right)$$

$$= 0{\cdot}2245 + 0{\cdot}2564 = 0{\cdot}48\ \mathrm{J/K}$$

2.218 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

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

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

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 refer to unit mass here). Thus

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

For water $C_p = \dfrac{R\gamma}{\gamma - 1}\cdot\dfrac{1}{M}$ with $\gamma = 1{\cdot}32$ and $M = 18$

So $$C_p = 1{\cdot}90\ \mathrm{J/gm\,K}$$

and $$C = -4{\cdot}13\ \mathrm{J/gm\,^\circ K} = -74\ \mathrm{J/mole\,K}$$

2.219 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.