TKP Exam Solutions 2007

Section A

A1)   The zeroth law of thermodynamics states that if bodies A and B are each separately in thermal equilibrium with a third body C then they must be in thermal equilibrium with each other.

A2)   The empirical temperature scale is defined as

$$T_R = 273.16 \left(\frac{R}{R_{TP}} \right)$$

Where R is the resistance at the unknown temperature and R_{TP} is the resistance at the triple point of water.

A3)   The ideal gas temperature scale is defined as

$$T_{Gas} = 273.16 \lim_{P_{TP} \to 0} \left(\frac{P}{P_{TP}} \right)$$

Where the limit $P_{TP} \to 0$ is taken to more closely approximate an ideal gas by reducing the effects of intermolecular interactions as the gas becomes dilute.

A4)   The mean kinetic energy of a molecule in a gas at temperature T is given by;

$$\frac{1}{2}\langle mv^2 \rangle = \langle KE \rangle = \frac{3}{2}k_B T$$

The kinetic energy of a CO_2 molecule is given as

$$\langle KE \rangle = 0.0285 eV = \frac{3}{2}k_B T$$

therefore

$$T = \frac{2}{3}\frac{0.0285 eV}{8.63 \times 10^{-5} eVK^{-1}} = 220K$$

And for CO_2

$$\frac{1}{2}\langle mv^2 \rangle = 0.0285 eV$$

$$\langle v^2 \rangle_{CO_2} = \frac{2 \times 0.0285 eV \times 1.6 \times 10^{-19} C}{44 amu \times 1.66 \times 10^{-27} kg} = 1.25 \times 10^5 m^2 s^{-2}$$

therefore

$$v_{rms}(CO_2) = 353.3 ms^{-1}$$

Similarly for N_2 as they are at the same temperature they will have the same average kinetic energy and

$$\langle v^2 \rangle_{N_2} = \frac{2 \times 0.0285 eV \times 1.6 \times 10^{-19} C}{28 amu \times 1.66 \times 10^{-27} kg} = 1.96 \times 10^5 m^2 s^{-2}$$

therefore

$$v_{rms}(N_2) = 443 ms^{-1}$$

A5) $dU = dQ + dW$ and the conventions used are that heat flowing into the system is positive and work done on the system is positive.

A6)   The work done on a gas is equal to the area between the volume axis and the curve representing the process being positive when traversed from right to left ie. when compressing the gas.

A7)   The equation of state of an ideal gas is

$$PV = nRT$$

Where P, V and T are the pressure, volume and temperature respectively and n is the number of moles of the gas.
In an isothermal process there will be no change in internal energy.

A8)   In an isobaric process $dP = 0$
in an isochoric process $dV = 0$ and
in an adiabatic process $dQ = 0$

A9)   During the process a $\rightarrow$ b, $dQ = +150J$, $dW = -60J$ from the first law

$$\Delta U_{a \rightarrow b} = 150J - 60J = 90J$$

A10)   During the process b $\rightarrow$ c, $dQ = -108J$, $dW = 0J$ from the first law

$$\Delta U_{b \rightarrow c} = -108J - 0J = -108J$$

A11)   During the adiabatic process c $\rightarrow$ a the change in internal energy must be

$$\Delta U_{a \rightarrow b} + \Delta U_{b \rightarrow c} = -\Delta U_{c \rightarrow a} = 90J - 108J = -18J$$

It is adiabatic so $dQ = 0J$ and therefore using the first law

$$dW_{c \rightarrow a} = \Delta U_{c \rightarrow a} - dQ = \Delta U_{c \rightarrow a} = 18J$$

A12)   we are given

$$U = \frac{7}{2} PV$$

The process is adiabatic and therefore $dQ = 0$

$$dU = \frac{7}{2}\left(PdV + VdP\right) = -PdV$$

rearranging

$$\frac{9}{2} PdV + \frac{7}{2} VdP = 0$$

$$\frac{9}{7} \frac{dV}{V} = -\frac{dP}{P}$$

After integration

$$\frac{9}{7} \ln V = -\ln P + const$$

$$PV^{9/7} = PV^{\gamma} = \left(PV\right)V^{\gamma-1} = nRTV^{\gamma-1} = const \qquad \text{QED}$$

$$\gamma = \frac{9}{7}$$

A13) $\gamma = \dfrac{C_P}{C_V}$ where C_P and C_V are the heat capacities of the gas at constant pressure and volume respectively.

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Section B

B1)   (a)

       i)   The Clausius statement of the second law is

It is impossible to devise a device that , when operating in a cycle, produces no other effect than the transfer of heat from a cooler to a hotter body (reservoir).

       ii)   The heat pump has a figure of merit defined as useful output, Q_1, divided by input required to achieve the desired effect, W.

$$\eta_{HP} = \frac{Q_1}{W}$$

From the first law we have $W = Q_1 - Q_2$

Therefore

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

       iii)

$$\eta_{HP} = \frac{Q_1}{Q_1 - Q_2} = 10 \qquad\qquad 10 = \frac{Q_1}{Q_1 - 9kW}$$
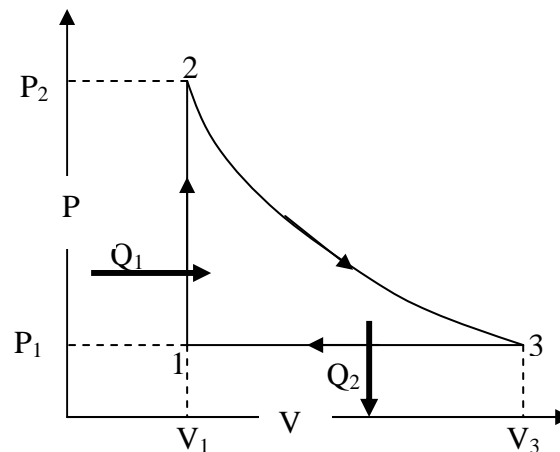
$$9Q_1 = 90kW$$

$$Q_1 = 10kW$$

$$W = Q_1 - Q_2 = 10kW - 9kW = 1kW$$

       (b)

       i)

ii)   The process $1 \to 2$ is isochoric and therefore no work is done leaving the first law as

$$\Delta U_{1 \to 2} = \Delta Q_{1 \to 2}$$

We are given $U = \dfrac{5}{2} PV$

$$dU_{1 \to 2} = \frac{5}{2}(P_2 - P_1)V_1 = \Delta Q_{1 \to 2} = Q_1$$

The process $3 \to 1$ is isobaric and therefore $\Delta W_{3 \to 1} = P_1(V_3 - V_1)$ whilst $\Delta U_{3 \to 1} = \dfrac{5}{2}(V_1 - V_3)P_1$ and from the first law

$$\Delta Q_{3 \to 1} = \Delta U_{3 \to 1} - \Delta W_{3 \to 1} = \frac{5}{2}(V_1 - V_3)P_1 + (V_1 - V_3)P_1$$

$$\Delta Q_{3 \to 1} = \frac{7}{2}(V_1 - V_3)P_1 = Q_2$$

iii)   We can define the engine efficiency as useful work out divided by heat in.

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

In this definition of efficiency the moduli of the heats are required and Q_2 as calculated in part ii) is a negative number (heat is expelled) and we therefore need to take the positive modulus in this case. Q_1 as calculated is positive in any case.

Thus using results from part ii)

$$\eta_E = 1 - \frac{\dfrac{7}{2}(V_3 - V_1)P_1}{\dfrac{5}{2}(P_2 - P_1)V_1}$$

The pressures and volumes at points 2 and 3 are related through the adiabatic rule

$$PV^{7/5} = const$$

$$\frac{V_2}{V_3} = \frac{V_1}{V_3} = \left(\frac{P_3}{P_2}\right)^{5/7} = \left(\frac{P_1}{P_2}\right)^{5/7} = p^{5/7}$$

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$$V_3 = V_1 p^{5/7}$$

To obtain V_3 in terms of V_1 in the equation for the efficiency

$$\eta_E = 1 - \frac{\frac{7}{2}(V_3 - V_1)P_1}{\frac{5}{2}(P_2 - P_1)V_1} = 1 - \frac{7}{5}\frac{V_1\left(p^{5/7} - 1\right)P_1}{(P_2 - P_1)V_1} = 1 - \frac{7}{5}\frac{p^{5/7} - 1}{p - 1} \qquad \text{QED}$$

(c)

i) To find p we first need P_2 which we find by noting $V_1 = V_3$ and

$$P_2 V_2^{7/5} = P_3 V_3^{7/5} = P_1 V_3^{7/5}$$

$$P_2 = P_1\left(\frac{V_3}{V_2}\right)^{7/5} = 1atm \times \left(\frac{0.001cc}{0.0001cc}\right)^{7/5} = 10^{1.4}\, atm = 25.11\ \ atm$$

ii) We have found the engine efficiency in part ii in terms of

$$p = \frac{P_2}{P_1} = 25.11$$

$$\eta_E = 1 - \frac{7}{5}\frac{p^{5/7} - 1}{p - 1} = 1 - 1.4 \times \frac{25.11^{0.714} - 1}{25.11 - 1} = 1 - 1.4 \times \frac{9.99 - 1}{24.11} = 0.477$$

iii) To calculate the work done in one cycle we need to know Q_1

$$Q_1 = \frac{5}{2}(P_2 - P_1)V_1 = 2.5 \times (25.11 - 1) \times 1.01 \times 10^5 \times 0.0001$$

$$Q_1 = 608.775J$$

Now we use the efficiency to calculate W

$$W = Q_1 \times \eta_E = 608.77 \times 0.477 = 290.38J$$

B2)   (a)

     i)   The entropy form of the second law of thermodynamics for an isolated system is given by the inequality

$$\Delta S \geq 0$$

where the equality applies for a reversible process.

     ii)   Boltzmann conjectured that the macroscopic entropy S was related to the number of accessible microstates available to make up that macrostate. He suggested that

Entropy is a measure of the MICROSCOPIC probability of finding the system under study in a given MACROSCOPIC equilibrium state.

     (b)

     i)   The final state of the water will be 3kg of ice at -5 ^{o}C or 268.15 K

     ii)   The calculation is to be carried out in 3 stages, the cooling from 15 ^{o}C (288.15 K) to 0 ^{o}C (273.15 K). The change of state at 273.15 K from water to ice and the final cooling of the ice from 273.15 K to 268.15 K.

1.   In cooling from 288.15 K to 273.15 K we need to calculate

$$\int_{288.15}^{273.15} dS = \Delta S = \int_{288.15}^{273.15} \frac{dQ}{T}$$

as an integral with the temperature changing. We do this by finding dQ in terms of dT using the assumption of constant pressure

$$dQ = mC_P dT$$

$$\Delta S = mC_P \int_{288.15}^{273.15} \frac{dT}{T} = mC_P \ln \frac{273.15}{288.15} = 3kg \times 4.2 \times 10^3 \, Jkg^{-1}K^{-1} \times -5.34 \times 10^{-2}$$

$$\Delta S = -9,419 JK^{-1}$$

2.   In changing state from water to ice at constant temperature we need to calculate the total latent heat and divide this by the temperature

$$\Delta S = \frac{ml^{LS}}{273.15} = \frac{-ml^{SL}}{273.15} = \frac{-3kg \times 3.33 \times 10^5 \, Jkg^{-1}}{273.15} = -10,971 JK^{-1}$$

3.   In cooling from 273.15 to 268.15 K the ice will change entropy by an amount

$$\Delta S = mC_P^{ice} \int\limits_{273.15}^{268.15} \frac{dT}{T} = mC_P \, ln\frac{268.15}{273.15} = 3kg \times 2.1 \times 10^3 \, Jkg^{-1}K^{-1} \times -1.847 \times 10^{-2}$$

$$\Delta S = -116JK^{-1}$$

The total entropy change is then the sum of these three

$$\Delta S^{Total} = -9.419 - 10,971 - 116 = -20506JK^{-1}$$

iii) The surrounding environment remains at the ambient temperature and all that is required is to find the heat input/output from part ii) in order to calculate ΔS

1. For the cooling down of the water there will be heat added to the environment that is lost from the water

$$\Delta Q = mC_P \int\limits_{288.15}^{273.15} dT = mC_P \Delta T = 3kg \times 4.2 \times 10^3 \, Jkg^{-1}K^{-1} \times 15 = 189,000J$$

$$\Delta S = \frac{189000}{268.15} = +704.82JK^{-1}$$

2. For the phase change water to ice again heat is added to the environment

$$\Delta S = \frac{ml^{SL}}{268.15} = \frac{3kg \times 3.33 \times 10^5 \, Jkg^{-1}}{268.15} = +3,725JK^{-1}$$

3. For the cooling of the ice

$$\Delta Q = -mC_P^{ice} \int\limits_{273.15}^{268.15} dT = -mC_P^{ice} \, ln\frac{268.15}{273.15} = 3kg \times 3.33 \times 10^5 \times 1.847 \times 10^{-2} \, JK^{-1} = 18,451J$$

$$\Delta S = \frac{18,451}{268.15} = +68.810JK^{-1}$$

$$\Delta S_{environment}^{Total} = 704,82 + 3,726 + 69 = +74,313JK^{-1}$$

iv) The second law requires that the total entropy change of an isolated system is greater than (or equal to in the case of reversible changes) zero.

The sum total of the entropy changes here ia

$$\Delta S_{Universe} = (74313 - 20506)JK^{-1} = +53,807\,JK^{-1}$$

The overall change in the entropy is positive as required by the second law. It can be noted that none of the three processes is reversible as water will not warm to 15 $^{\circ}$C when sitting outside in a garden at temperature -5 $^{\circ}$C. Ice will not spontaneously melt in theses circumstances and a block of ice at -5 $^{\circ}$C will not warm up to 0 $^{\circ}$C.

(c)

i)   Beginning with the thermodynamic identity

$$dU = TdS - PdV$$

$$dS = \frac{dQ_R}{T} = \frac{dU}{T} + \frac{P}{T}dV$$

We are given

$$U = \frac{5}{2}PV \qquad\qquad PV = Nk_BT$$

Which gives

$$U = \frac{5}{2}Nk_BT \Rightarrow dU = \frac{5}{2}Nk_BdT$$
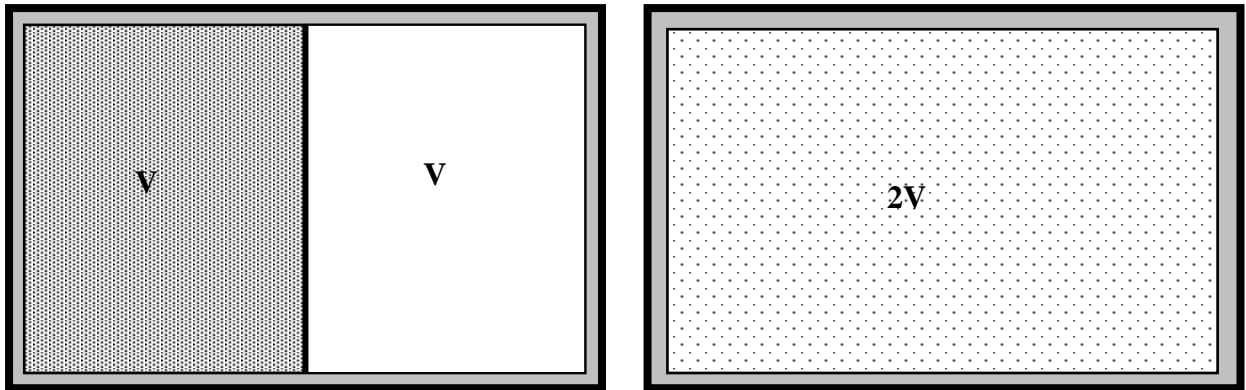
and

$$\frac{P}{T} = \frac{Nk_B}{V}$$

Using these in the equation for dS

$$dS = \frac{5}{2}Nk_B\frac{dT}{T} + Nk_B\frac{dV}{V}$$

$$\Delta S = \int_i^f dS = \frac{5}{2}Nk_B\int_{T_i}^{T_f}\frac{dT}{T} + Nk_B\int_{V_i}^{V_f}\frac{dV}{V} = \frac{5}{2}Nk_B\,ln\left(\frac{T_f}{T_i}\right) + Nk_B\,ln\left(\frac{V_f}{V_i}\right)$$

QED

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ii)

In the Joule free expansion gas is initially confined to a reduced volume in a container with walls *that are both rigid & adiabatic* by a secondary partition as in LHS of diagram. The expansion occurs without heat flow when this partition is broken allowing the gas to expand freely into the previously empty volume as in RHS of diagram.

For an ideal gas the internal energy remains constant as there is no work done (rigid walls) and no heat flow (adiabatic walls) $\Delta U = \Delta Q + \Delta W = 0$. This implies no temperature change between initial and final states.

iii)   If an ideal gas undergoes such a free expansion we may calculate the change in entropy from

$$\Delta S = \frac{5}{2} N k_B \, ln\left(\frac{T_f}{T_i}\right) + N k_B \, ln\left(\frac{V_f}{V_i}\right) = N k_B \, ln\, 3 = 1.098 \times N k_B$$

Where the fact that $\Delta T = 0$ has been used.

This is consistent with the Boltzmann interpretation of entropy as a measure of the number of accessible microstates that give rise to the macrostate. We have a slight increase in entropy after the expansion and Boltzmann would explain this as due to the increased number of positions available to the molecules of the gas in the larger volume. Many of the increased number of configurations (microstates) available to the *N* molecules would give rise to identical macrostates giving an increase in entropy according to Boltzmann's conjecture.

B3)   a)

   i) $F = U - TS$

   $dF = dU - TdS - SdT$

Using the thermodynamic identity $dU = TdS - PdV$ allows us to write this

$$dF = -PdV - SdT$$

The natural variables of F are then V and T which means we can also write the infinitesimal for F as

$$dF = \left(\frac{\partial F}{\partial V}\right)_T dV + \left(\frac{\partial F}{\partial T}\right)_V dT$$

This allows the identification

$$P = -\left(\frac{\partial F}{\partial V}\right)_T \qquad\qquad S = -\left(\frac{\partial F}{\partial T}\right)_V$$

$$\left(\frac{\partial P}{\partial T}\right)_V = -\left(\frac{\partial^2 F}{\partial V \partial T}\right) = -\left(\frac{\partial^2 F}{\partial T \partial V}\right) \qquad\qquad \left(\frac{\partial S}{\partial V}\right)_T = -\left(\frac{\partial^2 F}{\partial V \partial T}\right) = -\left(\frac{\partial^2 F}{\partial T \partial V}\right)$$

Giving the Maxwell relation

$$\left(\frac{\partial P}{\partial T}\right)_V = \left(\frac{\partial S}{\partial V}\right)_T \qquad\qquad \text{QED}$$

$$G = U - TS + PV$$

$$dG = dU - TdS - SdT + PdV + VdP$$

Using the thermodynamic identity

$$dG = -SdT + VdP$$

We identify the natural variables of G as T and P and can therefore also write the infinitesimal dG as

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

Allowing the identifications

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

$$\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial^2 G}{\partial P \partial T}\right) = -\left(\frac{\partial^2 G}{\partial T \partial P}\right) \qquad \left(\frac{\partial V}{\partial T}\right)_P = \left(\frac{\partial^2 G}{\partial T \partial P}\right)$$

Giving the Maxwell relation

$$\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P \qquad\qquad \text{QED}$$

ii)   Using the thermodynamic identity at constant V

$$dU = TdS - PdV = TdS$$

Therefore

$$C_V = \left(\frac{\partial U}{\partial T}\right)_V = T\left(\frac{\partial S}{\partial T}\right)_V$$

iii)   We may write using the thermodynamic identity

$$\left(\frac{\partial U}{\partial V}\right)_T = \frac{TdS - PdV}{dV} \qquad \Rightarrow \qquad \left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial S}{\partial V}\right)_T - P$$

Using the previously obtained Maxwell relation $\left(\frac{\partial P}{\partial T}\right)_V = \left(\frac{\partial S}{\partial V}\right)_T$

$$\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V - P \qquad\qquad \text{QED}$$

iv)   The equation of state given is $\left(P + \frac{n^2 a}{V^2}\right)(V - nb) = nRT$

By obtaining P as the subject

$$P = \frac{nRT}{V - nb} - \frac{n^2 a}{V^2}$$

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We can use the expression $\left(\dfrac{\partial U}{\partial V}\right)_T = T\left(\dfrac{\partial P}{\partial T}\right)_V - P$ derived in iii)

$$\left(\frac{\partial U}{\partial V}\right)_T = T\frac{nR}{V-nb} - P = \frac{nRT}{V-nb} - \frac{nRT}{V-nb} + \frac{n^2a}{V^2} = \frac{n^2a}{V^2}$$

We also have

$$\left(\frac{\partial U}{\partial T}\right)_V = C_V = \frac{3}{2}nR$$

Integrating these two equations wrt to dV and dT respectively

$$U(T,V) = -\frac{n^2a}{V} + g(T) \qquad\qquad U(T,V) = \frac{3}{2}nRT + f(V)$$

The only consistent solution is

$$U(T,V) = \frac{3}{2}nRT - \frac{n^2a}{V} + const$$

The first term on the RHS is the kinetic energy and the second term is the potential energy of intermolecular interaction. At $T = 0$ the first term, the KE $= 0$ and at infinite volume the second term, PE $= 0$ and therefore U should be zero at $T = 0$, $V \rightarrow \infty$ implying that the const $=- 0$.

$$U(T,V) = \frac{3}{2}nRT - \frac{n^2a}{V}$$

Is the required expression for the internal energy of the Van der Waals gas

(b)
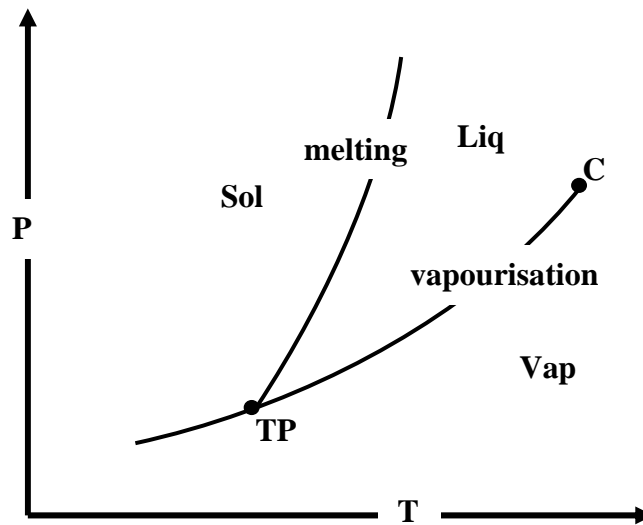
P-T diagram for simple substance

TP is the triple point being the pressure and temperature at which the solid liquid and vapour phases coexist.

C is the critical point beyond which (at higher temperatures and pressures) the vapour and liquid phases have the same density and become indistinguishable.

(c)

Given the Clausius Clapeyron equation for the liquid-vapour co-existence curve

$$\frac{dP}{dT} = \frac{l^{LV}}{T\left(v^V - v^L\right)}$$

We can make the approximation $v^V \gg v^L$ the molar volume of the vapour is much greater than that of the liquid.

Also as it is an ideal gas

$$v^V = \frac{RT}{P}$$

Giving an approximate form of the liquid vapour Clausius Clapeyron equation

$$\frac{dP}{dT} = \frac{l^{LV} P}{RT^2}$$

Re-arranging

$$\frac{dP}{P} = l^{LV} \frac{dT}{RT^2}$$

Integrating this equation

$$\ln P = -l^{LV} \frac{1}{RT} + const$$

Where P and T are any pair of points lying on the coexistence curve

$$\ln P_1 = -l^{LV} \frac{1}{RT_1} + const$$

$$\ln P_0 = -l^{LV} \frac{1}{RT_0} + const$$

We subtract one from the other giving

$$\ln \frac{P_1}{P_0} = -\frac{l^{LV}}{R} \left(\frac{1}{T_1} - \frac{1}{T_0} \right) \qquad \text{QED}$$

B4)   a) Cavity radiation is the radiation contained within a cavity that is at the same temperature as the cavity walls ie. the radiation is in thermal equilibrium with the cavity.

Its temperature is determined by the temperature T of the cavity walls and the volume of the cavity V.

i)   We are given $u(T) = \dfrac{4\sigma}{c}T^4$ and the equation of state $U = 3PV$

Writing

$$u(T) = \frac{U}{V} = 3P = \frac{4\sigma}{c}T^4$$

$$P = \frac{4}{3}\frac{\sigma}{c}T^4 = 1.333 \times \frac{5.67 \times 10^{-8}\, Js^{-1}m^{-2}T^{-4}}{3 \times 10^8\, ms^{-1}} \times 2.7^4$$

$$P = 1.333 \times \frac{5.67 \times 10^{-8}}{3 \times 10^8} \times 53.14 = 1.33 \times 10^{-14}\, Pa = \frac{1.33 \times 10^{-14}}{1.01 \times 10^5} = 1.32 \ \ Atm$$

ii)   For a photon gas at 1 Atm

$$T^4 = \left(\frac{3}{4}\frac{c}{\sigma}P\right) = 0.75 \times \frac{3 \times 10^8}{5.67 \times 10^{-8}} \times 1.01 \times 10^5 \ \ Pa = 4.00 \times 10^{20}$$

$$T = 1.4 \times 10^5 \ \ K$$

b)

Starting with the thermodynamic identity

$$dU = TdS - PdV$$

$$U(T) = u(T)V \qquad \Rightarrow \qquad dU = d(u(T)V) = TdS - PdV$$

We can use the equation of state rewritten as $P = \dfrac{1}{3}u$

$$d(u(T)V) = TdS - \frac{1}{3}u(T)dV$$

Rearranging this by expanding d(u(T)V) using the product and the chain rules.

$$TdS = \left(u(T)dV + u'(T)VdT\right) + \frac{1}{3}u(T)dV \qquad \left(u' = \frac{du(T)}{dT}\right)$$

$$dS = \left(\frac{u'(T)}{T}V\right)dT + \left(\frac{4}{3}\frac{u(T)}{T}\right)dV$$

We have been given previously

$$u(T) = \frac{U}{V} = 3P = \frac{4\sigma}{c}T^4$$

Allowing the expression for *dS* to be rewritten as

$$dS = \frac{16\sigma}{c}T^2VdT + \frac{16\sigma}{3c}T^3dV$$

We now know that *S* has *T* and *V* as natural variables and can write

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

By inspection of these two equations it is the case that

$$\left(\frac{\partial S}{\partial T}\right)_V = \frac{16\sigma}{c}T^2V$$

Integrating this wrt *T*

$$S = \frac{16\sigma}{3c}T^3V + f(V)$$

Also by inspection

$$\left(\frac{\partial S}{\partial V}\right)_T = \frac{16\sigma}{3c}T^3$$

Integrating this wrt *V*

$$S = \frac{16\sigma}{3c}T^3V + g(T)$$

The only consistent solution to these two forms of S is

$$S = \frac{16\sigma}{3c}T^3V + const \qquad\qquad \text{QED}$$

If the photon gas is expanded reversibly and adiabatically there is no change in S and therefore

$$T_1^3 V_1 = T_2^3 V_2 = T_2^3 64 V_1 \qquad \Rightarrow \qquad T_1^3 = 64 T_2^3 \qquad \Rightarrow \qquad T_2 = 0.25 T_1$$

c)

The mean free path in a gas is defined by the mean distance travelled by a molecule in a gas between collisions.

i) In the equation $\lambda = \frac{1}{n\sigma}$ the mean free path is λ, n is the number density of molecules and σ is an area called the collision cross section where we imagine a disc of area σ attached to a molecule in motion increasing the probability that the molecule may collide with a neighbour.

ii) Effusion describes the process whereby molecules or any particle in Brownian motion confined to a box escape from that box via a hole whose diameter is less than a mean free path.

iii) The number of molecules escaping will be determined by the rate of collision of particles with the holes. This is given by the particle flux multiplied by the mean speed

$$N \propto \frac{1}{4} n\bar{v} = \frac{1}{4} n \sqrt{\frac{8k_B T}{\pi m}}$$

The percentage of escaped He atoms is given by

$$\frac{n_{He}}{n_{He} + n_A} \times 100 = \frac{\dfrac{n_{He}}{\sqrt{m_{He}}}}{\dfrac{n_{He}}{\sqrt{m_{He}}} + \dfrac{n_A}{\sqrt{m_A}}} \times 100$$

$$\frac{n_{He}}{n_{He} + n_A} \times 100 = \frac{n_{He}\sqrt{m_A}}{n_{He}\sqrt{m_A} + n_A\sqrt{m_{He}}} \times 100$$

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Now dividing top and bottom by $\sqrt{m_{He}}$

$$\frac{n_{He}}{n_{He}+n_A}\times 100 = \frac{n_{He}\sqrt{m_A/m_{He}}}{n_{He}\sqrt{m_A/m_{He}}+n_A}\times 100$$

Divide top and bottom by n_{He}

$$\frac{n_{He}}{n_{He}+n_A}\times 100 = \frac{\sqrt{m_A/m_{He}}}{\sqrt{m_A/m_{He}}+n_A/n_{He}}\times 100$$

From data given

$$\sqrt{m_A/m_{He}} = \sqrt{40/4} = 3.16 \qquad \text{and} \qquad ` \qquad n_A/n_{He} = 0.9/0.1 = 9$$

Therefore the percentage of escaped He atoms is

$$\frac{n_{He}}{n_{He}+n_A}\times 100 = \frac{3.16}{3.16+9}\times 100 = 25.98\% \approx 26\%$$