THERMAL AND KINETIC PHYSICS (PHY 214)

EXERCISE 6 : WEEK 6

OUTLINE SOLUTIONS

Question 1.   1998 Exam Q1

a)   The Zeroth law of Thermodynamics states that if systems A and B are in thermal equilibrium with system C then they must both be in thermal equilibrium with each other.

Ideal gas temperature is that temperature measured by a constant volume gas thermometer with

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

The limit is taken in order that the gas approximates more closely to an ideal gas where U, its internal energy is only representative of the kinetic energies of its constituent parts. It is related to the observations of Robert Boyle that the product of pressure and temperature of a gas is equal to a constant in thermal equilibrium $PV = const$.

The kinetic temperature relates the internal energy (and therefore mean kinetic energy of a gas) to the temperature of that gas.

$$U = N \frac{1}{2} m v_{rms}^2 = \frac{3}{2} PV = \frac{3}{2} \frac{N}{N_A} RT$$

Rearranging gives

$$m v_{rms}^2 = 3 k_B T$$

$$\bar{v}_{rms} = \sqrt{\frac{3 k_B T}{m}} = \sqrt{\frac{3 \times 1.38 \times 10^{-23} J K^{-1} \times 300 K}{28 \times 1.66 \times 10^{-27} kg}} \approx 517 m s^{-1}$$

b)   The First Law of Thermodynamics in infinitesimal form is;

$$dU = dQ + dW$$

Where dU is the infinitesimal change in the internal energy of a system, dQ is the infinitesimal heat transfer to or from the system under consideration and dW the infinitesimal work carried out by or on the system under consideration.

NB. The sign convention is such that dQ is positive if the heat flows to the system and dW is positive if the work is done on the system.

c)   An adiabatic process is a process in which there is no heat flow into or out of the system under consideration.

The gas has an internal energy $U = \dfrac{5}{2}PV$ therefore using the first law and this equation of state we obtain

$$dU = \frac{5}{2}PdV + \frac{5}{2}VdP = dQ + dW = 0 - PdV$$

Re-arranging

$$\frac{7}{2}PdV = -\frac{5}{2}VdP$$

Collecting V and P on opposite sides
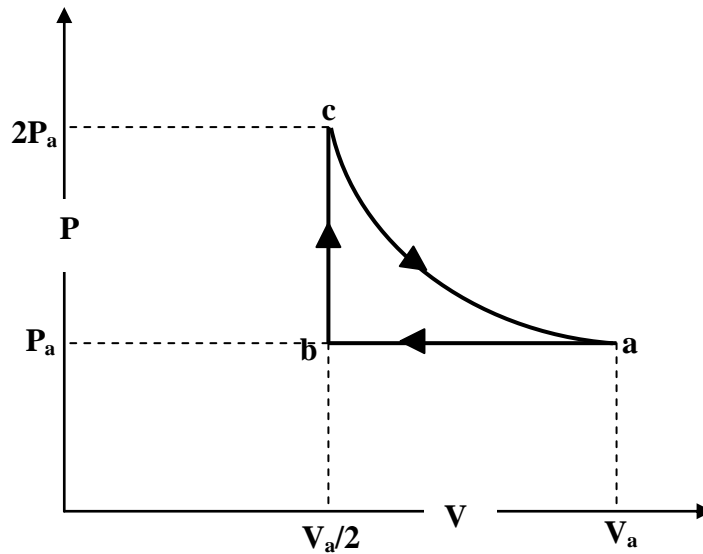
$$-\frac{7}{5}\frac{dV}{V} = \frac{dP}{P}$$

Integrating

$$-\frac{7}{5}\ln V = \ln P \qquad \Rightarrow \qquad \ln PV^{7/5} = const \qquad \Rightarrow \qquad PV^{7/5} = const$$

This is true of any equilibnrium state on the adiabatic.

Therefore

$$P_1 V_1^{7/5} = P_2 V_2^{7/5}$$

d)

i)

ii)   To calculate heat absorbed it is easiest to calculate work done in the cycle as change in internal energy is zero and therefore according to the first law

$$\Delta Q = -\Delta W$$

1.   On the isobar $\mathbf{a} \rightarrow \mathbf{b}$ the work done is

$$\Delta W_{a \rightarrow b} = \int_{a}^{b} -PdV = P\int_{b}^{a} dV = P\frac{V_a}{2}$$

2.   On the isochore, $\mathbf{b} \rightarrow \mathbf{c}$ there is no work done

$$\Delta W_{b \rightarrow c} = 0$$

3.   And on the isotherm, $\mathbf{c} \rightarrow \mathbf{a}$

$$\Delta W_{c \rightarrow a} = \int_{c}^{a} -PdV = -nRT\int_{c}^{a} \frac{dV}{V} = nRT\ln\frac{V_c}{V_a} = nRT\ln\left(\frac{1}{2}\right) = -0.693P_aV_a$$

Therefore

$$\Delta W_{Net} = 0.5P_aV_a - 0.693P_aV_a = -0.193P_aV_a$$

And finally

$$\Delta Q_{Net} = -\Delta W_{Net} = +0.193P_aV_a \quad \text{is the heat absorbed.}$$

e)

i) For 1 mole of an ideal gas

$$PV = RT \quad \Rightarrow \quad V = \frac{RT}{P}$$

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

$$\beta = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P = \frac{R}{PV} = \frac{1}{T}$$

ii) For 1 mole of a van der Waals gas

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

We would ideally like to find $\left(\dfrac{\partial V}{\partial T}\right)_P$ and there are two ways (at least) in which this may be done

A. We can find $\left(\dfrac{\partial T}{\partial V}\right)_P$ easily by making T the subject of the equation of state and then use the reciprocal relationship to find $\left(\dfrac{\partial V}{\partial T}\right)_P$

$$T = \frac{1}{R}\left(PV - Pb + \frac{a}{V} - \frac{ab}{V^2}\right)$$

$$\left(\frac{\partial T}{\partial V}\right)_P = \left(P - \frac{a}{V^2} + \frac{2ab}{V^3}\right)\frac{1}{R} = \left(\frac{PV^3 - aV + 2ab}{V^3}\right)\frac{1}{R}$$

Using the reciprocal relation

$$\left(\frac{\partial V}{\partial T}\right)_P = \frac{RV^3}{PV^3 - aV + 2ab}$$

B. Or we can use implicit differentiation by writing

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

Expanding bracket

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

and differentiate both sides wrt T holding P constant

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

We use $\dfrac{\partial}{\partial T} f(P,V) = \dfrac{\partial}{\partial V} f(P,V) \dfrac{\partial V}{\partial T}$

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

And solve for $\left(\dfrac{\partial V}{\partial T}\right)_P$

$$\left(\frac{\partial V}{\partial T}\right)_P = \frac{RV^3}{PV^3 - aV + 2ab}$$

As previously

It is now straightforward to use the definition of β

$$\beta = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P = \frac{RV^2}{PV^3 - aV + 2ab} = \frac{1}{T - a/RV + 2ab/RV^2}$$

Which is the same as the ideal gas for a, b $\rightarrow$ 0

Question 2   1999 Exam Q1

a)   The Zeroth law of Thermodynamics states that if systems A and B are in thermal equilibrium with system C then they must both be in thermal equilibrium with each other.

The empirical temperature is defined for any thermometric property as

$$T_X = 273.16 \times \frac{X}{X_{TP}}$$

Therefore, for the constant volume gas thermometer the temperature is defined as

$$T_{Gas} = 273.16 \times \frac{P}{P_{TP}}$$

It differs from the ideal gas temperature which is only defined *as the dilution of the gas in a constant volume gas thermometer tends to zero* (more closely to approximate an ideal gas) as

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

We know that all molecules/atoms will have the same mean kinetic energy irrespective of type.

$$\langle KE \rangle = \frac{1}{2} m v_{rms}^2 = 3 \times \frac{1}{2} k_B T$$

That is $\frac{1}{2} k_B T$ per degree of freedom

Therefore

$$\langle KE \rangle_{O_2} = \frac{3}{2} k_B T = 1.5 \times 1.38 \times 10^{-23} JK^{-1} \times 290K = 6.00 \times 10^{-21} J$$

And quite generally

$$\bar{v}_{rms} = \sqrt{\frac{3k_B T}{m}}$$

The velocity is proportional to $\sqrt{\frac{1}{m}}$ and so

$$\frac{\bar{v}_{rms}^{N_2}}{\bar{v}_{rms}^{A}} = \sqrt{\frac{m^A}{m^{N_2}}} = \sqrt{\frac{40}{28}} = 1.195$$

b) The First Law of Thermodynamics in infinitesimal form is

$$dU = dQ + dW$$

Where dU is the infinitesimal change in the internal energy of a system, dQ is the infinitesimal heat transfer to or from the system under consideration and dW the infinitesimal work carried out by or on the system under consideration.

The sign convention is such that dQ is positive if the heat flows to the system and dW is positive if the work is done on the system.

c) An adiabatic process is a process in which there is no heat flow into or out of the system under consideration.

Using the equation of state for the photon gas which has an internal energy

$$U = 3PV$$

With the first law

$$dU = 3PdV + 3VdP = dQ + dW = 0 - PdV$$

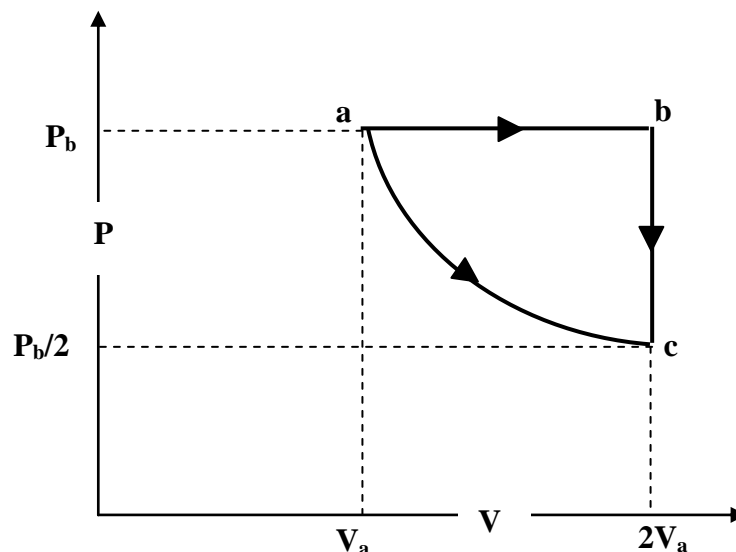Re-arranging

$$4PdV = -3VdP$$

Grouping V and P terms either side and then integrating

$$-\frac{4}{3}\frac{dV}{V} = \frac{dP}{P}$$

$$-\frac{4}{3}lnV = ln P \qquad PV^{4/3} = const$$

d)

i)

ii)   For the process **a → b → c** we split into two parts

In the isobaric process **a → b**

$$\Delta W_{a \to b} = -\int_a^b P dV = P \int_b^a dV = -P_a V_a$$

In the isochoric process **b → c** there is no work done

Therefore the net work is

$$\Delta W_{Net} = \Delta W_{a \to b \to c} = -P_a V_a$$

This a negative quantity and is work done BY the gas on the surroundings

For the isothermal process **a → c**

$$\Delta W_{a \to c} = -\int_a^c P dV = -nRT_a \int_a^c \frac{dV}{V} = nRT_a \ln \frac{V_a}{V_c} = P_a V_a \ln \frac{1}{2} = -0.693 P_a V_a$$

This is again a negative quantity representing work done BY the gas on its surroundings

This is no surprise as in both cases an expansion is involved and the gas does work.

iii)   For the process **a → b → c**

In the isobaric process **a → b** using the first law

$$\Delta Q = \Delta U - \Delta W$$

$$\Delta Q_{a \to b} = \frac{3}{2} \left(V_a P_a - V_a P_a \right) + P_a V_a = +\frac{5}{2} P_a V_a$$

And in the isochoric process **b → c**

$$\Delta Q = \Delta U - \Delta W = \Delta U = \frac{3}{2} \left(V_a P_a - 2 P_a V_a \right) = -\frac{3}{2} P_a V_a$$

$$\Delta Q_{Net} = \Delta Q_{a\to b\to c} = +\frac{5}{2}P_aV_a - \frac{3}{2}P_aV_a = +P_aV_a$$

For the isothermal process **a** → **c** there is no change in the internal energy and therefore from the First Law

$$\Delta Q_{a\to c} = \Delta U_{a\to c} - \Delta W_{a\to c} = -\Delta W_{a\to c} = +0.693P_aV_a$$

e)   For 1 mole of an ideal gas

$$PV = RT \qquad \Rightarrow \qquad V = \frac{RT}{P}$$

$$\left(\frac{\partial V}{\partial P}\right)_T = \frac{-RT}{P^2} = \frac{-PV}{P^2} = -\frac{V}{P} \qquad \Rightarrow \qquad \kappa = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T = \frac{1}{P}$$

For 1 mole of a van der Waals gas

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

We would ideally like to find $\left(\dfrac{\partial V}{\partial P}\right)_T$ but can find $\left(\dfrac{\partial P}{\partial V}\right)_T$ more easily and then use the reciprocal relationship

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

$$\left(\frac{\partial P}{\partial V}\right)_T = \frac{\partial}{\partial V}\left(\frac{RT}{\left(V-b\right)} - \frac{a}{V^2}\right) = \frac{-RT}{\left(V-b\right)^2} + \frac{2a}{V^3}$$

Using the reciprocal relation by inverting

$$\left(\frac{\partial V}{\partial P}\right)_T = \frac{V^3\left(V-b\right)^2}{-RTV^3 + 2a\left(V-b\right)^2}$$

thus

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$$\kappa = -\frac{1}{V}\frac{V^3(V-b)^2}{-RTV^3 + 2a(V-b)^2} = \frac{V^2(V-b)^2}{2a(V-b)^2 - RTV^3}$$

Dividing top and bottom by $(V-b)$

$$\kappa = \frac{(V-b)V^2}{2a(V-b) - RTV^3 \Big/ (V-b)} = \frac{V^2(V-b)}{2aV - 2ab - \left(P + a \Big/ V^2\right)V^3}$$

Or alternatively by implicit differentiation

$$\frac{\partial}{\partial P}\left[\left(P + \frac{a}{V^2}\right)(V-b)\right] = \frac{\partial}{\partial P}RT = 0$$

$$\frac{\partial}{\partial P}\left[PV + \frac{a}{V} - Pb - \frac{ab}{V^2}\right] = 0$$

$$V + P\frac{\partial V}{\partial P} - \frac{a}{V^2}\frac{\partial V}{\partial P} - b + \frac{2ab}{V^3}\frac{\partial V}{\partial P} = 0$$

$$\left[P - \frac{a}{V^2} + \frac{2ab}{V^3}\right]\frac{\partial V}{\partial P} = b - V \qquad \left[\frac{PV^3 - aV + 2ab}{V^3}\right]\frac{\partial V}{\partial P} = b - V$$

$$\kappa = \frac{-1}{V}\frac{V^3(b-V)}{PV^3 - aV + 2ab} \qquad \kappa = \frac{V^2(V-b)}{PV^3 - aV + 2ab}$$

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Question 3   1998 Exam Q2

a)   The Kelvin-Planck statement based on empirical observation states;

It is impossible to devise a device that , operating in a cycle, produces no other effect than the extraction of heat from a single body (a reservoir) with the production of an equivalent amount of work.

b)   We may define the efficiency of a heat engine in a simple manner

$$\eta = efficiency = figure \ of \ merit = \frac{What \ we \ want \ out}{What \ we \ put \ in}$$

And in turn with reference to the schematic diagram write this in terms of the heat flows

$$\eta_E = \frac{W}{Q_1} = \frac{Q_1 - Q_2}{Q_1} = 1 - \frac{Q_2}{Q_1}$$
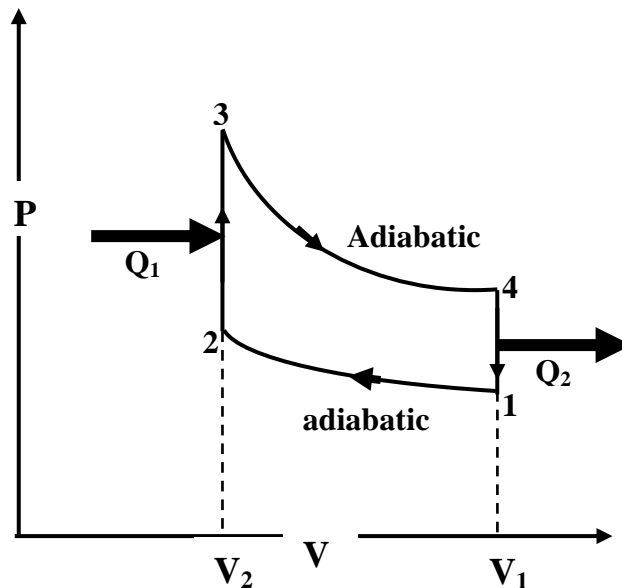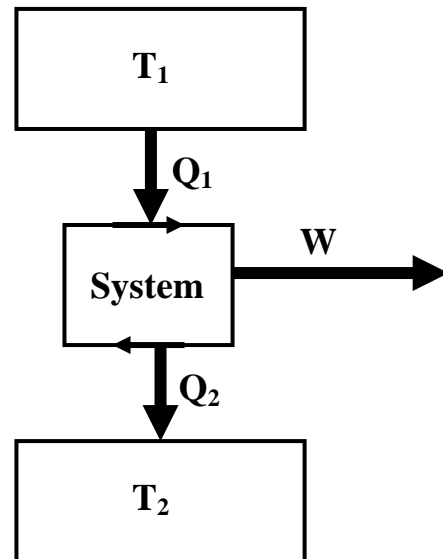
$1 \rightarrow 2$ is an adiabatic compression where work is done on the gas and the usual equation holds,

$$T_1 V_1^{\gamma-1} = T_2 V_2^{\gamma-1}$$

$3 \rightarrow 4$ is also an adiabatic expansion where work is done by the gas

$$T_4 V_1^{\gamma-1} = T_3 V_2^{\gamma-1}$$

where $V_1 = V_4$ and $V_2 = V_3$ were used.

$2 \rightarrow 3$ is an isochore and no work is done as $dV = 0$. The heat can be calculated from the first law

$$\Delta U = U_3 - U_2 = \frac{5}{2} nR(T_3 - T_2) = \Delta Q = Q_1$$

We can see that Q_1 is positive as $T_3 > T_2$ and it is therefore a flow of heat into the gas.

$4 \rightarrow 1$ is also an isochore and again no work is done as $dV = 0$. The heat can be calculated from the first law

$$\Delta U = U_1 - U_4 = \frac{5}{2} nR(T_1 - T_4) = \Delta Q = -Q_2$$

We can see that Q_2 is negative as $T_1 > T_4$ and it is therefore a flow of heat from the gas.

The efficiency is

$$\eta_E = 1 - \frac{Q_2}{Q_1} = 1 - \frac{C_V(T_4 - T_1)}{C_V(T_3 - T_2)}$$

NB. the modulus of Q_2 has been taken.

Taking the two results derived for the adiabats and subtracting one from the other we obtain

$$\left(T_4 - T_1 \right) V_1^{\gamma-1} = \left(T_3 - T_2 \right) V_2^{\gamma-1}$$

Thus

$$\eta_E = 1 - \left(\frac{V_b}{V_a} \right)^{\gamma-1}$$

Where $\gamma = \dfrac{C_P}{C_V} = \dfrac{7}{5}$

Defining **the compression ratio** $\gamma_C = \dfrac{V_a}{V_b}$

$$\eta_E = 1 - \frac{1}{\gamma_C^{\gamma-1}}$$

c) i) $\qquad \eta_E = 1 - \dfrac{1}{\gamma_C^{\gamma-1}} = 1 - \dfrac{1}{\left(\frac{400}{50}\right)^{1.4-1}} = 0.564$

ii) $\qquad P_1 V_1^{1.4} = P_2 V_2^{1.4}$

$$P_2 = P_1 \left(\frac{V_1}{V_2}\right)^{1.4} = 1 \ atm \times 8^{1.4} = 18.38 \ atm = 1.86 \times 10^6 \ Pa$$

$$T_2 = \frac{P_2 V_2}{nR} = \frac{1.86 \times 10^6 \times 50 \times 10^{-6} m^3}{8.31 J \ mol^{-1} \ K^{-1}} = 11.2 \ K$$

iii) $\qquad T_3 = \dfrac{P_3 V_3}{nR} = \dfrac{24 \times 1.01 \times 10^5 Pa \times 50 \times 10^{-6} m^3}{8.31 J \ mol^{-1} \ K^{-1}} = 14.6 \ K$

iv) $\qquad$ In process $2 \rightarrow 3$ which is isochoric there is no work done and the first law then reads

$$\Delta U_{2\rightarrow3} = \Delta Q_{2\rightarrow3}$$

$$\Delta Q_{2\rightarrow3} = \frac{5}{2} \left(P_3 V_3 - P_2 V_2 \right) = 2.5 \times V_2 \times \left(P_3 - P_2 \right)$$

$$\Delta Q_{2\rightarrow3} = Q_1 = 2.5 \times 50 \times 10^{-6} m^3 \times \left(24 - 18.38 \right) 1.01 \times 10^5 Pa = +71 \ J$$

v) $\qquad W = \eta_E \times Q_1 = 0.564 \times 71 \ J = 40.0 \ J$

This is the energy delivered as work in one cycle so if there are 60 cycles per second the power is

$$Power = 40.0 \ J \times 60 \ s^{-1} = 2400 \ Watts$$

Question 4   1999 Exam Q3

a)   Infinitesimal entropy change may be defined in terms of reversible heat flow as

$$dS = \frac{dQ_R}{T}$$

NB. The entropy is not defined in absolute terms with only entropy difference having absolute meaning between two equilibrium states

$$\Delta S = \int_i^f \frac{dQ_R}{T}$$

The second law of thermodynamics for processes undergone by a thermally isolated system may be expressed as

$$\Delta S \geq 0$$

Where the equality applies to a reversible process.

b)

i)   The final equilibrium state of the system is found by finding the final temperature T_f of the mixture accounting for the fact that no heat is exchanged with the external environment, $\Delta Q = 0$

$$c_P^{Water}\left(T_f - 273.15\right)m^{Ice} + c_P^{Water}\left(T_f - 300\right)m^{water} + l_{S \rightarrow L}m^{Ice} = 0$$

$$4.2 \times 10^3 \left(T_f - 273.15\right)0.5kg + 4.2 \times 10^3 \left(T_f - 300\right)5kg + 3.33 \times 10^5 \times 0.5kg = 0$$

$$4.2 \times 10^3 \times 5.5kg \times T_f = 4.2 \times 10^3 \times \left(0.5kg \times 273.15 + 5kg \times 300\right) - 3.33 \times 10^5 \times 0.5kg$$

$$T_f = \frac{4.2 \times 10^3 \times 1636 - 1.66 \times 10^5}{4.2 \times 10^3 \times 5.5} = \frac{6.7 \times 10^6}{2.31 \times 10^4} = 290 \ K$$

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Therefore the final equilibrium state is 5.5kg of water at 290 K

ii) The net entropy change is to be found by considering the entropy changes occurring during the three processes

1. The change as 5kg of water cools from 300K to 290 k

$$\Delta S_{Cooling} = \int_{300}^{290} \frac{dQ}{T} = m c_P \int_{300}^{290} \frac{dT}{T} = m c_P \ln \frac{290}{300} = 5kg \times 4.2 \times 10^3 \times \left(3.39 \times 10^{-2} \right)$$

$$\Delta S_{Cooling} = 5kg \times 4.2 \times 10^3 \times \left(3.39 \times 10^{-2} \right) = -712 \ JK^{-1}$$

2. The change as 0.5kg of water warms from 273.15 to 290 is calculated in an identical fashion

$$\Delta S_{Warming} = \int_{273.15}^{290} \frac{dQ}{T} = m c_P \int_{273.15}^{290} \frac{dT}{T} = m c_P \ln \frac{290}{273.15} = 0.5kg \times 4.2 \times 10^3 \times \left(5.98 \times 10^{-2} \right)$$

$$\Delta S_{Warming} = 0.5kg \times 4.2 \times 10^3 \times \left(5.98 \times 10^{-2} \right) = 125.6 \ JK^{-1}$$

3. Finally there is a change associated with the phase change as 0.5kg of ice turns to 0.5kg of water

$$\Delta S_{Ice \rightarrow Water} = + \frac{\Delta Q}{T} = + \frac{lm^{Ice}}{273.15} = \frac{1.665 \times 10^5}{273.15} = 609.5 \ JK^{-1}$$

The net change in entropy is then the sum of these three components

$$\Delta S_{Net} = -712 + 125.6 + 609.5 = +23.1 \ JK^{-1}$$

iii) As the system is thermally isolated the second law requires that the change in entropy must be greater than zero (the process are irreversible as the

final 5.5kg of water cannot separate out spontaneously into 0.5 kg of ice and 5 kg of water at 300K). This is indeed seen to be the case in ii)

c)   We are given the following

$$U = \frac{3}{2}nRT \qquad\qquad PV = nRT$$

From which we may deduce further that

$$dU = \frac{3}{2}nRdT \qquad \text{and} \qquad \frac{P}{T} = \frac{nR}{V}$$

Also we know $dQ = TdS$ and so the first law may be written in the form

$$dU = TdS + dW = TdS - PdV$$

known as the thermodynamic identity

Using all of this we may write

$$dS = \frac{dU}{T} + \frac{P}{T}dV = \frac{3}{2}nR\frac{dT}{T} + nR\frac{dV}{V}$$

Allowing us to first hold V constant on the RHS and integrate both sides to give

$$\Delta S = \frac{3}{2}nR\ln\frac{T_f}{T_i} + const$$

Where the constant of integration will depend on the value of V at which the integration was performed.

Similarly we may hold T constant and integrate both sides to give

$$\Delta S = nR\ln\frac{V_f}{V_i} + const$$

Where the constant of integration will depend on the value of T at which the integration was performed.

To bring these two expressions for ΔS together we must write

$$\Delta S = \frac{3}{2}nR\ln\frac{T_2}{T_1} + nR\ln\frac{V_2}{V_1}$$

for the change in entropy when the gas undergoes the process taking it from (T_1, V_1) to (T_2, V_2).

d)

  i) Boltzmann in seeking to explain entropy with a microscopic model conjectured that;

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

By probability Boltzmann was considering a number that is proportional to the number of distinct ways a system can arrange itself microscopically to achieve a particular macroscopic equilibrium state.

  ii) Using the result from c) we have

$$\Delta S = \frac{3}{2}nR\ln\frac{T_2}{T_1} + nR\ln\frac{V_2}{V_1} = nR\ln\frac{3V_1}{V_1} = nR\ln 3 = +1.1nR$$

  iii) Again using the result from c) we have

$$\Delta S = \frac{3}{2}nR\ln\frac{T_2}{T_1} + nR\ln\frac{V_2}{V_1} = \frac{3}{2}nR\ln\frac{2T_1}{T_1} = 1.5nR\ln 2 = +1.04nR$$

  iv) From Boltzmanns understanding of entropy based on the number microscopic arrangements that could represent a given macrostate we can see how these results agree as follows;

For the expansion where V goes to 3V the number of arrangements available is given by

$$\Omega_{Mom}\Omega_{Spatial}(V) = \Omega_{Mom}\frac{1}{N!}\left(\frac{V}{\Delta X^3}\right)^N$$

$$\Omega(V) = \Omega_{Mom}\frac{1}{N!}\left(\frac{3V}{\Delta X^3}\right)^N$$

$$S(V) = k\ln\Omega = k\ln\Omega_{Mom} + k\ln\frac{1}{N!} + kN\ln\left(\frac{V}{\Delta X^3}\right)$$

$$S(3V) = k\ln\Omega(3V) = k\ln\Omega_{Mom} + k\ln\frac{1}{N!} + kN\ln\left(\frac{3V}{\Delta X^3}\right) = k\ln\frac{1}{N!} + kN\ln 3 + kN\ln\left(\frac{V}{\Delta X^3}\right)$$

$$\Delta S = S(3V) - S(V) = N_A k \frac{N}{N_A} \ln 3 = nR \ln 3$$

Where we use $n = \dfrac{N}{N_A}$ and $k = \dfrac{R}{N_A}$ and R is the universal gas constant and

N_A is Avagadro's number.

This is the same change in entropy as in the previous answer obtained from macroscopic considerations.

For the heating where T goes to 2T the number of arrangements available is given by

$$\Omega_{Mom}(T)\Omega_{Spatial} = \Omega_{Spatial} \frac{1}{N!} \left(\frac{p_{rms}^3}{\Delta p^3} \right)^N$$

$$p_{rms} = m v_{rms} = \sqrt{\frac{3k\,T}{m}}$$

$$\Omega_{Mom}(T) = \frac{1}{N!} \left(\frac{\left(\frac{3k}{m}\right)^{3/2} T^{3/2}}{\Delta p^3} \right)^N$$

And

$$\Omega_{Mom}(2T) = \frac{1}{N!} \left(\frac{\left(\frac{3k}{m}\right)^{3/2} 2^{3/2} T^{3/2}}{\Delta p^3} \right)^N$$

$$S = k \ln \Omega_{Mon} = k \ln \frac{1}{N!} + kN \ln \left(\frac{\left(\frac{3k}{m}\right)^{3/2}}{\Delta p^3} \right) + \frac{3}{2} Nk \ln T$$

$$S(T) = k \ln \Omega_{Mon} = k \ln \frac{1}{N!} + kN \ln \left(\frac{\left(\frac{3k}{m}\right)^{3/2}}{\Delta p^3} \right) + \frac{3}{2} Nk \ln 2 + \frac{3}{2} Nk \ln T$$

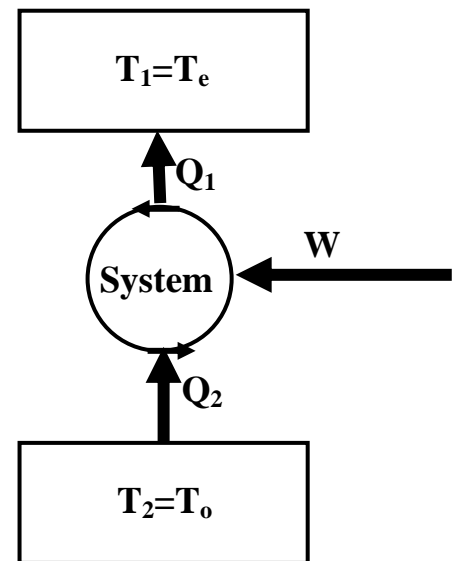$$\Delta S = S(2T) - S(T) = \frac{3}{2} Nk \ln 2 = \frac{3}{2} nR \ln 3$$

This is the same change in entropy as in the previous answer obtained from macroscopic considerations.

Tutorial Questions

(a) This is a heat balance problem. First we have an ideal (Carnot) heat pump whose efficiency is found by considering the following definition and diagram

$$\eta_{HP} = \frac{Heat\ flow\ Into\ hot\ reservoir}{Work\ in} = \frac{Q_1}{W}$$

$$\eta_{HP} = \frac{Q_1}{Q_1 - Q_2} = \frac{T_1}{T_1 - T_2}$$

We can identify T_2 the temperature of the cold reservoir as T_o
We can also identify T_1 as the temperature of the building, T_e

In equilibrium the heat pumped in must equate with the heat lost to the surroundings

$$\dot{Q}_1 = \eta_{HP} W = \frac{T_e}{T_e - T_o} W = \alpha (T_e - T_o)$$

We need to find an expression for T_e and so re-arrange the above equation

$$W T_e = \alpha (T_e - T_o)^2$$

Re-arranging into the form of a quadratic

$$\alpha T_e^2 - (W + 2\alpha T_o)T_e + \alpha T_o^2 = 0$$

We can solve this quadratic in T_e by the usual formula

$$T_e = \frac{(W + 2\alpha T_o) \pm \sqrt{(W + 2\alpha T_o)^2 - 4\alpha^2 T_o^2}}{2\alpha}$$

$$T_e = \frac{W}{2\alpha} + T_o \pm \sqrt{\frac{W^2 + 4\alpha W T_o}{4\alpha^2}}$$

$$T_e = T_o + \frac{W}{2\alpha}\left(1 + \sqrt{1 + \frac{4\alpha T_o}{W}}\right) \qquad \textbf{QED}$$

(b)

The engine we are considering is a Carnot engine and it has the property that the hot reservoir is gradually cooling as the engine operates.

$$\eta_E = \frac{dW}{dQ_1} \qquad\qquad \eta_E = 1 - \frac{T_2}{T_1}$$
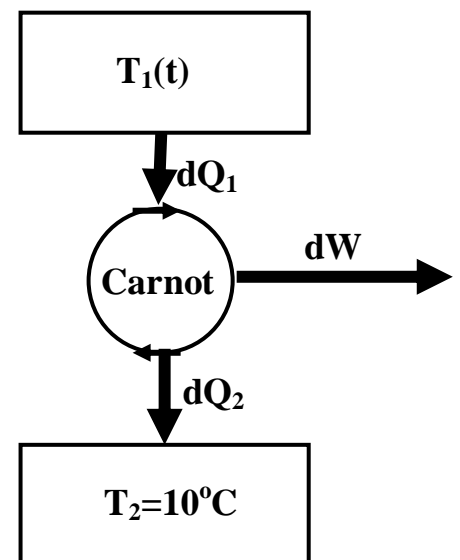
$$dW = \eta_E dQ_1$$

$$dQ_1 = -m c_P dT_1$$

The minus sign is required because the hot reservoir is cooling and dT_1 is negative whereas we require dQ_1 to be a positive quantity

$$\int_i^f dW = \int_{100}^{10} \eta_E dQ_1 = -m c_P \int_{373.15}^{283.15}\left(1 - \frac{T_2}{T_1}\right) dT_1$$

T_2 is a constant and we have

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$$W = mc_p \left(\int_{283.15}^{373.15} dT_1 - T_2 \int_{283.15}^{373.15} \frac{dT_1}{T_1} \right)$$

$$W = 4.2 \times 10^3 \times \left(\rho_{Water} \times 1000 m^3 \right) \left(90 - 283.15 \times ln \frac{373.15}{283.15} \right)$$

$$W = 4.2 \times 10^3 \times \left(\rho_{Water} \times 1000 m^3 \right) \left(90 + 78 \right)$$

$$\rho_{Water} = 1 kgLt^{-1} = 10^3 kgm^{-3}$$

$$W = 4.2 \times 10^3 \times \left(10^3 kgm^{-3} \times 1000 m^3 \right) 168 = 7.06 \times 10^{11} \ J$$