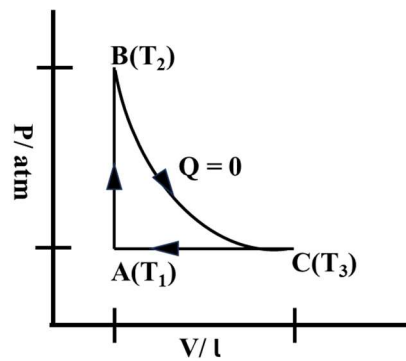


## Practice session IV

### Thermodynamics

1. One mole of an ideal monoatomic gas ( $C_V = 1.5R$ ) is allowed to undergo the following cyclic process ABC. Calculate the efficiency of the cycle.



Answer:

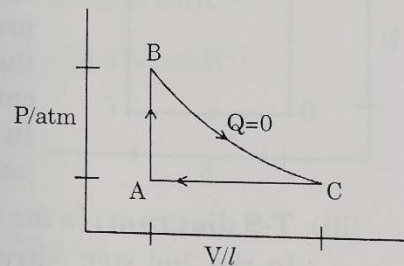
14. Let, temperatures at A, B and C be  $T_1$ ,  $T_2$  and  $T_3$ . State C is attained by adiabatic reversible expansion from B. So  $T_3 < T_2$ . Moreover  $T_3 > T_1$  as  $V_C > V_A$  at constant pressure.

$$W_{AB} = 0 \text{ since } \Delta V = 0$$

$$W_{BC} = \Delta U = C_V(T_3 - T_2)$$

$$W_{CA} = -P(V_A - V_C) = -R(T_1 - T_3)$$

$$\begin{aligned} W_{cycle} &= C_V(T_3 - T_2) - R(T_1 - T_3) \\ &= -\frac{3}{2}R(T_2 - T_3) - R(T_1 - T_3) \end{aligned}$$



$$\therefore |W_{cycle}| = R \left[ \frac{3}{2}T_2 - \frac{5}{2}T_3 + T_1 \right] = R \left[ \frac{3}{2}(T_2 - T_1) - \frac{5}{2}(T_3 - T_1) \right]$$

$$\text{Heat absorbed, } Q_1 = C_V(T_2 - T_1) = \frac{3}{2}R(T_2 - T_1)$$

$$\therefore \eta = \frac{R \left[ \frac{3}{2}(T_2 - T_1) - \frac{5}{2}(T_3 - T_1) \right]}{\frac{3}{2}R(T_2 - T_1)} = 1 - \frac{5(T_3 - T_1)}{3(T_2 - T_1)}$$

2. Calculate the entropy change of a sample of perfect gas under reversible isothermal expansion. (Given: the volume occupied by 2 mole of any perfect gas molecules is tripled at any constant temperature).

$$\Delta S = \frac{1}{T} \int_i^f dq_{\text{rev}} = \frac{q_{\text{rev}}}{T}$$

From eqn 2.11, we know that

$$q_{\text{rev}} = -w_{\text{rev}} = nRT \ln \frac{V_f}{V_i}$$

It follows that

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

$$\Delta S = (2 \text{ mol}) \times (8.314 \text{ JK}^{-1}\text{mol}^{-1}) \times \ln 3$$

$$\Delta S = 18.27 \text{ JK}^{-1}$$

3. Calculate the entropy change when 1 mole of argon gas at 25°C and 1.00 bar in a container of volume 0.8 dm<sup>3</sup> is allowed to expand to 1.2 dm<sup>3</sup> and is simultaneously heated to 75°C. (C<sub>V</sub>=3/2 R)

**For a reversible process involving changes in  $T$  and  $V$  of 1 mole of an ideal gas**

$$\delta q_{\text{rev}} = dU + pdV \Rightarrow \frac{\delta q_{\text{rev}}}{T} = \frac{dU}{T} + \frac{p}{T} dV$$

$$dS = \frac{C_V}{T} dT + \frac{R}{V} dV$$

$$\int_1^2 dS = S_2 - S_1 = \Delta S = C_V \int_{T_1}^{T_2} \frac{dT}{T} + R \int_{V_1}^{V_2} \frac{dV}{V}$$

$$\Delta S = C_V \ln \left( \frac{T_2}{T_1} \right) + R \ln \left( \frac{V_2}{V_1} \right)$$

$$\Delta S = (3/2)R \times \ln(T_2/T_1) + R \times \ln(V_2/V_1)$$

$$\Delta S = (3/2) \times 8.314 \times \ln(348/298) + 8.314 \times \ln(1.2/0.8)$$

$$\Delta S = 1.93 + 3.37$$

$$\Delta S = 5.3 \text{ JK}^{-1}$$

4. Find entropy change for the melting of 3 g of ice (heat of fusion 79.7 cal/g) at STP. Find the same for the reverse process.

The change in entropy ( $\Delta S$ ) during a phase transition like melting can be calculated using the formula:

$\Delta S = \Delta H/T$ , where:

$\Delta H$  is the enthalpy of fusion (the heat absorbed during melting).

T is the melting point in K

STP means 1 atm pressure and 0°C temperature

$\text{H}_2\text{O (s) to H}_2\text{O (l)}$  ;  $\Delta H = 79.7 \text{ cal/g}$

The entropy change for the melting of ice is positive, meaning entropy increases, as the ordered solid state transitions to the more disordered liquid state.

Entropy change for the melting

$$\begin{aligned}\Delta S &= \Delta H/T \\ &= (79.7 \text{ cal/g} \times 3 \text{ g})/273 \text{ K} \\ &= 0.88 \text{ cal/K} \\ &= 3.68 \text{ J/K}\end{aligned}$$

For entropy change in case of freezing,  $q_{\text{rev}}$  is negative

$$\begin{aligned}\Delta S &= -0.88 \text{ cal/K} \\ &= -3.68 \text{ J/K}\end{aligned}$$

For one mole the molar mass would be 18 g

$$\begin{aligned}\text{Then, } \Delta S &= \Delta H/T \\ &= (79.7 \text{ cal/g} \times 18 \text{ g})/273 \text{ K} \\ &= 5.25 \text{ cal/K} \\ &= 21.97 \text{ J/K}\end{aligned}$$

5. Show that  $\Delta S_{\text{mix,molar}} = R \ln 2$  if equal volumes of two gases under the same conditions are mixed. Calculate the entropy of mixing if two moles of  $\text{N}_2$  (g) are mixed with three moles of  $\text{O}_2$  (g) at the same temperature and pressure. (Assume ideal behaviour).

When ideal gases mix, the entropy of the system increases because the gases expand into a larger volume, leading to a greater number of available microstates.

Because there are equal volumes of ideal gases under the same conditions,  $y_1 = y_2 = 0.5$  (Problem 20–28). Now Equation 20.30 gives

$$\begin{aligned}\Delta_{\text{mix}} \bar{S} &= -R y_1 \ln y_1 - R y_2 \ln y_2 \\ &= -\frac{R}{2} \ln \frac{1}{2} - \frac{R}{2} \ln \frac{1}{2} \\ &= -R \ln \frac{1}{2} = R \ln 2\end{aligned}$$

The mole fractions  $x$  are  $2/5$  for  $\text{N}_2$  (g) and  $3/5$  for  $\text{O}_2$  (g)

$$\begin{aligned}\Delta S_{\text{mix}} &= -R n_1 \ln x_1 - R n_2 \ln x_2 \\ &= \{-2x \ln(2/5) - 3x \ln(3/5)\} \times 8.314 \\ &= (1.83 + 1.53) \times 8.314 \\ &= 27.94 \text{ JK}^{-1}\end{aligned}$$

To calculate the entropy change, let us treat this mixing as two separate gas expansions, one for gas A and another for B. From the statistical definition of entropy, we know that

$$\Delta S = nR \ln \frac{V_2}{V_1}.$$

Now, for each gas, the volume  $V_1$  is the initial volume of the gas, and  $V_2$  is the final volume, which is both the gases combined,  $V_A + V_B$ . So for the two separate gas expansions,

$$\begin{aligned}\Delta S_A &= n_A R \ln \frac{V_A + V_B}{V_A} \\ \Delta S_B &= n_B R \ln \frac{V_A + V_B}{V_B}\end{aligned}$$

So to find the total entropy change for both these processes, because they are happening at the same time, we simply add the two changes in entropy together.

$$\Delta_{\text{mix}} S = \Delta S_A + \Delta S_B = n_A R \ln \frac{V_A + V_B}{V_A} + n_B R \ln \frac{V_A + V_B}{V_B}$$

Recalling the ideal gas law,  $PV = nRT$ , we see that the volume is directly proportional to the number of moles (Avogadro's Law), and since we know the number of moles we can substitute this for the volume:

$$\Delta_{\text{mix}} S = n_A R \ln \frac{n_A + n_B}{n_A} + n_B R \ln \frac{n_A + n_B}{n_B}$$

Now we recognize that the inverse of the term  $\frac{n_A + n_B}{n_A}$  is the mole fraction  $\chi_A = \frac{n_A}{n_A + n_B}$ , and taking the inverse of these two terms in the above equation, we have:

$$\Delta_{\text{mix}} S = -n_A R \ln \frac{n_A}{n_A + n_B} - n_B R \ln \frac{n_B}{n_A + n_B} = -n_A R \ln \chi_A - n_B R \ln \chi_B$$

since  $\ln x^{-1} = -\ln x$  from the rules for logarithms. If we now factor out  $R$  from each term:

$$\Delta_{\text{mix}} S = -R(n_A \ln \chi_A + n_B \ln \chi_B)$$

represents the equation for the entropy change of mixing. This equation is also commonly written with the total number of moles:

$$\Delta_{\text{mix}} S = -nR(\chi_A \ln \chi_A + \chi_B \ln \chi_B) \quad (1)$$

where the total number of moles is  $n = n_A + n_B$