

EXERCISE (S-I)

1. The efficiency of a carnot cycle is $1/6$. On decreasing the temperature of the sink by 65°C , the efficiency increases to $1/3$. Calculate the temperature of source and sink.

Ans. 117°C , 52°C

$$\eta = 1 - \frac{T_L}{T_H}$$

$$\frac{1}{6} = 1 - \frac{T_L}{T_H} \quad \text{--- (1)}$$

$$\frac{1}{3} = 1 - \frac{(T_L - 65)}{T_H} \quad \text{--- (2)}$$

$$\frac{1}{3} = \frac{1}{6} + \frac{65}{T_H}$$

$$T_H = 6 \times 65 = 390 \text{ K} \\ = 117^\circ\text{C}$$

$$T_L = \frac{5}{6} \times 390 = 325 \text{ K} \\ = 52^\circ\text{C}$$

2. A carnot cycle has an efficiency of 40%. Its low temperature reservoir is at 9°C . What is the temperature of source ?

Ans. 197°C

$$\eta = 1 - T_L/T_H$$

$$\eta = 0.40 = 1 - \frac{(273 + 9)}{T_H}$$

$$T_H = T_{\text{Source}} = 470 \text{ K} \\ = 197^\circ\text{C}$$

3. A diatomic ideal gas is expanded isothermally to 32 times of its initial volume then it is cooled to restore to initial entropy at constant volume. Calculate ratio of initial temperature to final temperature

3. Ans. (4)

Sol. $nC_{v,m} \ln \frac{T_i}{T_f} = nR \ln \frac{V_2}{V_1}$

$$n \times \frac{5}{2} R \ln \frac{T_i}{T_f} = nR \ln 32$$

$$\frac{T_i}{T_f} = (32)^{2/5} \Rightarrow \frac{T_i}{T_f} = 4$$

4. One mole of an ideal monoatomic gas was taken through reversible isochoric heating from 100 K to 1000 K. Calculate ΔS_{system} , ΔS_{surr} and ΔS_{total}

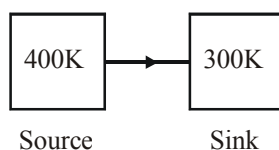
(i) when the process is carried out reversibly

(ii) when the process is carried out irreversibly (one step)

4. Ans. (i) $\Delta S_{\text{syst}} = 28.72 \text{ J/K}$; $\Delta S_{\text{surr}} = -28.72 \text{ J/K}$; $\Delta S_{\text{total}} = 0$

(ii) $\Delta S_{\text{sys}} = 28.72 \text{ J/K}$; $\Delta S_{\text{surr}} = -11.22 \text{ J/K}$; $\Delta S_{\text{total}} = 17.50 \text{ J/K}$

5. 100 kJ heat is transferred from a large heat reservoir at 400 K to another large heat reservoir at 300 K. Suppose there is no change in temperature due to exchange of heat and combinedly source and sink form isolated system.



Find (a) ΔS_{source} , (b) ΔS_{sink} and (c) ΔS_{total} . Also comment on spontaneity of process.

4. Ans. (a) -250 J/K (b) 333.33 J/K (c) $+83.33 \text{ J/K}$. Process is spontaneous.

(i) $\Delta S_{\text{sys}} = nC_v \ln \frac{T_2}{T_1} = 1 \times \frac{3}{2} \times 8.314 \ln \frac{1000}{100} = 28.72 \text{ J/K}$

$\Delta S_{\text{surr}} = -\Delta S_{\text{sys}} \text{ (Rev.)}$ and $\Delta S_{\text{Total}} = 0 \text{ (Rev.)}$

(ii) $\Delta S_{\text{sys}} = \Delta S_{\text{sys}} = 28.72 \text{ J/K}$ (Rev) | $\Delta S_{\text{surr}} = -nC_v(T_2 - T_1)/T_2$
 $= -1 \times \frac{3}{2} \times 8.314 \times 900/1000$
 $= -11.22 \text{ J/K}$
 $\Delta S_{\text{Total}} = 28.72 - 11.22 = 17.5 \text{ J/K}$

(a) $\Delta S_{\text{Source}} = -100 \text{ kJ}/400 \text{ K} = -250 \text{ J/K}$

(b) $\Delta S_{\text{Sink}} = \frac{+100 \times 10^3 \text{ J}}{300} = 333.33 \text{ J/K}$

(c) $\Delta S_{\text{Total}} = 333.33 - 250 = +83.33 \text{ J/K}$

2 Since $\Delta S_{\text{Total}} > 0 \Rightarrow$ Spontaneous.

6. A system of 100 kg mass undergoes a process in which its specific entropy increases from $0.3 \text{ kJkg}^{-1}\text{K}^{-1}$ to $0.4 \text{ kJkg}^{-1}\text{K}^{-1}$. At the same time, the entropy of the surrounding decreases from 80 kJkg^{-1} to 75 kJkg^{-1} . Find the $(\Delta S)_{\text{universe}}$ in kJK^{-1} .

6. Ans.(5)

$$(\Delta S)_{\text{system}} = 0.1 \times 100 = 10 \text{ kJ/K}$$

$$(\Delta S)_{\text{surrounding}} = -5 \text{ kJ/K}$$

$$(\Delta S)_{\text{universe}} = 5 \text{ kJ/K}$$

7. Calculate $(\Delta S)_{\text{universe}}$ (in cal/K) when 1kg water at 300K is brought into contact with a heat reservoir at 600K. Specific heat capacity of water is $1 \text{ cal/gm}^\circ\text{C}$. Assume no change in physical state of water.

$$(\ln 2 = 0.7)$$

7. Ans (200)

$$\Delta S_{\text{universe}} = \Delta S_{\text{system}} + \Delta S_{\text{surrounding}}$$

$$= ms \ln \frac{T_2}{T_1} + \left(\frac{-ms\Delta T}{T_2} \right)$$

$$= 1000 \times 1 \times \ln 2 + \left(\frac{-1 \times 1000 \times 300}{600} \right)$$

$$= 700 - 500$$

$$= 200 \text{ cal/K}$$

8. 1 mole of ideal monoatomic gas is heated by supplying 5 kJ heat from a reservoir maintained at 400 K from 300 K to 400 K. In the process volume of gas increased from 1 L to 10 L. Find ΔS_{total} (in J/K-mol) in the process

$$\text{Use : } \ln \left(\frac{4}{3} \right) = 0.3, \ln 10 = 2.3, R = 8.3 \text{ J/K-mol and } \ln x = 2.3 \log x$$

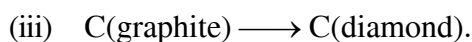
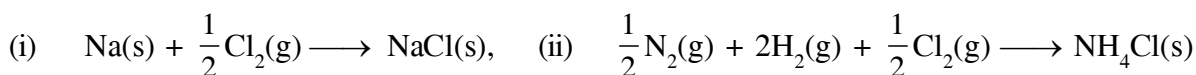
8. Ans. 10.325

$$[\text{Sol. } \Delta S_{\text{system}} = C_v \ln \frac{T_2}{T_1} + R \ln \frac{V_2}{V_1} ; \Delta S_{\text{surr}} = \frac{-q}{400}]$$

$$\Delta S_{\text{total}} = - \frac{5000}{400} + \frac{3}{2} \times (8.3) \times \ln \frac{4}{3} + (8.3) (2.3)$$

$$\Delta S_{\text{total}} = + 10.325 \text{ J/K-mol Ans.]}$$

9. Calculate ΔS_r° at 298K of



The values of S° of Na, Cl_2 , NaCl, NH_4Cl , N_2 , H_2 diamond & graphite are 51, 223, 72, 95, 192, 131, 2.43 & 5.69 $\text{JK}^{-1} \text{mol}^{-1}$ respectively.

9. Ans. (i) -90.5 (ii) -374.5 (iii) -3.26 (all in $\text{J mol}^{-1} \text{K}^{-1}$)

$$\begin{aligned} \text{(i)} \quad \Delta_r S^\circ &= \left\{ (S_f^\circ)_{\text{NaCl(s)}} \right\} - \left\{ (S_f^\circ)_{\text{Na(s)}} + \frac{1}{2} (S_f^\circ)_{\text{Cl}_2(\text{g})} \right\} \\ &= \{ 72 \} - \left\{ 51 + \frac{1}{2} \times 223 \right\} \\ &= -90.5 \text{ J/K} \end{aligned}$$

$$\begin{aligned} \text{(ii)} \quad \Delta_r S^\circ &= \{ 95 \} - \left\{ \frac{1}{2} \times 192 + 2 \times 131 + \frac{1}{2} \times 223 \right\} \\ &= -374.5 \text{ J/K} \end{aligned}$$

$$\begin{aligned} \text{(iii)} \quad \Delta_r S^\circ &= (S_f^\circ)_{\text{C(dia)}} - (S_f^\circ)_{\text{C(gr)}} \\ &= 2.43 - 5.69 = -3.26 \text{ J/K} \end{aligned}$$

10. Identify the substance in each of the following pairs of samples that has the higher entropy?

(A) $\text{Br}_2(\text{l})$ or $\text{Br}_2(\text{g})$

(B) $\text{C}_2\text{H}_6(\text{g})$ or $\text{C}_3\text{H}_8(\text{g})$

(C) MgO(s) or NaCl(s)

(D) KOH(s) or KOH(aq)

10. Ans. [A] - II ; [B] - II ; [C] - II ; [D] - II

(A) $S(\text{liq}) < S(\text{gas})$

(B) $S \propto$ More no. of Atoms per molecule

(C) $S \propto$ Weak Ionic Bonds -

(D) $S_{\text{solid solute}} < S_{\text{Aq. Solute}}$

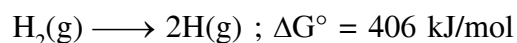
11. Calculate the ΔG° change at 300 K for the reaction;

$\text{Br}_2(\ell) + \text{Cl}_2(\text{g}) \longrightarrow 2\text{BrCl}(\text{g})$. For the reaction $\Delta H^\circ = 29.3 \text{ kJ}$ & the standard entropies of $\text{Br}_2(\ell)$, $\text{Cl}_2(\text{g})$ & $\text{BrCl}(\text{g})$ at the 300 K are 150, 220, 240 $\text{J mol}^{-1}\text{K}^{-1}$ respectively.

11. Ans. -3.7 kJ

$$\begin{aligned} \textcircled{11} \quad \Delta G^\circ &= \Delta H^\circ - T \Delta S^\circ = 29.3 - 300 \left[\frac{2 \times 240 - 150 - 220}{1000} \right] \\ &= \textcircled{-3.7} \text{ kJ} \end{aligned}$$

12. The standard entropies of $\text{H}_2(\text{g})$ and $\text{H}(\text{g})$ are 130 and 115 $\text{J mol}^{-1}\text{K}^{-1}$ respectively at 300K. Using the data given below calculate the bond energy of H_2 (in kJ/mol) :-

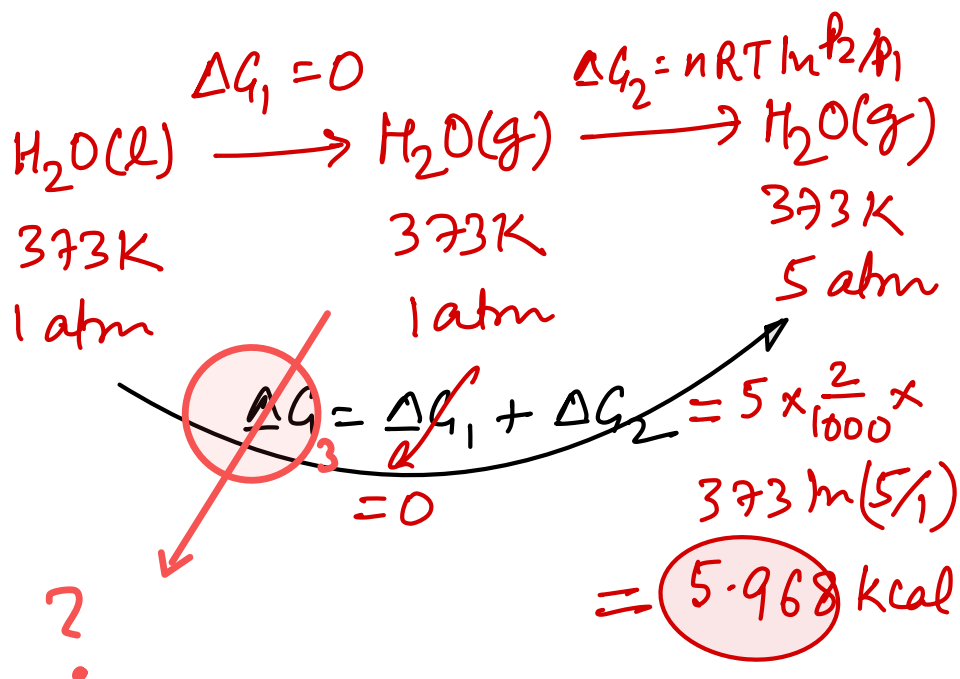


- Ans 436 kJ

$$\begin{aligned} \Delta G^\circ &= \Delta H^\circ - T \Delta S^\circ \\ 406 &= \Delta H^\circ - 300 \left[\frac{2 \times 115 - 130}{1000} \right] \\ \Delta H^\circ &= \textcircled{436 \text{ kJ}} = E_{\text{H-H}} \end{aligned}$$

13. 5 mole $\text{H}_2\text{O}(\ell)$ at 373K and 1 atm is converted into $\text{H}_2\text{O}(\text{g})$ at 373K and 5 atm. Calculate ΔG for this process. [Given : $R = 2\text{Cal/K-mol}$, $\ln 5 = 1.6$]

Ans. 5.968 kcal



14. Calculate ΔG (in bar-L) when a definite mass of a monoatomic ideal gas at 1 bar & 27°C is expanded adiabatically against vacuum from 10 L to 20 L ($\ln 2 = 0.7$)
14. Ans. (-7)

$$\Delta G = nRT \ln \frac{V_1}{V_2} = P_1 V_1 \ln \frac{V_1}{V_2}$$

$$= 1 \times 10 \ln \frac{10}{20}$$

$$= -10 \times \ln 2$$

$$= -10 \times 0.7$$

$$= -7 \text{ bar-L}$$

15. Find $(\Delta S)_{\text{universe}}$ (in Joule/mole/K) at 1 bar for a chemical reaction at 300 K if $\Delta H_{300\text{ K}}^{\circ} = 75 \text{ kJ/mol}$
 $\Delta S_{300\text{ K}}^{\circ} = 300 \text{ J/K}$

15. **Ans. (50)**

$$\begin{aligned}(\Delta S)_{\text{uni}} &= (\Delta S)_{\text{sys}} + (\Delta S)_{\text{surr.}} \\ &= 300 - \frac{75 \times 1000}{300} = 50 \text{ J/mole-K}\end{aligned}$$

16. A liquid freezes into a solid ($\Delta H = -1000 \text{ J/mole}$) at 200 K and 1 atm, (it's normal melting point).

(i) What is the value of ΔG at 200 K ?

(ii) What is the ΔS value at 200 K ?

(iii) Will the freezing be spontaneous at 150 K and 1 atm ? Calculate ΔS_{total} .

(iv) What is the value of ΔG at 250 K and 1 atm ?

(And it is assumed that ΔS and ΔH do not depend on temperature)

[Sol. (i) $L \rightleftharpoons S$: $\Delta H = -1000 \text{ Joule. mole}$: at $T = 200 \text{ K}$ and $P = 1 \text{ atm}$. At normal melting point, this transformation is reversible – Hence

$$\Delta G = 0 \text{ Ans.}$$

$$(ii) \quad \Delta S = -\frac{\Delta H}{T} = \frac{-1000}{200} = -5 \text{ J/mole. K}$$

$$(iii) \quad \Delta S_{\text{total}} = \Delta S_{\text{syst}} + \Delta S_{\text{surr}}$$

assuming that ΔS and ΔH do not vary temperature

$$\Delta S_{\text{total}} = -5 \text{ J/mole. K} + \left(\frac{\Delta H}{T} \right)$$

$$= -5 + \frac{1000}{150} = +1.66 \text{ J/ mole .K process is spontaneous}$$

$$(iv) \quad \Delta G = -T\Delta S_{\text{total}}$$

at 250 K : $\Delta S_{\text{total}} = \Delta S_{\text{syst}} + \Delta S_{\text{surr}}$

$$= -5 + \left(\frac{\Delta H}{T} \right)$$

$$= -5 + \frac{1000}{250} = -1 \text{ J/mole. K}$$

$$\Rightarrow \Delta G = - (250) (-1) = +250 \text{ J/mole. K}$$

The process is non-spontaneous at 250 K

Ans.

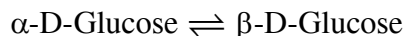
$$(i) \quad \Delta G = 0$$

$$(ii) \quad \Delta S = -5 \text{ J/mole.K}$$

$$(iii) \quad \Delta S_{\text{total}} = +1.66 \text{ J/ mole. K ; process is spontaneous}$$

$$(iv) \quad \Delta S_{\text{total}} = -1 \text{ J/mole. K} = \Delta G = +250 \text{ J/mole. K]}$$

17. α -D Glucose undergoes mutarotation to β -D-Glucose in aqueous solution. If at 300K there is 60% conversion. Calculate ΔG° of the reaction. ($\ln 2 = 0.7$, $\ln 3 = 1.1$)



Ans. -997.68 J/mol

$$\begin{aligned}\Delta_r G^\circ &= -RT \ln K_{eq} \\ &= -8.314 \times 300 \ln \frac{60}{40} \\ &= -8.314 \times 300 \ln \frac{3}{2} \\ &= -8.314 \times 300 [\ln 3 - \ln 2] \\ &= -8.314 \times 300 [1.1 - 0.7] \\ &= -997.68 \text{ J/mol}\end{aligned}$$

18. The equilibrium constant of the reaction $2\text{C}_3\text{H}_6(\text{g}) \rightleftharpoons \text{C}_2\text{H}_4(\text{g}) + \text{C}_4\text{H}_8(\text{g})$ is found to fit the expression

$$\ln K = -1.04 - \frac{1088\text{K}}{T}$$

Calculate the standard reaction enthalpy and entropy at 400 K.

Ans. $\Delta H^\circ = 9.04 \text{ kJ/mol}$; $\Delta S^\circ = -8.64 \text{ J/mol}^{-1} \text{ K}^{-1}$

$$\begin{aligned}\ln K &= -\frac{\Delta H^\circ}{R} \cdot \frac{1}{T} + \frac{\Delta S^\circ}{R} \\ \ln K &= -1088 \frac{1}{T} + (-1.04) \\ -\frac{\Delta H^\circ}{R} &= -1088 \Rightarrow \Delta H^\circ = 1088R \\ &= 9.04 \frac{\text{kJ}}{\text{mol}} \\ \Delta S^\circ &= -1.04R = -8.64 \frac{\text{J}}{\text{mol-K}}\end{aligned}$$

19. For the reaction $\text{SO}_2(\text{g}) + 1/2 \text{O}_2(\text{g}) \rightleftharpoons \text{SO}_3(\text{g})$; $\Delta H^\circ_{300} = -95 \text{ kJ/mole}$,
 $\Delta S^\circ_{300} = -95.0 \text{ J/K mole}$. Find the value of $\ln K_p$ for this reaction at 300 K.

Ans. 26.7

$$\Delta G^\circ = -RT \ln K_p^\circ = \Delta H^\circ - T \Delta S^\circ$$

$$\ln K_p^\circ = \frac{(\Delta H^\circ - T \Delta S^\circ)}{(-RT)}$$

$$= \frac{\left(-95 - 300 \left(\frac{-95}{1000} \right) \right)}{\left(- \frac{8.314}{1000} \times 300 \right)}$$

$$= 26.7$$