THERMODYNAMICS

PROBLEM 189 Suppose that a gas obeys the modified van der Waals' equation $P \times (V_m - b) = RT$ and $b = 0.02\ \text{L mol}^{-1}$. If 0.5 mol of the gas is reversibly compressed from an initial volume of $2\ \text{dm}^3$ to a final volume of $0.5\ \text{dm}^3$, how much work is done on the system at 27°C.

PROBLEM 190 One mole of a monoatomic, ideal gas confined in a 5 L piston fitted cylinder at 300 K is heated such that its temperature increased to 400 K but at the same time gas also expanded to a volume of 8 L. Calculate change in enthalpy of the system.

PROBLEM 191 One mole of a monoatomic ideal gas confined in a 5 L, piston fitted cylinder at 300 K is heated to 800 K as well as allowed to expand to a volume of 8 L simultaneously. Calculate change in enthalpy of the system.

PROBLEM 192 100 g of nitrogen gas at 300 K are held by a piston under 30 atmosphere. The pressure is suddenly released to 10 atmosphere and gas is allowed to expand adiabatically. If $C_V = 20.8\ \text{JK}^{-1}\text{mol}^{-1}$, calculate ΔS_{System}.

PROBLEM 193 Calculate entropy change when 0.5 L of an ideal gas ($C_V = 12.6\ \text{JK}^{-1}\text{mol}^{-1}$) at 300 K and one atmosphere is allowed to expand to double its volume and simultaneously heated to 373 K.

PROBLEM 194 10 g of ice at 0°C are added to 20 g water at 90°C in a thermally insulated flask of negligible heat capacity. The heat of fusion of ice is 6 kJ/mol. What is the final temperature, ΔS_{System}? $C_p = 75.42\ \text{JK}^{-1}\text{mol}^{-1}$.

PROBLEM 195 One mole of a supercooled liquid water at – 10°C and one atmosphere turns into ice at – 10°C. Calculate entropy change for the system. C_p for liquid water and ice are 75.42 and $37.2\ \text{JK}^{-1}\text{mol}^{-1}$ respectively.

PROBLEM 196 In an open beaker at 27°C and one atm pressure, 100 g of zinc are caused to react with dilute sulphuric acid. Calculate the work done by the liberated hydrogen gas assuming it to behave ideally. What would be the work done if the reaction took place in a sealed vessel?

PROBLEM 197 A balloon is 0.5 m in diameter and contains air at 25°C and 1 bar pressure. It is then filled with air isothermally and reversibly until the pressure reaches to 5 bar. Assume that pressure is proportional to the diameter of the balloon, calculate (a) final diameter and (b) work done in the process.

PROBLEM 198 One mole of an ideal gas initially at 10 bar and 300 K is allowed to expand against a constant external pressure of 2.00 bar to a final pressure of 2 bar. During this process, the temperature of this gas falls to 250 K. Construct a reversible path connecting this initial and final state as a combination of reversible isothermal expansion followed by reversible adiabatic expansion so that the final state is attained and calculate work done by the system in attaining the final state. $C_{vm} = 3/2\ R$.

PROBLEM 199 With the temperature maintained at 0°C, 2 mole of an ideal gas are allowed to expand against a piston that supports 2.0 bar pressure. The initial pressure of the gas is 10 bar and the final pressure 2 bar.

(a) How much energy is transferred to the surrounding during the expansion?
(b) What is the change in internal energy and enthalpy of the gas?
(c) How much heat the gas has absorbed?

PROBLEM 200 A gas behaving ideally was allowed to expand reversibly and adiabatically to twice its volume. Its initial temperature was 25°C and $C_{vm} = (5/2)\,R$, calculate ΔE_m and ΔH_m.

PROBLEM 201 One mole of a gas at 300 K is compressed isothermally and reversibly from an initial volume of $10\,\text{dm}^3$ to a final volume of $0.2\,\text{dm}^3\text{mol}^{-1}$. Calculate work done on the system if the equation of state of the gas is $(V_m - b)P = RT$ with $b = 0.03\,\text{dm}^3\text{mol}^{-3}$.

PROBLEM 202 One mole of a gas at 100 K is compressed isothermally from an initial volume of $20\,\text{dm}^3$ to a final volume of $5\,\text{dm}^3$. Calculate the work done on the system if the equation state is:

$$\left(P + \frac{a}{V_m^2}\right)V_m = RT \qquad \text{where } a = 0.384\ \text{m}^6\ \text{Pa mol}^{-1}$$

PROBLEM 203 Find $q, W, \Delta U$ and ΔH if 2.0 g of He undergoes a reversible isobaric expansion from 20 to 40 L at 0.8 atm pressure followed by reversible isochoric heating till pressure reaches to 1.0 atm. Depict the change of state on a *P-V* diagram.

PROBLEM 204 One mole of liquid water at 30°C is adiabatically compressed, pressure increasing from 1.0 atm to 10.0 atm. Since, liquids and solids are rather incompressible, it is a fairly approximastion to take *V* constant. Calculate q, ΔU and ΔH for the process. C_p of $H_2O(l) = 75.42\ \text{JK}^{-1}\text{mol}^{-1}$.

PROBLEM 205 For a perfect gas, $C_v = 2.5\,R$. 2.0 moles of this gas undergoes following change of state:

(a) A reversible isobaric expansion from 1.0 atm, 20 L to 1.0 atm, 40 L.

(b) A reversible isochoric change from 1.0 atm, 40 L to 0.5 atm, 40 L

(c) A reversible isothermal compression from 0.5 atm, 40 L to 1.0 atm, 20 L. Sketch each process on the *P-V* diagram and calculate : q, W, ΔU and ΔH.

PROBLEM 206 A sample of an ideal gas underwent an adiabatic expansion from 298 K, 15 bar to 2.5 bar against a constant external pressure of 1.0 bar. What is the final temperature of the system and work done by the system, assume $C_{vm} = 2.5\,R$?

PROBLEM 207 A gas behaves ideally and its C_v is given by: $C_v = 21.52 + 8.2 \times 10^{-3}\ T$ (all parameters in SI unit). A sample of this gas is initially at $T_1 = 300$ K, $P_1 = 10$ bar and $V_1 = 1$ L. It is allowed to expand until $P_2 = 1$ atm and $V_2 = 10$ L. What are ΔU and ΔH for this process? Could the process be carried out adiabatically. Calculate C_p at 300 K.

PROBLEM 208 The entropy change of argon is given to a good approximation by the expression:

$$\text{Sm}/\text{JK}^{-1}\text{mol}^{-1} = 36.36 + 20.79 \ln T$$

Calculate change in Gibb's free energy of one mole of argon gas if it is heated at constant pressure from 25°C to 50°C.

PROBLEM 209 Initially at 300 K and 10 atm pressure, 1.0 mole of an ideal gas is allowed to expand adiabatically against a constant pressure of 4.0 atm until equilibrium is established. Assume the gas to be ideal with:

$$C_p = 28.58 + 1.76 \times 10^{-2}\ T$$

Calculate ΔU, ΔH, and ΔS.

PROBLEM 210 An ideal gas expand against a constant external pressure of 2.0 atmosphere from 20 L to 50 L and absorb 20 kJ of energy from surrounding. What is the change in internal energy of the system?

PROBLEM 211 A gas expands against a variable pressure given by $P = \frac{10}{V}$ atm, where V is volume of gas at each stage of expansion. Further during expansion from volume 10 L to 100 L, the gas undergoes a change in internal energy of 420 J. How much heat is absorbed by the gas during expansion?

PROBLEM 212 Three moles of an ideal gas is heated at constant pressure of one atmosphere from 27°C to 127°C. If C_v is expressed as: $C_v = 30 + 14 \times 10^{-3}\, T\, \text{JK}^{-1}\ \text{mol}^{-1}$, determine W, ΔE and q.

PROBLEM 213 One mole of an ideal gas at state A (500 K, 5.0 atm) is cooled at constant volume to B (300 K) and then expanded isothermally and reversibly to C and finally compressed adiabatically to A. Sketch the change on a P-V diagram and determine the net work done in this cyclic process. $\gamma = \frac{5}{3}$.

PROBLEM 214 One mole of an ideal gas is subjected the following change of state:

$$A(5.0\ \text{atm, } 500\ \text{K}) \xrightarrow[\text{Isothermal expansion}]{\text{Reversible}} B$$

$$B \xrightarrow{\text{Isochoric cooling}} C\ (300\ \text{K}) \xrightarrow[\text{Adiabatic compression}]{\text{Reversible}} A$$

Depicting the above mentioned change on a P-V diagram, determine the net work done in the cyclic process. $C_v = 1.5\, R$.

PROBLEM 215 One mole of an ideal gas initially at A (300 K and 5.0 bar) is heated at constant pressure to double its volume (B). The gas is then expanded isothermally and reversibly to a new state C. The gas is then cooled at constant pressure to another new state D (200 K) and finally compressed adiabatically and reversibly to A. Depicting on a P-V diagram, determine the net work done in the above cyclic process. $C_v = 1.5\, R$.

PROBLEM 216 One mole of an ideal gas at A (500 K, 5.0 bar) is expanded isothermally and reversibly to a new state B and then cooled at constant pressure to C (250 K) and finally compressed adiabatically and reversibly to A. Depicting on a P-V diagram, determine the net work done in the cyclic process. $C_v = 1.5\, R$.

PROBLEM 217 One mole of an ideal gas at 500 K and 10 bar, defined by state A is allowed to expand isothermally and does a work equal to 4200 J. Construct a combination of initial irreversible expansion upto 2.0 bar followed by reversible expansion so that final state is reached and determine final pressure of the gas.

PROBLEM 218 One mole of an ideal gas at 500 K and 10 bar is allowed to expand till the final pressure falls to 1.0 atmosphere and final temperature falls to 250 K. Construct a combination of reversible path of:

(a) initial adiabatic expansion followed by isothermal expansion so that final state is reached and determine the total work done. $C_v = 1.5\, R$.

(b) Determine the work by reversing the order of combination in (a) and compare the two work done.

PROBLEM 219 One mole of an ideal gas at 300 K and 1.0 atmosphere is heated to 500 K and expanded simultaneously to 36 litre. Determine ΔH assuming heat capacity to be independent of temperature and $C_v = 1.5\,R$.

PROBLEM 220 One mole of a gas initially at 300 K is heated to 500 K. Determine the Gibb's free energy change, ΔG if $S = 1.5 + 3 \times 10^{-3}\ T[\mathrm{JK^{-1}mol^{-1}}]$ and $C_v = 1.5\,R$.

PROBLEM 221 One mole of an ideal gas at 300 K and 1.0 atmosphere is heated as well as expanded simultaneously to 500 K and 2.0 atmosphere. Determine ΔS if $C_v = 2.5\,R$.

PROBLEM 222 One mole of an ideal gas is taken in a one litre sealed flask at 300 K and heated till the pressure becomes equal to 40 atmosphere. If $C_v = 12 + 28 \times 10^{-3}\ T$ (in SI unit), determine ΔS.

PROBLEM 223 A gaseous reactant A forms two different product in a parallel reaction B and C as follows:

$$A \longrightarrow B; \quad \Delta H^\circ = -3\ \mathrm{kJ},\ \Delta S^\circ = 20\ \mathrm{JK^{-1}}$$

$$A \longrightarrow C; \quad \Delta H^\circ = -3.6\ \mathrm{kJ},\ \Delta S^\circ = 10\ \mathrm{JK^{-1}}$$

Discuss the relative stability of B and C on the basis of Gibb's free energy change at 27°C.

PROBLEM 224 One mole of an ideal gas contained in a sealed flask at 1.0 bar is heated from 27°C to 127°C. Determine ΔG if: $S(\mathrm{JK^{-1}}) = 10 + 12 \times 10^{-3}\ T$.

PROBLEM 225 Two moles of NO_2 is heated at constant volume from 27°C to 127°C and

$$C_p\ (\mathrm{JK^{-1}mol^{-1}}) = 28 + 31 \times 10^{-3}\ T$$

Determine ΔS.

PROBLEM 226 Two moles of an ideal gas is expanded isothermally and irreversibly at 27°C from volume V_1 to $2.5\,V_1$ and 4.17 kJ heat is absorbed from surroundines. Determine ΔS_{sys}, ΔS_{surr} and ΔS_{univ}.

PROBLEM 227 One mole of He(g) is mixed isothermally and reversibly with 2.0 mole of Ne(g). Determine ΔS.

PROBLEM 228 C_{vm} for an ideal gas is 2.5 R and it is independent of temperature. If 2.0 moles of this gas is subjected to the following change of state :

$$A(1.0\ \text{bar, } 20\ \text{L}) \xrightarrow[\text{Isobaric heating}]{\text{Reversible}} B(1.0\ \text{bar, } 40\ \text{L})$$

$$B \xrightarrow{\text{Isochoric cooling}} C(0.5\ \text{bar, } 40\text{L}) \xrightarrow[\text{Isothermal compression}]{\text{Reversible}} A$$

Representing the above change of states on a P-V diagram, determine the net work done.

PROBLEM 229 An ideal gas has

$$C_{vm} = a + bT$$

where $a = 25\ \text{JK}^{-1}\ \text{mol}^{-1}$ and $b = 0.03\ \text{JK}^{-2}\ \text{mol}^{-1}$. If 3.0 moles of this gas is subjected to a thermodynamic change of state from A (300 K, 2.0 bar) to B (500 K, 3.0 bar), determine q, W, ΔE, ΔH and ΔS.

PROBLEM 230 One mole of an ideal gas defined by state A (400 K, 5.0 bar) is heated at constant pressure to B (500 K) and then cooled at constant volume to C. The gas is then expanded isothermally and reversibly to a new state D (1.0 bar) and finally compressed adibatically to A. Depicting on a P-V diagram, determine the net work done in this cyclic process. $C_v = 1.5\,R$..

PROBLEM 231 One mole of an ideal gas is subjected to the following change of state:

$$A(500\ \text{K}, 5.0\ \text{bar}) \xrightarrow[\text{Isothermal expansion}]{\text{Reversible}} B \xrightarrow{\text{Isochoric cooling}} C(250\text{K}, 1.0\ \text{bar})$$

$$C \xrightarrow[\text{Adiabatic compression}]{\text{Reversible}} D(3.0\ \text{bar});\ C_v = 1.5\,R$$

Depicting the above change on a P-V diagram, determine the net work done.

PROBLEM 232 The entropy of vaporization of benzene is $85\ \text{JK}^{-1}\text{mol}^{-1}$.

(a) Estimate the enthalpy of vaporization of benzene at its normal boiling point of 80°C.

(b) Determine the entropy change of surroundings when 100 g benzene vaporizes at its normal boiling point.

PROBLEM 233 The entropy of vaporization of acetone is $85\ \text{JK}^{-1}\text{mol}^{-1}$.

(a) Estimate enthalpy of vaporization of acetone at its normal boiling point 56°C.

(b) Determine entropy change of surrounding if 100 g of acetone condenses at its boiling point.

PROBLEM 234 With the help of following reduction reactions:

$$\text{TiO}_2(s) + 2\text{C}(s) \longrightarrow \text{Ti}(s) + 2\text{CO}(g) \qquad \text{...(i)}$$

$$\text{TiO}_2(s) + \text{C}(s) \longrightarrow \text{Ti}(s) + \text{CO}_2(g) \qquad \text{...(ii)}$$

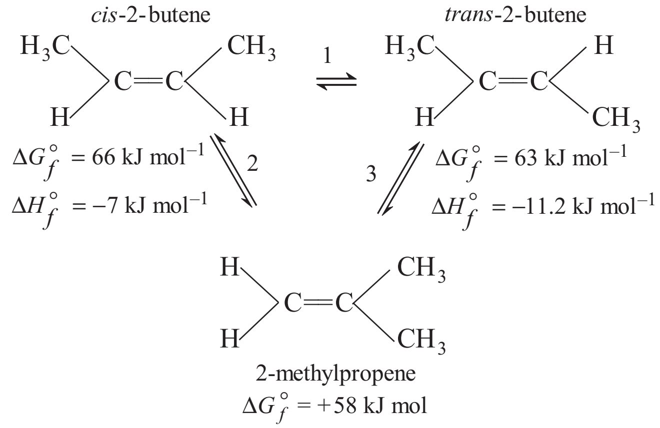
at 1000 K, given $\Delta G_f^\circ(\text{CO}) = -200\ \text{kJ mol}^{-1}$, $\Delta G_f^\circ(\text{CO}_2) = -396\ \text{kJ mol}^{-1}$ and $\Delta G_f^\circ\ \text{TiO}_2(s) = -762\ \text{kJ mol}^{-1}$, determine which will be the predominant mode of reduction of $\text{TiO}_2(s)$ at 1000 K.

PROBLEM 235 The reaction for the production of synthetic fuel 'water gas' from coal is:

$$\text{C}(gr) + \text{H}_2\text{O}(g) \longrightarrow \text{CO}(g) + \text{H}_2(g)$$

Standard molar entropies of $\text{C}(gr)$, $\text{H}_2\text{O}(g)$, $\text{CO}(g)$ and $\text{H}_2(g)$ are 5.7, 70, 190 and 131 $\text{JK}^{-1}\text{mol}^{-1}$ respectively. Also, standard enthalpy of formations of H_2O and CO are –242 and –111 kJ mol^{-1} respectively. Determine the standard reaction free energy of reaction at 27°C. Also, predict about the spontaneity and effect of temperature on direction of reaction.

PROBLEM 236 The thermodynamic informations for isomerization of alkene (C_4H_8) at 300 K are as follows:



$\Delta G_f^\circ = 66\ \text{kJ mol}^{-1}$

$\Delta H_f^\circ = -7\ \text{kJ mol}^{-1}$

$\Delta G_f^\circ = 63\ \text{kJ mol}^{-1}$

$\Delta H_f^\circ = -11.2\ \text{kJ mol}^{-1}$

$\Delta G_f^\circ = +58\ \text{kJ mol}$

If the temperature of the above system is increased to 400 K and equilibrium was allowed to re-establish, mole percentage of *trans*-2-butene at new equilibrium was 18. Determine ΔH° and ΔS° for the isomerization reactions below:

$$\textit{cis}\text{-2-butene} \rightleftharpoons \text{2-methylpropene}$$

$$\textit{trans}\text{-2-butene} \rightleftharpoons \text{2-methylpropene}$$

PROBLEM 237 At a temperature above 65 K, decarboxylation of acetic acid, (*i.e.,* loss of CO_2) becomes spontaneous. If ΔH_f° of CH_3COOH, $CO_2(g)$ and CH_4 are −484.5, − 394 and − 74.8 kJ/mol respectively, determine standard state entropy change (ΔS°) for the decarboxylation reaction. What is the driving force for getting this reaction to proceed?

PROBLEM 238 For the reaction:

$$H_2(g) + CO_2(g) \rightleftharpoons H_2O(g) + CO(g)$$

ΔG at 2000 K is 2540 J, where partial pressures of the species are $P_{H_2} = 0.25$, $P_{CO_2} = 0.78$, $P_{H_2O(g)} = 0.66$ and $P_{CO} = 1.2$ atm respectively. Determine equilibrium composition of the gaseous mixture.

PROBLEM 239 Consider the thermal decomposition of solid $CaCO_3$ as:

$$CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g).$$

The equilibrium vapour pressure of CO_2 at 700°C and 950°C are 22.6 and 1830 mm of Hg. Calculate ΔH° and ΔS° for the reaction.

PROBLEM 240 A certain reaction is spontaneous at 72°C. If the enthalpy change for the reaction is 19 kJ, what is the minimum value of ΔS for the reaction?

PROBLEM 241 The internal engine of a 1200 kg car is designed to run on octane whose enthalpy of combustion is 5510 kJ/mol. If the car is moving up a slope, calculate the maximum height to which the car can be driven on 2.0 gallon of the fuel. Assume the cylinder temperature is 2200°C and the exit temperature is 760°C and ignore all form of friction. The mass of 1.0 gallon of fuel is 3.1 kg.

PROBLEM 242 One gram sample of oxygen undergoes free expansion from 0.75 L to 3.0 L at 298 K. Calculate ΔS, q, W, ΔH and ΔE.

PROBLEM 243 A 550 ml sample of an ideal gas at 300 K exerts 3 atm. The thermodynamic state of the system changes in a process. In the final state, $P = 3.5$ atm and $V = 730$ mL. Calculate ΔS and ΔE and ΔH, $C_{vm} = (5/2)R$.

PROBLEM 244 A sample of 0.0133 mole of an ideal gas, initially at 5.00 atm, expands isothermally and reversibly from 3.00 L to 10 L. Calculate ΔS, ΔG and ΔH.

PROBLEM 245 One mole of an ideal gas originally at a volume of 8.00 Lit. at 1000 K, is allowed to expand adiabatically until final volume is 16.00 Lit. For the gas $C_v = 1.5\,R$. Calculate values of ΔS for the process when:

(a) The expansion takes place reversibly.
(b) The expansion takes place against a constant pressure of 3.00 atm.
(c) The change in volume involves a free expansion.

PROBLEM 246 One mole of an ideal gas at 0°C and 1.0 atm pressure is mixed adiabatically with one mole of a different gas at 100°C and 1.0 atm to yield a mixture. If C_P for each gas is (5/2) R, determine ΔS (mixing).

PROBLEM 247 For chloroform gas C_{PM} is expressed as:

$$C_{PM} = 24.9 + 14.8 \times 10^{-2}\ \mathrm{T} - 9 \times 10^{-5} \mathrm{T}^2\ \mathrm{JK^{-1}mol^{-1}}.$$

Assuming this gas to be ideal, determine entropy change involved in heating 2.0 mole of gas from volume 100 L at 500 K to a volume of 70 Lit. at 700 K.

PROBLEM 248 For $N_2(g)$, entropy function as a function of temperature is expressed as:

$$S = 25.1 + 29.3 \ln \mathrm{T}$$

Determine Gibb's free energy change ΔG of one mole of nitrogen if it is heated from 298 K to 348 K at 2.0 atm pressure.

PROBLEM 249 One mole of an ideal gas initially at 400 K and 10 atm, is adiabatically expanded against a constant pressure of 5.0 atm until equilibrium is attained. If $C_V = 18.8 + 0.021\,\mathrm{T}\ \mathrm{JK^{-1}mol^{-1}}$, determine ΔE, ΔH and ΔS.

PROBLEM 250 Molar volume of $C_6H_6\,(l)$ is 89 c.c. at 27°C and 1.0 atm pressure. Assuming the volume to be constant, determine ΔG for compression of 5.00 moles of liquid benzene from 1.0 atm to 100 atm.

PROBLEM 251 One mole of an ideal gas at 25°C is subjected to a reversible isoentropic expansion until final temperature reached to 75°C. If the initial pressure was 1.0 atm, determine final pressure $C_V = (3/2)\,R$.

PROBLEM 252 A flask containing 1.00 mol of N_2 at 4.00 atm and 298 K was connected to a flask containing 1.00 mol of N_2 gas at 2.00 bar and 298 K. The gases were allowed to mix isothermally. Determine the entropy change for the system.

PROBLEM 253 One mole of solid iron was vaporized in an oven at 3500 K. If iron boils at 3133 K and enthalpy of vaporization is 349 $\mathrm{JK^{-1}mol^{-1}}$, determine ΔS_{system}, $\Delta S_{\text{surroundings}}$ and $\Delta S_{\text{universe}}$.

Solutions

THERMODYNAMICS

189. $-W = nRT \ln \frac{V_2 - nb}{V_1 - nb} = 0.5 \times 8.314 \times 300 \ln \frac{0.5 - 0.5 \times 0.02}{2 - 0.5 \times 0.02} = -1747.8 \text{ J} \quad \Rightarrow \quad W = 1747.8 \text{ J}$

190. $\Delta H = \Delta E + P\Delta V + V\Delta P \;:\; \Delta E = nC_V \Delta T = \frac{3}{2} \times 8.314 \times 100 = \mathbf{1247.1\ J}$

$$P_1 = 4.92 \text{ atm and } P_2 = 4.1 \text{ atm}$$

$\Rightarrow \; P_1 \Delta V = 4.92 \times 3 = 14.76$ L atm and $V_2 \Delta P = 8(4.1 - 4.92) = -6.56$ L atm

$\Rightarrow \; P_1 \Delta V + V_2 \Delta P = 8.2$ L atm $= 831.48$ J

$\Rightarrow \quad \Delta H = 1247.1 + 831.48 = \mathbf{2078.58\ J}$

191. $\Delta H = \Delta E + P_1 \Delta V + V_2 \Delta P = \frac{3}{2} \times 8.314 \times 500 + [4.92 \times 3 + 8\,(8.2 - 4.92)] \times 101.4$

$$= \mathbf{6.236 \times 10^3\ J}$$

192.

$$\Delta S = \frac{100}{28}\left[20.8 \ln \frac{T_2}{T_1} + 8.314 \ln \frac{V_2}{V_1}\right] \qquad \ldots\text{(i)}$$

For irreversible adiabatic expansion :

$$T_2 = \left[\frac{C_V + (P_2/P_1)}{C_P}\right] T_1 = 217.76 \text{ K}$$

Also,

$$\frac{V_2}{V_1} = \frac{P_1 T_2}{P_2 T_1} = \frac{30 \times 217.76}{10 \times 300} = 2.1776$$

Substituting in Eq. (i) gives $\Delta S = \mathbf{-0.692\ JK^{-1}}$

193. $\Delta S = nC_V \ln \frac{T_2}{T_1} + nR \ln \frac{V_2}{V_1} = 0.02\left(12.6 \ln \frac{373}{300} + 8.314 \ln 2\right) = \mathbf{0.17\ JK^{-1}}$

194. Applying conservation of heat to :

$$\underset{0°\text{C}}{H_2O(s)} \xrightarrow[q_1]{\Delta S_1} \underset{0°\text{C}}{H_2O(l)} \xrightarrow[q_2]{\Delta S_2} \underset{T\text{K}}{H_2O(l)} \xleftarrow[q_3]{\Delta S_3} \underset{363\text{ K}}{H_2O(l)}$$

$$\frac{10}{18}[6000 + 75.42\,(T - 273)] = \frac{20}{18} \times 75.42\,(363 - T)$$

$$\Rightarrow \qquad T = 306.48 \text{ K}$$

Also,

$$\Delta S_1 = \frac{10}{18} \times \frac{6000}{273} = 12.21 \text{ JK}^{-1}$$

$$\Delta S_2 = \frac{10}{18} \times 75.42 \ln \frac{306.48}{273} = 4.85 \text{ JK}^{-1}$$

$$\Delta S_3 = \frac{20}{18} \times 75.42 \ln \frac{306}{363} = -14.31 \text{ JK}^{-1}$$

$$\Rightarrow \qquad \Delta S_{\text{system}} = \Delta S_1 + \Delta S_2 + \Delta S_3 = \mathbf{2.75\ JK^{-1}}$$

195. Process involved are :

$$\underset{-10°C}{H_2O(l)} \xrightarrow[\Delta S_1]{} \underset{0°C}{H_2O(l)} \xrightarrow[\Delta S_2]{} \underset{0°C}{H_2O(s)} \xrightarrow[\Delta S_3]{} \underset{-10°C}{H_2O(s)}$$

$$\Delta S_1 = C_P \ \ln \frac{T_2}{T_1} = 75.42 \ln \frac{273}{263} = 2.814 \text{ JK}^{-1}$$

$$\Delta S_2 = \frac{-6000}{273} = -21.98 \text{ JK}^{-1} \text{ and } \Delta S_3 = 37.2 \ln \frac{263}{273} = -1.388 \text{ JK}^{-1}$$

$$\Delta S = \Delta S_1 + \Delta S_2 + \Delta S_3 = -20.554 \text{ JK}^{-1}$$

196.

$$\text{Zn} + H_2SO_4 \longrightarrow \text{ZnSO}_4 + H_2$$

$$-W_{\text{irr}} = \Delta n_g RT = \frac{100}{65} \times 8.314 \times 300 = 3.84 \text{ kJ}$$

In sealed vessel, $\Delta V = 0 \Rightarrow -W = 0$

197. $P \propto d \Rightarrow d_{(\text{final})} = 2.5$ m. Also $P = kd \Rightarrow k = 2$ atm m^{-1}

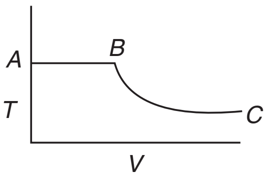
$$-dW_{\text{rev}} = P\ dV = k.d.\frac{\pi}{2} d^2\ dd = \frac{k\pi}{2} d^3\ dd$$

$$\Rightarrow \quad -W = \frac{k\pi}{2} \int_{0.5}^{2.5} d^3 dd = \frac{k\pi}{8}\ [(2.5)^4 - (0.5)^4] = \frac{2 \text{ atm m}^{-1} \times \pi}{8} \times 39 \text{ m}^4$$

$$= 30.63 \text{ atm m}^3 = \mathbf{3.1 \times 10^6\ J}$$

198. $A : P = 10$ bar, $T = 300$ K, B: P = ? $T = 300$K

$C : P = 2$ bar, $T = 250$ K, $C_V = \frac{3}{2} R$



Connecting reversible adiabatic points B and C :

$$P_B = P_C \left(\frac{T_C}{T_B}\right)^{\frac{\gamma}{1-\gamma}} = 2 \left(\frac{250}{300}\right)^{\frac{-5}{2}} = 3.15 \text{ bar}$$

$$\Rightarrow \quad -W_{AB} = 8.314 \times 300 \ln \frac{10}{3.15} = 2.88 \text{ kJ}$$

$$-W_{BC} = C_V\ (T_1 - T_2) = 1.5 \times 8.314 \times 50 = 623.55 \text{ J}$$

$$-W_{AC} = \mathbf{3.50355\ kJ}$$

199. Process is irreversible :

(a) $-W = P_{\text{ext}}\ \Delta V = 2 \text{ atm} \left(\frac{2 \times R}{2} - \frac{2R}{10}\right) \times 273 = 2 \times \frac{4}{5} \times 8.314 \times 273 = 3631.55 \text{ J}$

(b) $\Delta H = \Delta E = 0 \quad \therefore\ \Delta T = 0$

200. In reversible adiabatic process : $TV^{\gamma - 1} = $ constant

$$\Rightarrow \quad T_1 = T_2 \left(\frac{V_2}{V_1}\right)^{\gamma - 1} = T_2 (2)^{2/5} \Rightarrow T_2 = 225.84 \text{ K}$$

$$\Delta E_m = \frac{5}{2} \times 8.314 \times 72.16 = \mathbf{1499.84\ J}$$

$$\Delta H_m = \frac{7}{2} \times 8.314 \times 72.16 = \mathbf{2099.78\ J}$$

201.

$$-dW = \frac{RT}{V - b} dV \Rightarrow -W = RT \ln \frac{V_2 - b}{V_1 - b}$$

$$-W = 8.314 \times 300 \ln \frac{0.2 - 0.03}{10 - 0.03} = -10.155 \text{ kJ}$$

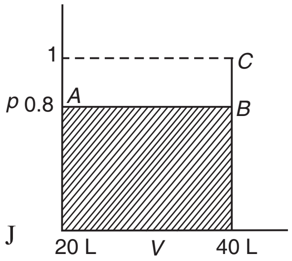
$$\Rightarrow \quad W = \mathbf{+\ 10.155\ kJ}$$

202.
$$-\,dW = \left(\frac{RT}{V} - \frac{a}{V^2}\right) dV$$

$$\Rightarrow \qquad -\,W = RT\,\ln\frac{V_2}{V_1} + a\left(\frac{1}{V_2} - \frac{1}{V_1}\right) = -\,1152.56 + \frac{0.384\times 0.15}{10^{-3}} = -\,1095\text{ J}$$

$$\Rightarrow \qquad \boldsymbol{W = +\,1095\text{ J}}$$

203. Work will be done only between $A - B$



$$\Rightarrow \qquad -W_{AB} = P\Delta V = 0.8\times 20\text{ L atm} = \mathbf{1622.4\ J}$$

Initial temperature $\qquad T_A = \dfrac{0.8\times 20}{0.5\times 0.082} = 390.25\text{ K}$

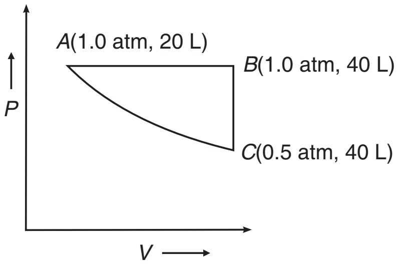
$$T_B = 2T_A = 780.5\text{ K}$$
$$T_C = 975.625\text{ K}$$

$$\Rightarrow \qquad \Delta E_{AB} = 0.5\times 1.5\times 8.314\times 390.25 = 2433.4\text{ J}$$
$$\Delta E_{BC} = 0.5\times 1.5\times 8.314\times 195.125 = 1216.7\text{ J}$$
$$\Rightarrow \qquad \Delta E_{AC} = \Delta E_{AB} + \Delta E_{BC} = \mathbf{3650.1\ J}$$
$$q = \Delta E - W_{AB} = 4461.3\text{ J} \;\text{ and } \Delta H = \Delta E + P\,\Delta V = q$$

204. At constant n and V, $P \propto T \;\Rightarrow\; T_2 = 3030\text{ K}$

$$\Rightarrow \qquad q = \Delta E = C_V\Delta T = (75.42 - 8.314)\times 2727 = \mathbf{183\ kJ}$$
$$\Delta H = C_P\Delta T = \mathbf{205.67\ kJ}$$

205. $-\,W_{AB} = P\Delta V = 20\text{ L atm} = 2028\text{ J}$



$$W_{BC} = 0$$
$$-\,W_{CA} = 2\times 8.314\,\ln\frac{0.5}{1} = -11.52$$
$$-\,W_{A\leftrightarrow A} = \mathbf{2016.48\ J}$$

Since process in cyclic, ΔU and $\Delta H = 0$ and $q = -\,W = \mathbf{2016.48\ J}$

206. In adiabatic irreversible expansion :

$$0 = C_V\,(T_2 - T_1) + P_{ext}\,(V_2 - V_1)$$

Solving for T_2 : $\qquad T_2 = \left[\dfrac{C_V + R\,(P_{ext}/P_1)}{C_V + R\,(P_{ext}/P_2)}\right] T_1 = \mathbf{263.74\ K}$

$$-\,W = nC_V\,(T_1 - T_2) = 3.22\times 20.785 = \mathbf{2293\ J}$$

207. Process is isothermal $\qquad n = \dfrac{10\times 1}{0.082\times 300} = 0.4$

$$\Delta U = \Delta H = 0$$
$$-\,W = 0.4\times 8.314\,\ln 10 = 7.66\text{ J}$$
$$C_V\,(300) = 21.52 + 8.2\times 10^{-3}\times 300 = 23.98\text{ JK}^{-1}$$
$$\Rightarrow \qquad C_P\,(300\text{ K}) = C_V + R = \mathbf{32.294\ JK^{-1}}$$

208. $dG = VdP - SdT$ at constant P, $dG = -SdT$

$$\Rightarrow \qquad \int dG = -36.36 \int dT - 20.79 \int \ln T dT$$

$$\Delta G = -36.36\,(T_2 - T_1) - 20.79\,[T \ln T - T]_{T_1}^{T_2}$$

$$= -909 - 20.79\,(1543.18 - 1399.73) = \mathbf{-3891.33\ J}$$

209.

$$C_V = 20.266 + 1.76 \times 10^{-2}\, T$$

$$dE = C_V\, dT = (20.266 + 1.76 \times 10^{-2}\, T)dT$$

$$\Rightarrow \quad \Delta E = 20.266(T_2 - T_1) + \frac{1.76}{2} \times 10^{-2}\,(T_2^2 - T_1^2) = P_2(V_1 - V_2) = R\left(\frac{P_2}{P_1} T_1 - T_2\right)$$

$$\Rightarrow \qquad \frac{1.76}{2} \times 10^{-2}\, T_2^2 + 28.58\, T_2 - 7869.48 = 0$$

Solving, $T_2 = 255.3$ K

Also, $$dS = C_p \frac{dT}{T} - R\frac{dP}{P} = (28.58 + 1.76 \times 10^{-2} T)\frac{dT}{T} - R\frac{dP}{P}$$

$$\Rightarrow \qquad \Delta S = 28.58 \ln \frac{T_2}{T_1} + 1.76 \times 10^{-2}\,(T_2 - T_1) + R \ln \frac{P_1}{P_2} = \mathbf{2.22\ JK^{-1}}$$

$$\Delta U = \int C_V\, dT = \int (20.266 + 1.76 \times 10^{-2} T)\, dT$$

$$= 20.266\,(255.3 - 300) + \frac{1.76 \times 10^{-2}}{2}[(255.3)^2 - (300)^2] = \mathbf{-1124.32\ J}$$

$$\Delta H = \int C_p\ dT = \int (28.58 + 1.76 \times 10^{-2}\ \mathrm{T})\, dT$$

$$= 28.58(255.3 - 300) + \frac{1.76}{2} \times 10^{-2}[(255.3)^2 - (300)^2] = \mathbf{-1496 J}$$

210. $-W = 2 \times 30$ L atm $= 6084$ J $\Rightarrow \Delta E = (20000 - 6084)$ J $=$ **13.916 kJ**

211. $-W = \int PdV = \int 10 \cdot \frac{dV}{V} = 10 \ln \frac{V_2}{V_1} = 10 \times \ln 10$ L atm $= 23$ L atm $= 2332.2$ J

$$q = 420 + 2332.2 = \mathbf{2752.2\ J}$$

212.

$$\Delta E = n\int C_V\, dT = 3\int (30 + 14 \times 10^{-3}\, T)dT$$

$$= 3 \times 30\,(T_2 - T_1) + 42 \times 10^{-3}\,(T_2^2 - T_1^2)$$

$$= 9000 + 2940 = \mathbf{11.94\ kJ}$$

$$-W = (T_2 - T_1)\, nR = 3 \times 8.314 \times 100 = \mathbf{2494.2\ J}$$

$$q = 11.94 \times 10^3 + 2494.2 = \mathbf{14.4342\ kJ}$$

213. Applying adiabatic conditions between C and A.

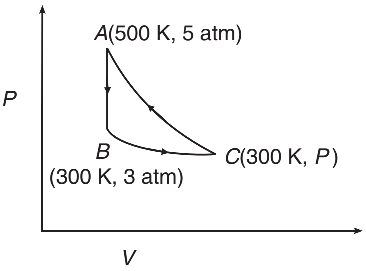
$$P = \left(\frac{500}{300}\right)^{-2.5} \times 5 = 1.39 \text{ atm.}$$

$$W_{AB} = 0 \quad \because \ \Delta V = 0$$

$$W_{BC} = -8.314 \times 300 \ \ln \frac{3}{1.39} = -\ 1918.8 \text{ J}$$

$$W_{CA} = \frac{3}{2} \times 8.314 \times 200 = 2494.2$$

$$W = \mathbf{575.4\ J}$$



214. $$P_C = \left(\frac{500}{300}\right)^{-2.5} \times 5 = 1.39 \text{ atm}$$

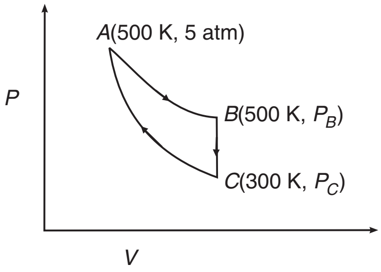
$$P_B = \frac{5}{3} \times 1.39 = 2.32 \text{ atm}$$

$$\Rightarrow \quad W_{AB} = -8.314 \times 500 \ \ln \frac{5}{2.32} = -3192 \text{ J}$$

$$W_{BC} = 0$$

$$W_{CA} = 1.5 \times 8.314 \times 200 = 2494.2 \text{ J}$$

$$W = \mathbf{-\ 697.8\ J}$$



215. Applying adiabatic condition between A and D

$$P = \left(\frac{300}{200}\right)^{-2.5} \times 5 = 1.82 \text{ atm}$$

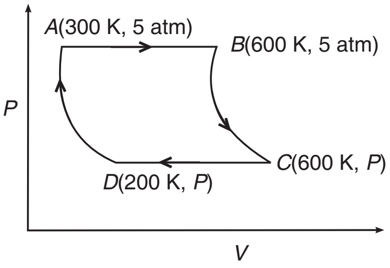
$$W_1 = -PV_1 = -nRT_1 = -300\,R$$

$$W_2 = -\,nR \times 600 \ \ln \frac{5}{1.82} = -606.4\,R$$

$$W_3 = 1.82\,(V_C - V_D) = 400\,R$$

$$W_4 = C_V \times 100 = 150\,R$$

$$\Rightarrow \quad W = -356.4\,R = -\ \mathbf{2.963\ kJ}$$



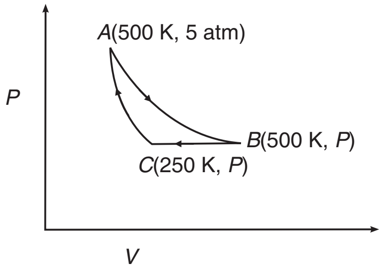
216. $$P = (2)^{-2.5} \times 5 = 0.88 \text{ atm}$$

$$W_{AB} = -\,R \times 500 \ \ln \frac{5}{0.88} = -868.63\,R$$

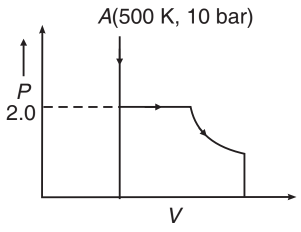
$$W_{BC} = 0.88\,(500R - 250R) \times \frac{1}{0.88} = 250R$$

$$W_{CA} = 1.5R \times 250 = 375\,R$$

$$\Rightarrow \quad W = -243.63\,R = -\ \mathbf{2.026\ kJ}$$



217.



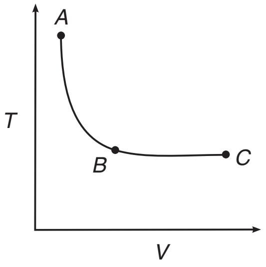
$$-\,W_{\text{irr}} = P_2\,(V_2 - V_1) = P_2 \left(\frac{RT}{P_2} - \frac{RT}{P_1}\right) = 0.8RT$$

$$-\,W_{\text{rev}} = RT \ \ln \frac{2}{P}$$

Adding : $RT \ln \frac{2}{P} + 0.8RT = 4200$

$$\Rightarrow \qquad \boldsymbol{P = 1.62 \text{ atm}}$$

218. (a) $$P_B = (2)^{-2.5} \times 10 = 1.77 \text{ atm}$$

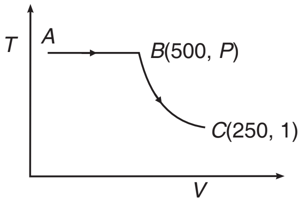


$$W_{AB} = -1.5\,R \times 250 = -375\,R$$

$$W_{BC} = -250\,R \ln \frac{1.77}{1} = -142.75\,R$$

$$W = -517.75\,R = \mathbf{-\,4.304 \text{ kJ}}$$

(b) $$P = \left(\frac{250}{500}\right)^{-2.5} = 5.65 \text{ atm}$$



$$\Rightarrow \qquad W = -500R \ln \frac{10}{5.6} - 1.5R \times 250$$

$$= -664.9\,R$$

$$= \mathbf{-\,5.528 \text{ kJ}}$$

219. $$V_1 = 0.082 \times 300 = 24.6 \text{ L},$$

$$P_2 = \frac{0.082 \times 500}{36} = 1.138 \text{ atm}$$

$$\Delta H = \Delta E + P_1 \Delta V + V_2 \Delta P = 1.5\,R \times 200 + [11.4 + 36 \times 0.138] \times 101.4$$

$$= \mathbf{4.154 \text{ kJ}}$$

220. $$dG = C_P\,dT - TdS - SdT = C_P\,dT - T\,(3 \times 10^{-3}\ dT) - (1.5 + 3 \times 10^{-3}\,T)\,dT$$

$$= (C_P - 1.5)\,dT - 6 \times 10^{-3}\ T\,dT$$

$$\Rightarrow \qquad \Delta G = (C_P - 1.5)\,(T_2 - T_1) - \frac{6}{2} \times 10^{-3}\ (T_2^2 - T_1^2) = \mathbf{3377 \text{ J}}$$

221. $$\Delta S = C_P \ln \frac{T_2}{T_1} + R \ln \frac{P_1}{P_2} = 3.5\,R \ln \frac{5}{3} + R \ln \frac{1}{2} = \mathbf{9.1 \text{ J}}$$

222. $$\Delta V = 0 \quad \Rightarrow \quad dS = C_V \frac{dT}{T} = (12 + 28 \times 10^{-3}\ T)\frac{dT}{T} = 12\frac{dT}{T} + 28 \times 10^{-3}\ dT$$

$$\Rightarrow \qquad \Delta S = 12 \ln \frac{T_2}{T_1} + 28 \times 10^{-3}\ (T_2 - T_1), \ T_2 = \frac{40 \times 1}{0.082} = 487.8 \text{ K}$$

$$\Delta S = 12 \ln \frac{487.8}{300} + 28 \times 10^{-3} \times 187.8 = \mathbf{11.09 \text{ JK}^{-1}}$$

223. $$A \longrightarrow B \quad \Delta G^\circ = -3 \times 1000 - T \times 20 = -9000 \text{ J}$$

$$A \longrightarrow C \quad \Delta G^\circ = -3600 - 10T = -6600 \text{ J}$$

ΔG° indicates that *B* is more stable than *C*.

224. $$dG = V\,dP - S\,dT = V\,dP - (10 + 12 \times 10^{-3}\,T)\,dT$$

$$\Rightarrow \qquad \Delta G = V\,\Delta P - 10\,\Delta T - 6\times10^{-3}\ (T_2^2 - T_1^2)$$

$$V = \frac{0.082\times300}{1} = 24.6\ \text{L}$$

$$P_2 = \frac{400}{300} = \frac{4}{3}\ \text{atm.}$$

$$\Rightarrow \qquad \Delta G = 24.6\times\frac{1}{3}\times101.4 - 10\times100 - 6\times10^{-3}[(400)^2 - (300^2)] = \mathbf{-\ 588.52\ J}$$

225.

$$dS = nC_V\ \frac{dT}{T} = 2(19.686 + 31\times10^{-3}T)\,\frac{dT}{T}$$

$$\Delta S = 2\times19.686\ \ln\frac{T_2}{T_1} + 31\times10^{-3}\ (T_2 - T_1) = \mathbf{14.43\ JK^{-1}}$$

226.

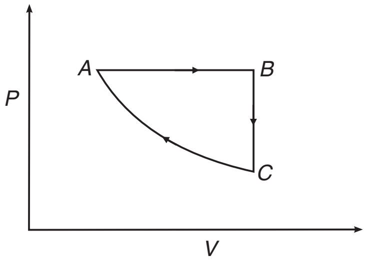
$$\Delta S_{\text{system}} = nR\ \ln\frac{V_2}{V_1} = 2\times8.314\ \ln 2.5 = \mathbf{15.236\ J}$$

$$\Delta S_{\text{surr}} = -\frac{4.17\times10^3}{300} = \mathbf{-\ 13.9\ J}$$

$$\Delta S_{\text{univ}} = \mathbf{1.336\ J}$$

227.

$$\Delta S = R\ \ln 3 + 2R\ \ln\frac{3}{2} = 15.87\ \text{JK}^{-1}$$



228.

$$T_A = 122\ \text{K} \quad \text{and} \quad T_B = 244\ \text{K}$$

$$\Rightarrow \qquad W_{AB} = -1(T_2 - T_1)\,\frac{nR}{1} = -244\,R$$

$$W_{BC} = 0, \qquad W_{CA} = 2R\times122\ \ln 2 = 169.12\,R$$

$$W = -\ 74.88\,R$$

$$= \mathbf{-\ 622.5\ J}$$

229. $\Delta E = \int C_V\ dT = \int (a + bT)\ dT = a(T_2 - T_1) + \frac{b}{2}(T_2^2 - T_1^2) = \mathbf{7.4\ kJ\ /\ mol}$

$$\Delta H = \int C_P\ dT = \int (33.314 + bT)\ dT = 33.314(T_2 - T_1) + \frac{b}{2}(T_2^2 - T_1^2) = \mathbf{9.063\ kJ/mol}$$

$$V_1 = \frac{3\times0.082\times300}{2} = 36.9\ \text{L}$$

$$V_2 = \frac{3\times0.082\times500}{3} = 41\ \text{L}$$

We can construct a path as:

$$A(2.0\ \text{bar},\ 36.9\ \text{L},\ 300\ \text{K}) \xrightarrow{W_1} B(2.0\ \text{bar},\ 41\ \text{L},\ T)$$

$$\xrightarrow{W_2} C(3\ \text{bar},\ 41\ \text{L},\ 500\ \text{K})$$

$$T = \frac{2\times41\times300}{2\times36.9} = 333.33\ \text{K}$$

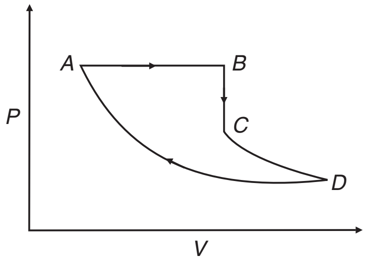
Then, $W_1 = P\,\Delta V = 2 \times 4.1 \times 101.4 = \mathbf{831.48\ J}$ and $W_2 = 0$

$\Rightarrow$ $q = 7.4 \times 10^3 + 831.48 = \mathbf{8.23 \times 10^3\ J}$

$$dS = n\left[C_V \frac{dT}{T} + R\frac{dV}{V}\right] = n\left[(a+bT)\frac{dT}{T} + R\frac{dV}{V}\right]$$

$$\Delta S = n\left[a \ln\frac{T_2}{T_1} + b(T_2 - T_1) + R \ln\frac{V_2}{V_1}\right] = \mathbf{59\ J}$$

230. $W_{AB} = -5(500-400)\frac{R}{5} = -100\,R$



$W_{BC} = 0$

Connecting adiabatic points A and D.

Applying $P^{1-\gamma}T^{\gamma} = K$ gives $T_D = 210\text{ K} = T_C$

$\Rightarrow$ $P_C = 2.1\text{ atm}$

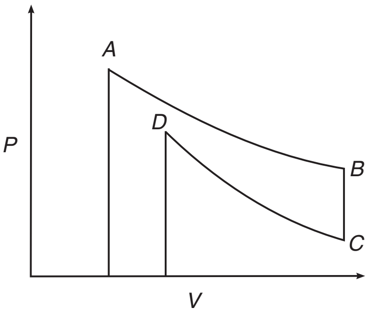
$\Rightarrow$ $W_{CD} = -210\,R \ln\frac{2.1}{1} = -155.8\,R$

$W_{DA} = 1.5\,R \times 190 = 285\,R$

$W = W_{AB} + W_{CD} + W_{DA} = 29.2\,R$

$= \mathbf{242.76\ J}$

231. $T_D = 388\text{ K}$, $P_B = 2\text{ bar}$,



$$W_{AB} = -500\,R \ln\frac{5}{2} = -458.14\,R$$

$$W_{CD} = 1.5R \times (388-250) = 270\,R$$

$$W = -251.14\,R$$

$$= \mathbf{-2.088\ kJ}$$

232. According to second law of thermodynamics:

$$\Delta S_v = \frac{\Delta H_v}{T_b}$$

$\Rightarrow$ $\Delta H_v = \Delta S_v \times T_b = 85 \times 353 = 30.005\text{ kJ mol}^{-1}$.

(b) Since vaporization process is endothermic, heat lost by surrounding in vaporization of 100 g benzene is:

$$Q = \frac{30005}{78} \times 100 = 38468\text{ J}$$

$\Rightarrow$ $\Delta S_{\text{surrounding}} = -\frac{Q}{T} = -\frac{38468}{353} = -108.97\text{ JK}^{-1}$.

233. (a) $\Delta H_v = \Delta S_v \cdot T_b = 85 \times 329 = 2796\,5\text{ J mol}^{-1}$

(b) Heat gained by surrounding $= \frac{100 \times 27965}{58} = 48215.5\text{ J}$

Increasing in entropy of surrounding $= \frac{48215.5}{329} = 146.55\text{ J}$

234. For a reaction:

$$\Delta G_R^\circ = \Sigma\, \Delta G_f^\circ \text{ (Products)} - \Sigma\, \Delta G_f^\circ \text{ (Reactants)}$$

$$\Rightarrow \qquad \Delta G^\circ \text{(i)} = -2 \times 200 + 762 = +362 \text{ kJ}$$

$$\Delta G^\circ \text{(ii)} = -396 + 762 = +366 \text{ kJ}$$

Since, both ΔG° are positive, a reaction with less positive ΔG° will be more likely to occur. Therefore, reduction of TiO_2 will be more favourable through reaction (i).

235.

$$\Delta H_r^\circ = -111 + 242 = 131 \text{ kJ}$$

$$\Delta S_r^\circ = 190 + 131 - (5.7 + 70) = 245.3 \text{ JK}^{-1}$$

$$\Rightarrow \qquad \Delta G^\circ = \Delta H^\circ - T\Delta S^\circ = 131 \times 10^3 - 300 \times 245.3 = 57.41 \text{ kJ}$$

Positive value of ΔG° indicates that reaction is non spontaneous at 300 K. Increasing temperature will decrease ΔG° and after certain value of T, ΔG° will become negative, *i.e.,* reaction will turn from non-spontaneous to spontaneous. That specific temperature at which reaction turns from non-spontaneous to spontaneous can be determined by equating $\Delta G^\circ = 0$ as:

$$0 = 131 \times 10^3 - T \times 245.3 \quad \Rightarrow \quad T = \frac{131000}{245.3} = 534 \text{ K}$$

i.e., at temperature above 534 K, reaction will become spontaneous.

236. At 300 K,

$$\Delta G^\circ \,(\textit{cis}\text{-2-butene} \longrightarrow \textit{trans}\text{-2-butene}) = -3 \text{ kJ mol}^{-1}$$

$$\Delta H^\circ \,(\textit{cis}\text{-2-butene} \longrightarrow \textit{trans}\text{-2-butene}) = -4.2 \text{ kJ mol}^{-1}$$

$$\Rightarrow \qquad \Delta S^\circ \,(\textit{cis}\text{-2-butene} \longrightarrow \textit{trans}\text{-2-butene}) = \frac{\Delta H^\circ - \Delta G^\circ}{T}$$

$$= \frac{-4.2 + 3}{300} \times 1000 = -4 \text{ JK}^{-1}$$

$$\Rightarrow \qquad \Delta G^\circ \text{ (1) at 400 K} = -4.2 \times 10^3 + 400 \times 4 = -2600 \text{ J}$$

$$\text{Also,} \qquad \ln K \text{ (1)} = -\frac{\Delta G^\circ \text{ (1)}}{RT} = \frac{3000}{8.314 \times 300}$$

$$\Rightarrow \qquad K \text{ (1)} = 3.33 \text{ at 300 K}$$

$$\text{and} \qquad K \text{ (1)} = 2.20 \text{ at 400 K}$$

$$\Delta G^\circ \text{ (2)} = -8 \text{ kJ mol}^{-1} \text{ at 300 K}$$

$$\Rightarrow \qquad \ln K \text{ (2)} = -\frac{\Delta G^\circ \text{ (2)}}{RT} = \frac{8000}{8.314 \times 300}$$

$$\Rightarrow \qquad K \text{ (2)} = 24.7 \text{ at 300 K.}$$

Now, let at 400 K, mixture contain x% *trans-2*-butene and y% 2-methyl propene.

$$\Rightarrow \text{ At } \qquad 400 \text{ K, } K(1) = 2.2 = \frac{x}{100 - x - y} = \frac{18}{82 - y}$$

$$\Rightarrow \qquad y = 73.8\%$$

$\Rightarrow$ $$K\text{ (2) at 400 K} = \frac{y}{100 - x - y} = \frac{73.8}{8.2} = 9$$

$\Rightarrow$ $$\Delta G^\circ\text{ (2) at 400 K} = -8.314 \times 400 \ln q = -7.3\text{ kJ}$$

$\Rightarrow$ $$\Delta G^\circ\text{ (2) at 300 K} = -8000 = \Delta H^\circ\text{ (2)} - 300\,\Delta S^\circ\text{ (2)}$$

$$\Delta G^\circ\text{ (2) at 400 K} = -7300 = \Delta H^\circ\text{ (2)} - 400\,\Delta S^\circ\text{ (2)}$$

$\Rightarrow$ $$\Delta S^\circ\text{ (2)} = -\mathbf{7\ JK^{-1}}$$

$$\Delta H^\circ\text{ (2)} = -8000 + 300\,(-7) = -\mathbf{10.1 \times 10^3\ J}$$

Also, $$K\text{ (3)} = \frac{K\text{ (2)}}{K\text{ (1)}}$$

$\Rightarrow$ At 300 K: $$K\text{ (3)} = \frac{24.7}{3.33} = 7.41$$

$\Rightarrow$ $$\Delta G^\circ\text{ (3)} = -8.314 \times 300 \ln 7.41 = -4995\text{ J}$$

At 400 K: $$K\text{ (3)} = \frac{9}{2.2} = 4$$

$\Rightarrow$ $$\Delta G^\circ\text{ (3)} = -8.314 \times 400 \ln 4 = -4610\text{ J}$$

$\Rightarrow$ $$-4995 = \Delta H^\circ\text{ (3)} - 300\,\Delta S^\circ\text{ (3)}$$

$$-4610 = \Delta H^\circ\text{ (3)} - 400\,\Delta S^\circ\text{ (3)}$$

$\Rightarrow$ $$\Delta S^\circ\text{ (3)} = -\mathbf{3.85\ JK^{-1}} \quad\text{and}\quad \Delta H^\circ\text{ (3)} = -\mathbf{6.15\ kJ}.$$

237. For the decarboxylation reaction:

$$CH_3COOH \rightleftharpoons CH_4 + CO_2 \qquad \Delta H^\circ = -394 - 74.8 + 484.5 = 15.7\text{ kJ}$$

Also, above 65 K, reaction is spontaneous

$\Rightarrow$ $$\Delta G^\circ = 0\text{ at 65 K}$$

$\Rightarrow$ $$0 = 15.7 \times 10^3 - 65\,\Delta S^\circ$$

$\Rightarrow$ $$\Delta S^\circ = 241.54\text{ JK}^{-1}.$$

For a spontaneous reaction $\Delta G^\circ < 0$. Since, $\Delta H^\circ > 0$, spontaneity of reaction is due to $\Delta S^\circ > 0$.

238. Since, $$\Delta G = \Delta G^\circ + RT \ln Q = RT \ln Q - RT \ln K$$

$\Rightarrow$ $$\Delta G = RT \ln\left(\frac{Q}{K}\right)$$

In the present condition:

$$Q = \frac{0.66 \times 1.2}{0.25 \times 0.78} = 4.06$$

$\Rightarrow$ $$\ln\left(\frac{Q}{K}\right) = \frac{\Delta G}{RT} = \frac{2540}{8.314 \times 2000} = 15.275 \times 10^{-2}$$

$\Rightarrow$ $$\frac{Q}{K} = 1.165 \quad\Rightarrow\quad K = 3.48$$

$\because$ $Q > K$, reaction will proceed in backward direction as:

$$\underset{0.25+x}{H_2} + \underset{0.78+x}{CO_2} \rightleftharpoons \underset{0.66-x}{H_2O(g)} + \underset{1.2-x}{CO}$$

$$K = 3.48 = \frac{(1.2-x)\,(0.66-x)}{(0.25+x)\,(0.78+x)}$$

Solving : $x = 0.02.$

$\Rightarrow \quad P_{H_2} = 0.27$ atm, $P_{CO_2} = 0.80$ atm, $P_{H_2O} = 0.64$ atm. $P_{CO} = 1.18$ atm.

239. For the above reaction:

$$K_p = p_{CO_2}$$

Also, $$\ln\left(\frac{K_p(2)}{K_p(1)}\right) = \frac{\Delta H^\circ}{R}\left(\frac{T_2-T_1}{T_1T_2}\right)$$

$$\Rightarrow \quad \ln\frac{1830}{22.6} = \frac{\Delta H^\circ}{R}\left(\frac{250}{973\times1223}\right) = 4.394 \quad \Rightarrow \quad \Delta H^\circ = 173.88 \text{ kJ mol}^{-1}.$$

Also, $$\Delta G^\circ = -RT\ln K_p^\circ = -8.314\times973\ln\frac{22.6}{760} = 28.43\times10^3 \text{ J}$$

$$\Rightarrow \quad \Delta S^\circ = \frac{\Delta H^\circ - \Delta G^\circ}{T} = \frac{173.88-28.43}{973}\times1000 = 149.5 \text{ JK}^{-1}\text{mol}^{-1}.$$

240. The minimum value of ΔS will occur at $\Delta G = 0$ for spontaneous reaction.

$$\Rightarrow \quad 0 = 19000 - 345\,\Delta S^\circ \quad \Rightarrow \quad \Delta S^\circ = \frac{19000}{345} = 55.07 \text{ JK}^{-1}.$$

241. $$\text{Efficiency of engine } = \frac{T_h - T_c}{T_h} = \frac{2200-760}{2200} = 0.6545$$

$$\text{Total heat produced} = \frac{2\times3.1\times1000}{114}\times5510 = 299666.67 \text{ J}$$

$$\text{Heat converted into work} = 299666.67\times0.6545 = 196132 \text{ J}$$

$$\Rightarrow \quad Q = mgh$$

$$h = \frac{196132}{1200\times9.8} = \mathbf{16.67\ m}$$

242. Since, expansion occurred at constant temperature,

$$\Delta S = nR\ln\frac{V_2}{V_1} = \frac{1}{32}\times8.314\ln\frac{3.0}{0.75} = 0.36 \text{ JK}^{-1}$$

Since, this is case of free expansion, $P_{ext} = 0.$ $\Rightarrow$ $-W = P_{ext}\,\Delta V = 0,\quad q = 0$

Also, since, $\Delta T = 0,\quad \Delta H = \Delta E = 0.$

243. $\because$ $$\Delta S = nC_v\ln\frac{T_2}{T_1} + nR\ln\frac{V_2}{V_1}$$

$$n = \frac{3\times550\times10^{-3}}{0.082\times300} = 0.067 \quad \text{and} \quad T_{\text{final}} = \frac{3.5\times0.73}{3\times0.55}\times300 = 464.5 \text{ K}$$

$$\Rightarrow \qquad \Delta S = 0.067 \times \frac{5}{2} R \ln \frac{464.5}{300} + 0.067 R \ln \frac{0.73}{0.55} = 0.767 \text{ JK}^{-1}$$

$$\Delta E = nC_v \Delta T = 0.067 \times \frac{5}{2} R \times (464.5 - 300) = 229 \text{ J}$$

$$\Delta H = \Delta E + P\Delta V + V\Delta P = 229 + [3(0.73 - 0.55) + 0.73 \times 0.5] \times 101.4 = 320.767 \text{ J.}$$

244. Under isothermal condition,

$$\Delta S = nR \ln \frac{V_2}{V_1} = 0.133 \times 8.314 \ln \frac{10}{3} = 1.33 \text{ JK}^{-1}$$

$$\Delta G = nRT \ln \frac{P_2}{P_1} = 5 \times 3 \times 101.4 \ln \frac{3}{10} = -1831.25 \text{ J}$$

245. (a) In case of adiabatic reversible expansion, $dq_{\text{rev}} = 0 \quad \Rightarrow \quad \Delta S = 0.$

(b) In case of irreversible adiabatic expansion:

$$0 = P_{ext} (V_2 - V_1) + nC_v (T_2 - T_1)$$

$$T_2 = \frac{P_{ext} (V_1 - V_2)}{nC_v} + T_1 = \frac{-3 \times 8}{0.0821 \times 1.5} + 1000 = 805 \text{ K}$$

$$\Delta S = C_v \ln \frac{T_2}{T_1} + R \ln \frac{V_2}{V_1} = 1.5 \times 8.314 \ln \frac{805}{1000} + 8.314 \ln 2 = 3.06 \text{ JK}^{-1}.$$

(c) In case of free adiabatic expansion $P_{ext} = 0$

$$\Rightarrow \qquad 0 = P_{\text{ext}} \Delta V + nC_v (T_2 - T_1)$$

$$\Rightarrow \qquad T_1 = T_2$$

$$\Rightarrow \qquad \Delta S = R \ln \frac{V_2}{V_1} = 5.76 \text{ JK}^{-1}$$

246. Since, the two gases have same heat capacities, equal amounts, final temperature will be $(T_1 + T_2)/2 = 323$ K.
Also, final $P = 1$ atm, *i.e.,* partial pressure of each gas in the final mixture will be 0.5 atm.

Now,
$$\Delta S_1 \text{ (for cold gas)} = C_P \ln \frac{323}{273} + R \ln \frac{1}{0.5}$$

$$\Delta S_2 \text{ (for hot gas)} = C_P \ln \frac{323}{373} + R \ln \frac{1}{0.5}$$

$$\Rightarrow \qquad \Delta S = \Delta S_1 + \Delta S_2 = 2R \ln 2 + C_P \ln \left[\frac{323 \times 323}{273 \times 373}\right] = 12.03 \text{ JK}^{-1}.$$

247.
$$dS = nC_v \frac{dT}{T} + nR \frac{dV}{V} = n(C_p - R) \frac{dT}{T} + nR \frac{dV}{V}$$

$$= n\left[\left(16.6 \frac{dT}{T} + 14.8 \times 10^{-2} dT - 9 \times 10^{-5} T dT\right) + R \frac{dV}{V}\right]$$

$$\Rightarrow \qquad \Delta S = n\left[16.6 \ln \frac{T_2}{T_1} + 14.8\times 10^{-2}(T_2 - T_1) - \frac{9\times 10^{-5}}{2}(T_2^2 - T_1^2) + R \ln \frac{V_2}{V_1}\right]$$

$$= n\,[5.585 + 29.6 - 10.8 + (-2.965)] = 42.84 \text{ JK}^{-1}.$$

248. $dG = -SdT \quad \text{at} \quad \Delta P = 0$

$= -(25.1 + 29.3 \ln T)\,dT$, on integration

$$\Delta G = -(25.1 - 29.3)\,\Delta T - 29.3\,(T_2 \ln T_2 - T_1 \ln T_1)$$

Substituting, $T_1 = 298,\ T_2 = 348.$

$$\Delta G = -9750 \text{ J}$$

249. Since, the process is irreversible adiabatic expansion:

$$0 = \Delta E + P_{ext}\,\Delta V = \Delta E + P_{ext}\,(V_2 - V_1) \qquad \ldots\text{(i)}$$

Also, $\quad dE = nC_v dT = (18.8 + 0.021\,T)\,dT$

$$\Delta E = 18.8\,(T_2 - T_1) + \frac{0.021}{2}(T_2^2 - T_1^2) \qquad \ldots\text{(ii)}$$

Substituting in Eq. (i), $\quad 18.8\,(T_2 - T_1) + 0.0105\,(T_2^2 - T_1^2) + R\left(T_2 - \frac{T_1}{2}\right) = 0$

Substituting, $T_1 = 400$ K, solving yields $T_2 = 352.5$ K.

Now, $\quad dS = C_v \frac{dT}{T} + R\frac{dV}{V} = (18.8 + 0.021\,T)\frac{dT}{T} + R\frac{dV}{V}$

Integrating: $\quad \Delta S = 18.8 \ln \frac{T_2}{T_1} + 0.021\,(T_2 - T_1) + R \ln \frac{V_2}{V_1}$

$$= 18.8 \ln \frac{352.5}{400} + 0.021\,(352.5 - 400) + R \ln \frac{352.5\times 10}{400\times 5}$$

$$= \mathbf{1.338\ JK^{-1}mol^{-1}}$$

From Eq. (ii), $\quad \Delta E = 18.8\,(352.5 - 400) + \frac{0.021}{2}[(352.5)^2 - (400)^2] = \mathbf{-\ 1268.3\ J}$

$$dH = (R + C_v)\,dT = (27.114 + 0.021\,T)\,dT$$

$$\Rightarrow \qquad \Delta H = 27.114\,(T_2 - T_1) + \frac{0.021}{2}(T_2^2 - T_1^2) = \mathbf{-\ 1663.22\ J}$$

250. $\quad \Delta G = nV\,\Delta P = 5\times 0.089\times 99 \text{ L-atm} = 4467.18 \text{ J}$

251. For isoentropic process:

$$0 = nC_P \ln \frac{T_2}{T_1} + nR \ln \frac{P_1}{P_2} \qquad \Rightarrow \qquad R \ln\left(\frac{P_2}{P_1}\right) = \frac{5}{2} R \ln \frac{T_2}{T_1}$$

Solving, $P_2 =$ **1.474 atm**.

252. Under isothermal condition:

$\Delta S = nR \ln P_1/P_2$ where P_1 = initial pressure, P_2 = final pressure

Let, flask *A* has N_2 at 4 bar and flask *B* at 2 bar. After mixing final pressure in the combined system = (8/3) bar.

$$\Rightarrow \qquad \Delta S_A = R \ln \frac{12}{8} \quad \text{and} \quad \Delta S_B = R \ln \frac{6}{8}$$

$$\Delta S_A + \Delta S_B = \Delta S = \mathbf{0.98\ JK^{-1}}.$$

253. At boiling point,

$$\Delta S_{\text{system}} = \frac{\Delta H_{\text{vap}}}{T_b} = \frac{349 \times 10^3}{3133} = 111.4\ \text{JK}^{-1}$$

$$\text{Heat change in surrounding} = -349\ \text{kJ}$$

$$\Delta S_{\text{surr}} = -\frac{349 \times 1000}{3500} = -99.71\ \text{JK}^{-1}$$

$$\Rightarrow \qquad \Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}} = 111.4 - 99.71 = \mathbf{+\,11.69\ JK^{-1}}.$$