

Practice session III (Homework)

Thermodynamics

1. The heats of solution of one mole of KCl in 200 moles of H₂O under one atmospheric pressure are $\Delta H = 4339$ cal at 21°C and $\Delta H = 4260$ cal at 23°C. Calculate ΔH value at 25°C. (Hint: Kirchhoff's equation)

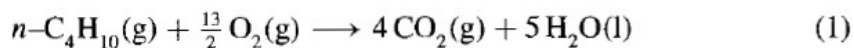
Answer:

From Kirchhoff's equation

$$\Delta H_{T_2} = \Delta H_{T_1} + \Delta C_P(T_2 - T_1) \text{ assuming that } C_P \text{ remains constant with the temperature range.}$$
$$\therefore \Delta C_P = \frac{\Delta H_{T_2} - \Delta H_{T_1}}{T_2 - T_1} = \frac{4260 - 4339}{296 - 294} \text{ cal K}^{-1} = -39.5 \text{ cal K}^{-1}$$
$$\therefore \Delta H_{25^\circ\text{C}} = \Delta H_{23^\circ\text{C}} + \Delta C_P(298 - 296) = 4260 - 39.5 \times 2 = 4181 \text{ cal}$$

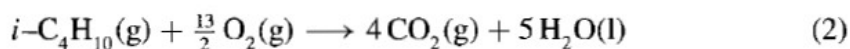
2. The molar enthalpies of combustion of isobutane and n-butane are -2871 kJ \cdot mol⁻¹ and -2878 kJ \cdot mol⁻¹, respectively at 298K and 1 atm. Calculate $\Delta_r H$ for the conversion of one mole of n-butane to one mole of isobutane.

SOLUTION: The equations for the two combustion reactions are



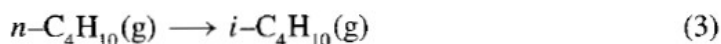
$$\Delta_r H(1) = -2877 \text{ kJ} \cdot \text{mol}^{-1}$$

and



$$\Delta_r H(2) = -2869 \text{ kJ} \cdot \text{mol}^{-1}$$

If we reverse the second equation and add the result to the first equation, then we obtain the desired equation



$$\begin{aligned} \Delta_r H(3) &= \Delta_r H(1) - \Delta_r H(2) \\ &= -2877 \text{ kJ} \cdot \text{mol}^{-1} - (-2869 \text{ kJ} \cdot \text{mol}^{-1}) = -8 \text{ kJ} \cdot \text{mol}^{-1} \end{aligned}$$

The heat of this reaction cannot be measured directly because competing reactions occur.

3. n mole of ideal gas undergoes isothermal free expansion from volume V_i to V_f at temperature T . Calculate the (a) $\Delta_{\text{sys}}S$, (b) $\Delta_{\text{surr}}S$, (c) $\Delta_{\text{total}}S$. Comment on the result considering an isolated situation.

Answer:

⊗ It is an irreversible process:
 For isothermal free expansion, $P_{\text{opp}} = 0$,
 Hence, $w = 0$
 Also, for ideal gas in isothermal process, $\Delta U = 0$.
 Hence, from first law of thermodynamics,
 $q_{\text{sys}} = 0$

i) $\Delta_{\text{sys}}S = nR \ln \frac{V_f}{V_i} > 0$ for expansion.

ii) $\Delta_{\text{surr}}S = \frac{q_{\text{surr}}}{T_{\text{surr}}} = \frac{-q_{\text{sys}}}{T_{\text{surr}}} = 0$.

iii) $\Delta_{\text{total}}S = \Delta_{\text{sys}}S + \Delta_{\text{surr}}S$
 $= nR \ln \frac{V_f}{V_i} + 0$
 $= nR \ln \frac{V_f}{V_i} = (+ve) \text{ quantity.}$

4. The Joule Thompson coefficient of a van der Waal's gas is given by the expression,

$$\mu_{JT} = -\frac{1}{C_p} \left(\frac{\partial H}{\partial P} \right)_T = -\frac{1}{C_p} \left(\frac{2a}{RT} - b \right)$$

Calculate ΔH for the isothermal expansion of one mole of CO_2 from 100 atm to 1 atm at 200K. Given, $a = 3.59 \text{ atm.lit}^2.\text{mol}^{-2}$ and $b = 0.043 \text{ lit.mol}^{-1}$

Answer:

From the expression of $\mu_{J.T}$,

$$\left(\frac{dH}{dP} \right)_T = \left(b - \frac{2a}{RT} \right)$$

$$\therefore \Delta H = \left(b - \frac{2a}{RT} \right) (P_2 - P_1)$$

$$= \left[0.043 \text{ lit mol}^{-1} - \frac{2 \times 3.59 \text{ atm lit}^2 \text{ mol}^{-2}}{0.082 \text{ lit atm K}^{-1} \text{ mol}^{-1} \times 300 \text{ K}} \right] (1 - 100) \text{ atm}$$

$$= 596.24 \text{ cal mol}^{-1}$$

5. Show that, the difference in $(C_p - C_v)$ value for a non-ideal gas differs from that of a perfect gas by the expression: $\left(\frac{\partial V}{\partial T}\right)_P \left(\frac{\partial U}{\partial V}\right)_T$

Answer:

$$\begin{aligned}(C_p - C_v)_{\text{ideal}} &= nR \equiv P \left(\frac{\partial V}{\partial T}\right)_P \quad \text{and} \\(C_p - C_v)_{\text{real}} &= T \left(\frac{\partial P}{\partial T}\right)_V \cdot \left(\frac{\partial V}{\partial T}\right)_P \\(C_p - C_v)_{\text{real}} - (C_p - C_v)_{\text{ideal}} &= \\&= T \left(\frac{\partial P}{\partial T}\right)_V \cdot \left(\frac{\partial V}{\partial T}\right)_P - P \left(\frac{\partial V}{\partial T}\right)_P \\&= \left(\frac{\partial V}{\partial T}\right)_P \left[T \left(\frac{\partial P}{\partial T}\right)_V - P \right] \\&= \left(\frac{\partial V}{\partial T}\right)_P \cdot \left(\frac{\partial U}{\partial V}\right)_T\end{aligned}$$