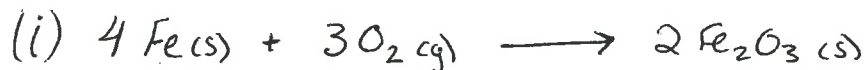


Homework #6

Chapter 20

①



$$\text{Fe (s)}: S^\circ = 27.3 \text{ J/mol}\cdot\text{K}$$

$$\text{O}_2 \text{(g)}: S^\circ = 205.0 \text{ J/mol}\cdot\text{K}$$

$$\text{Fe}_2\text{O}_3: S^\circ = 87.4 \text{ J/mol}\cdot\text{K}$$

$$\Delta S_r^\circ = 2(87.4) - 3(205.0) - 4(27.3)$$

$$\Delta S_r^\circ = -549.4 \text{ J/K}$$

(i) \ominus products more ordered

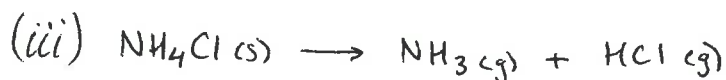


$$\text{O (g)}: S^\circ = 160.95 \text{ J/mol}\cdot\text{K}$$

$$\Delta S_r^\circ = 205.0 - 2(160.95) = -116.9 \text{ J/K}$$

$$\text{O}_2 \text{(g)}: S^\circ = 205.0 \text{ J/mol}\cdot\text{K}$$

(ii) \ominus products more ordered



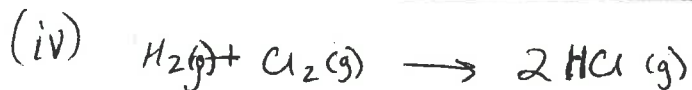
$$\text{NH}_4\text{Cl (s)}: S^\circ = 94.6 \text{ J/mol}\cdot\text{K}$$

$$\text{NH}_3 \text{(g)}: S^\circ = 193 \text{ J/mol}\cdot\text{K}$$

$$\text{HCl (g)}: S^\circ = 186.79 \text{ J/mol}\cdot\text{K}$$

$$\Delta S_r^\circ = 193 + 186.79 - 94.6 = 285.19 \text{ J/mol}\cdot\text{K}$$

(iii) \oplus reactants more ordered



$$\text{H}_2 \text{(g)}: S^\circ = 130.6 \text{ J/mol}\cdot\text{K}$$

$$\text{Cl}_2 \text{(g)}: S^\circ = 223.0 \text{ J/mol}\cdot\text{K}$$

$$\text{HCl (g)}: S^\circ = 186.79 \text{ J/mol}\cdot\text{K}$$

$$\Delta S_r^\circ = 2(186.79) - 223.0 - 130.6 = 19.98 \text{ J/K}$$

(iv) \oplus reactants more ordered

2

a) Ar... it has a greater mass

b) (i) CO₂ ... it has a greater mass

(ii) D₂O ... it has a greater mass

(iii) Ethane... it has a greater mass and it has more vibrational DoF

3

1 mole of ideal gas expanded reversibly and isothermally from 10.0 dm³ to 20.0 dm³

$$(\Delta T = 0)$$

$$(\therefore du = 0)$$

$$\int dq_{rev} = -\int dw_{rev}$$

$$\int dw_{rev} = -P dV$$

$$w_{rev} = -\int P dV = -\int_{10}^{20} \frac{nRT}{V} dV = -nRT \ln\left(\frac{20}{10}\right)$$

$$q_{rev} = nRT \ln\left(\frac{20}{10}\right)$$

$$\Delta S = q_{rev}/T = nR \ln(20/10) = 5.76 \text{ J/K}$$

ΔS is positive because gas is expanding

4

Show $\Delta S = c_p \ln T_2/T_1$ if c_p is independent of T

ΔS is a state function... you can choose any path to calculate it.

I chose constant pressure reversible process.

$$\int dq_p = \Delta H = c_p(T) dT$$

$$\Delta S = \int_{T_1}^{T_2} q_{rev}/T = c_p \ln(T_2/T_1)$$

Find ΔS of 2.00 moles H₂O(l) if $\bar{c}_p = 75.2 \text{ J/K}\cdot\text{mol}$

$$T_2 = 90^\circ\text{C} \quad T_1 = 10^\circ\text{C}$$

$$(363\text{K}) \quad (283\text{K})$$

$$\Delta S = n\bar{c}_p \ln(T_2/T_1) = (2.00 \text{ mol})(75.2 \frac{\text{J}}{\text{K}\cdot\text{mol}}) \ln\left(\frac{363\text{K}}{283\text{K}}\right)$$

$$\Delta S = 37.4 \text{ J/K}$$

5.) Pressure constant, reversible process

$$100^\circ\text{C} = 373\text{ K}$$

$$q_{\text{rev},p} = \Delta H_{\text{vap}} = n \overline{\Delta H_{\text{vap}}}$$

$$\Delta S_{\text{vap}} = \frac{q_{\text{rev}}}{T} = \frac{n \overline{\Delta H_{\text{vap}}}}{T} = \frac{(2.00 \text{ mol}) (40.65 \text{ kJ/mol})}{373 \text{ K}} = 0.21796 \frac{\text{kJ}}{\text{K}}$$

$$\Delta S_{\text{vap}} = 217.96 \text{ J/K}$$

ΔS_{vap} is positive because gas is more disordered than liquid.

6.)

$$\overline{\Delta S_{\text{mix}}} = -R \sum_{j=1}^N y_j \ln(y_j) \quad (\text{where } y_j = \text{mole fraction})$$

$$y_{\text{N}_2} = \frac{2}{2+1} = \frac{2}{3}$$

$$y_{\text{O}_2} = \frac{1}{2+1} = \frac{1}{3}$$

$$\Delta S_{\text{mix}} = -n_{\text{N}_2} R \ln\left(\frac{n_{\text{N}_2}}{n_{\text{N}_2} + n_{\text{O}_2}}\right) - n_{\text{O}_2} R \ln\left(\frac{n_{\text{O}_2}}{n_{\text{N}_2} + n_{\text{O}_2}}\right)$$

$$= 15.87 \text{ J/mol}\cdot\text{K}$$

$$\overline{\Delta S_{\text{mix}}} = -R \left(\frac{2}{3} \ln\left(\frac{2}{3}\right) + \frac{1}{3} \ln\left(\frac{1}{3}\right) \right)$$

$$R = 8.314 \text{ J/mol}\cdot\text{K}$$

$$\overline{\Delta S_{\text{mix}}} = 5.29 \text{ J/K}$$

Chapter 21

① $\bar{C}_V(T)/R = 16.4105 - \frac{6085.929 \text{ K}}{T} + \frac{822826 \text{ K}^2}{T^2}$ 300 to 1000 K

$$\Delta S = \int_{T_1}^{T_2} \frac{n \bar{C}_V}{T} dT \quad n = 1 \text{ mol}$$

$$\int_{T_1}^{T_2} \frac{\bar{C}_V}{T} dT = \int_{300}^{600} \left(\frac{16.4105}{T} - \frac{6085.929 \text{ K}}{T^2} + \frac{822826}{T^3} \right) dT$$

$$= 16.4105 \ln T - \frac{6085.929 \text{ K}}{-T} + \frac{822826 \text{ K}^2}{(-2) T^2} \Big|_{300}^{600}$$

$$= 16.4105 \ln(600) - 16.4105 \ln(300) + \frac{6085.929}{600} - \frac{6085.929}{300} - \frac{411413}{600^2} + \frac{411413}{300^2}$$

$$\int_{T_1}^{T_2} \frac{\bar{C}_V}{T} dT = 4.66$$

$$\Delta S = (4.66 R)(1 \text{ mol}) = 38.75 \text{ J/K}$$

a) $\Delta S = 38.75 \text{ J/K}$

We need \bar{C}_p . For an ideal gas $\bar{C}_p = R + \bar{C}_V$

$$\text{So } \bar{C}_p/R = 1 + 16.4105 - \frac{6085.929 \text{ K}}{T} + \frac{822826 \text{ K}^2}{T^2}$$

$$\int_{T_1}^{T_2} \frac{\bar{C}_p}{T} dT = \int_{300}^{600} \left(\frac{17.4105}{T} - \frac{6085.929}{T^2} + \frac{822826}{T^3} \right) dT$$

$$= 17.4105 \ln T - \frac{6085.929}{(-T)} + \frac{822826}{(-2) T^2} \Big|_{300}^{600}$$

$$\int_{T_1}^{T_2} \frac{\bar{C}_p}{T} dT = 5.353$$

$$\Delta S = (5.353 R)(1 \text{ mol}) = 44.51 \text{ J/K}$$

b) $\Delta S = 44.51 \text{ J/K}$

c) Compare and contrast ...

2
*

Why is $\Delta_{\text{vap}} \bar{S} > \Delta_{\text{fus}} \bar{S}$?

~ $\Delta_{\text{vap}} \bar{S}$ is a transition from liquid to gas. Gases are much more disordered than liquids

~ $\Delta_{\text{fus}} \bar{S}$ is a transition from solid to liquid. Liquids are somewhat more disordered than solids.

3

a) CO_2 (more atoms)

b) $\text{CH}_3\text{CH}_2\text{CH}_3$ (more flexibility / vibrations)

c) $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ (more flexibility / vibrations)

4

Debye approx.

$$\bar{S}(T) = \frac{C_p(10\text{K})}{3} + \int_{10}^{35.61} \frac{\bar{C}_p[\text{N}_2(\text{s}_1)]}{T} dT + \frac{\Delta_{\text{trs}} \bar{H}}{35.61}$$

$$+ \int_{35.61}^{63.51} \frac{\bar{C}_p[\text{N}_2(\text{s}_2)]}{T} dT + \frac{\Delta_{\text{fus}} \bar{H}}{63.51}$$

$$+ \int_{63.51}^{77.36} \frac{\bar{C}_p[\text{N}_2^{(g)}]}{T} dT + \frac{\Delta_{\text{vap}} \bar{H}}{77.36}$$

$$+ \int_{77.36}^{298.15} \frac{\bar{C}_p[\text{N}_2(\text{g})]}{T} dT + \text{Correction}$$

5) CO $\Theta_{rot} = 2.77 \text{ K}$ $T = 81.6 \text{ K}$ $P = 1 \text{ bar}$
 $\Theta_{vib} = 3103 \text{ K}$ $\sigma = 1, g_{el} = 1$ (normal b.p.)

(21.28) $\frac{\bar{S}}{R} = \ln \left[\left(\frac{2\pi M k_B T}{h^2} \right)^{3/2} \frac{V e^{5/2}}{N_A} \right] + \ln \frac{T e}{2\Theta_{rot}} - \ln(1 - e^{-\Theta_{vib}/T}) + \frac{\Theta_{vib}/T}{e^{\Theta_{vib}/T} - 1} + \ln g_{el}$

$\left[\frac{2\pi M k_B T}{h^2} \right]^{3/2} \left[\frac{2\pi (4.65 \times 10^{-26} \text{ kg}) (1.3807 \times 10^{-23} \text{ J/K}) (81.6 \text{ K})}{(6.626 \times 10^{-34} \text{ J}\cdot\text{s})^2} \right]^{3/2} = 2.05 \times 10^{31} \text{ m}^{-3}$

$\frac{V}{N_A} = \frac{RT}{N_A P} = \frac{(0.08314 \text{ L}\cdot\text{Bar/mol}\cdot\text{K})(81.6 \text{ K})}{(6.022 \times 10^{23} \text{ mol}^{-1})(1 \text{ bar})} = 1.127 \times 10^{-23} \text{ L} = 1.127 \times 10^{-24} \text{ m}^3$

$\frac{T e}{\Theta_{rot}} = \frac{(81.6 \text{ K})(2.71828)}{(1)(2.77 \text{ K})} = 80.076$

$1 - e^{-\Theta_{vib}/T} = 1 - e^{-3103/81.6} \approx 1$

$\ln g_{el} = 0$

$\frac{\Theta_{vib}/T}{e^{\Theta_{vib}/T} - 1} = \frac{3103/81.6}{e^{3103/81.6} - 1} = 1.162 \times 10^{-15}$

$\frac{\bar{S}}{R} = 14.85 + 4.38 - 0 + 1.162 \times 10^{-15} + 0$

$\bar{S} = 159.9 \text{ J/K}\cdot\text{mol}$

a) $\bar{S} = 159.9 \text{ J/K}\cdot\text{mol}$

b) Due to residual entropy, this value differs from experimental value by $\sim 5 \text{ J/K}\cdot\text{mol}$

(Recall: residual entropy is caused by compounds not crystallizing perfectly)