Homework #6

Chapter 20

①

(i) $4\,Fe_{(s)} + 3O_{2\,(g)} \longrightarrow 2\,Fe_2O_{3\,(s)}$

$Fe_{(s)}$: $S° = 27.3$ J/mol·K

$O_{2\,(g)}$: $S° = 205.0$ J/mol·K

Fe_2O_3: $S° = 87.4$ J/mol·K

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

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

(i) ⊖ products more ordered

(ii) $O_{(g)} + O_{(g)} \longrightarrow O_{2\,(g)}$

$O_{(g)}$: $S° = 160.95$ J/mol·K

$O_{2\,(g)}$: $S° = 205.0$ J/mol·K

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

(ii) ⊖ products more ordered

(iii) $NH_4Cl_{(s)} \longrightarrow NH_{3\,(g)} + HCl_{(g)}$

$NH_4Cl_{(s)}$: $S° = 94.6$ J/mol·K

$NH_{3\,(g)}$: $S° = 193$ J/mol·K

$HCl_{(g)}$: $S° = 186.79$ J/mol·K

$\Delta S_r^\circ = 193 + 186.79 - 94.6 = 285.19$ J/mol·K

(iii) ⊕ reactants more ordered

(iv) $H_{2\,(g)} + Cl_{2\,(g)} \longrightarrow 2\,HCl_{(g)}$

$H_{2\,(g)}$: $S° = 130.6$ J/mol·K

$Cl_{2\,(g)}$: $S° = 223.0$ J/mol·K

$HCl_{(g)}$: $S° = 186.79$ J/mol·K

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

(iv) ⊕ reactants more ordered

② a) Ar... it has a greater mass

b) (i) CO_2 ... it has a greater mass

(ii) D_2O ... 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 $10.0\ dm^3$ to $20.0\ dm^3$

$(\Delta T = 0)$
$(\therefore dU = 0)$

$$\delta q_{rev} = -\delta w_{rev}$$

$$\delta w_{rev} = -PdV$$

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

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

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

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.

$$\delta q_p = \Delta H = c_p(T)\, dT$$

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

Find ΔS of 2.00 moles $H_2O_{(l)}$ if $\bar{C}_p = 75.2\ J/K{\cdot}mol$

$T_2 = 90°C$ (363 K) $T_1 = 10°C$ (283 K)

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

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

⑤ Pressure constant, reversible process

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

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

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

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

ΔS_{vap} is positive because gas is <u>more disordered</u> than liquid.

⑥

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

$y_{N_2} = \frac{2}{2+1} = \frac{2}{3}$

$y_{O_2} = \frac{1}{2+1} = \frac{1}{3}$

$$\Delta S_{mix} = -n_{N_2} R \ln\left(\frac{n_{N_2}}{n_{N_2}+n_{O_2}}\right) - n_{O_2} R \ln\left(\frac{n_{O_2}}{n_{N_2}+n_{O_2}}\right)$$

$= 15.87\ J/mol \cdot K$

$$\Delta \overline{S}_{mix} = -R\left(\tfrac{2}{3}\ln(2/3) + \tfrac{1}{3}\ln(1/3)\right)$$

$R = 8.314\ J/mol \cdot K$

$$\Delta \overline{S}_{mix} = 5.29\ J/K$$

Chapter 21

①

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

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

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

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

$$= 16.4105 \ln(600) - 16.4105 \ln(300) + \frac{6085.929}{600} - \frac{6085.929}{300} - \frac{411413}{600^2} + \frac{4114}{30}$$

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

$$\Delta S = (4.66R)(1\,mol) = 38.75\ J/K$$

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

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

So $$\bar{C}_P/R = 1 + 16.4105 - \frac{6085.929k}{T} + \frac{822826\,k^2}{T^2}$$

$$\int_{T_1}^{T_2} \frac{\bar{C}_V}{T}\,dT = \int_{300}^{600} \frac{17.4105}{T} - \frac{6085.929}{T^2} + \frac{822826}{T^3}\,dT$$

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

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

$$\Delta S = (5.353R)(1\,mol) = 44.51\ J/K$$

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

c) Compare and contrast . . .

② $\star$ Why is $\Delta_{vap}\bar{S} > \Delta_{fus}\bar{S}$?

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

~ $\Delta_{fus}\bar{S}$ is a transition from solid to liquid. Liquids are <u>Somewhat</u> more disordered than solids.

③

a) CO_2 (more atoms)

b) $CH_3CH_2CH_3$ (more flexibility / vibrations)

c) $CH_3CH_2CH_2CH_2CH_3$ (more flexibility / vibrations)

④

$$\bar{S}(T) = \underbrace{\frac{\bar{C}_p(10K)}{3}}_{\text{Debye approx.}} + \int_{10}^{35.61} \frac{\bar{C}_p[N_2(s_1)]}{T}\,dT + \frac{\Delta_{trs}\bar{H}}{35.61}$$

$$+ \int_{35.61}^{63.51} \frac{\bar{C}_p[N_2(s_2)]}{T}\,dT + \frac{\Delta_{fus}\bar{H}}{63.51}$$

$$+ \int_{63.51}^{77.36} \frac{\bar{C}_p[N_2(\ell)]}{T}\,dT + \frac{\Delta_{vap}\bar{H}}{77.36}$$

$$+ \int_{77.36}^{298.15} \frac{\bar{C}_p[N_2(g)]}{T}\,dT + \text{Correction}$$

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

$$\left(\frac{2\pi M k_B T}{h^2}\right)^{3/2} = \left[\frac{2\pi\,(4.65\times10^{-26}\text{ kg})(1.3807\times10^{-23}\text{ J/K})(81.6\text{ K})}{(6.626\times10^{-34}\text{ J.s})^2}\right]^{3/2} = 2.05\times10^{31}\text{ m}^{-3}$$

$$\frac{\bar{V}}{N_A} = \frac{RT}{N_A P} = \frac{(0.08314\text{ L}\cdot\text{Bar/mol}\cdot\text{K})(81.6\text{ K})}{(6.022\times10^{23}\text{ mol}^{-1})(1\text{ bar})} = 1.127\times10^{-23}\text{ L} = 1.127\times10^{-26}\text{ m}^3$$

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

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

$$\ln g_{el} = 0$$

$$\frac{\Theta_{vib}/T}{e^{\Theta_{vib}/T}-1} = \frac{3103/81.6}{e^{3103/81.6}-1} = 1.162\times10^{-15}$$

$$\frac{\bar{S}}{R} = 14.85 + 4.38 - 0 + 1.162\times10^{-15} + 0$$

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

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

b) Due to residual entropy, this value differs from experimental value by ~5 J/K·mol

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

#6) p.6