

*(This assignment is optional. You lose no marks if you don't hand it in.)

1. a) The equation

$$dS = \left(\frac{\partial S}{\partial T}\right)_p dT + \left(\frac{\partial S}{\partial p}\right)_T dp \quad (1.1)$$

[5]

is mathematically correct, but not very convenient for calculating entropy changes. Explain.

- b) Starting with equation 1.1, show

$$dS = \frac{C_p}{T} dT - \beta V dp \quad (1.2)$$

where $C_p = (\partial H/\partial T)_p$ is the heat capacity at constant pressure and $\beta = V^{-1}(\partial V/\partial T)_p$ is the thermal expansivity. (*Hint*: the Maxwell relation from $dG = -SdT + Vdp$ is useful)

- c) Why is equation (1.2) more convenient for calculating entropy changes than equation (1.1)?
 d) Are equations (1.1) and (1.2) restricted to ideal gases, or do they apply to any system? Explain.

2. a) Similarly, the equation

$$dS = \left(\frac{\partial S}{\partial T}\right)_V dT + \left(\frac{\partial S}{\partial V}\right)_T dV \quad (2.1)$$

[5]

is mathematically correct, but not very convenient for calculating entropy changes. Explain.

- b) Starting with equation 2.1, show

$$dS = \frac{C_V}{T} dT + \frac{\beta}{\kappa} dV \quad (2.2)$$

where $C_V = (\partial U/\partial T)_V$ is the heat capacity at constant volume and $\kappa = -V^{-1}(\partial V/\partial p)_T$ is the isothermal compressibility.

- c) Why is equation (2.2) more convenient for calculating entropy changes than equation (2.1)?
 d) Are equations (2.1) and (2.2) restricted to ideal gases, or do they apply to any system? Explain.

3. a) Use $(\partial S/\partial p)_T = -\beta V$ derived in Question 1 to calculate $(\partial S/\partial p)_T$ at 25 °C and 1.00 bar for

i) one mole of an ideal gas

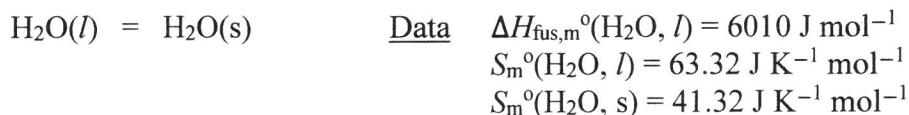
[3] ii) one mole of liquid water (density 0.997 g cm⁻³, $\beta = 0.000204$ K⁻¹)

- b) Explain briefly and qualitatively in molecular terms why values of $(\partial S/\partial p)_T$ for liquids and solids are much smaller than those for gases.

4. In class, we used the Second Law and $(\Delta S > 0)_{\text{isolated system}}$ for a spontaneous process to show freezing liquid water at 1 bar is spontaneous at temperatures below 0 °C. But to calculate ΔS using $dS = dq_{\text{rev}}/T$ for the irreversible freezing water at -10 °C (not an isolated system), we had to reversibly heat the supercooled liquid water from -10 °C to 0 °C, reversibly freeze it at 0 °C, reversibly cool the ice to -10 °C, and then include the entropy change of the surroundings.

[4] Is there an easier way to show freezing liquid water is spontaneous below 0 °C (with applications to other phase transitions and other processes)? **Yes!** At fixed temperature and pressure, use $\Delta G_{T,p} = 0$ for reversible processes and $\Delta G_{T,p} < 0$ for spontaneous processes:

a) Calculate q , ΔS and ΔG for the freezing of water at 0 °C and 1 bar.



b) Use the value of $\Delta G_{T,p}$ to show freezing liquid water is reversible at 0 °C.

c) Use $(\partial G/\partial T)_p = -S$ and therefore $(\partial \Delta G/\partial T)_p = -\Delta S$ to show freezing liquid water is spontaneous at temperatures below 0 °C.

5. 0.200 mol pure O₂ and 0.800 mol pure N₂ (assumed to be ideal gases) mix at 300 K and 1.00 bar.

ΔU and ΔH are zero (isothermal ideal gases), and the volume is constant (ideal gases at fixed temperature and pressure), so $w = 0$ and $q = \Delta U - w = 0$.

a) Calculate ΔG . Use the result to show the mixing process is spontaneous.

[3] b) Why is it incorrect to use q/T to calculate ΔS ?

c) Use the values of ΔG and ΔH to calculate ΔS . Can the value of ΔS also be used to show the mixing process is spontaneous? Explain.

Q1 a) The entropy equation $ds = \left(\frac{\partial S}{\partial T}\right)_p dT + \left(\frac{\partial S}{\partial p}\right)_T dp$

is mathematically correct, but not convenient for calculating entropy changes unless the partial derivatives $\left(\frac{\partial S}{\partial p}\right)_T$ and $\left(\frac{\partial S}{\partial T}\right)_p$ can be evaluated

b) Evaluate $\left(\frac{\partial S}{\partial T}\right)_p$?

$$dH = Tds + Vdp \quad \text{for the enthalpy}$$

recall $dq_p = dH_p$ at constant pressure ($dp=0$)

$$dH_p = Tds_p + \cancel{Vdp}^0 = dq_p$$

$$C_p = \frac{dq_p}{dT} = \frac{dH_p}{dT} = T \frac{ds_p}{dT} = T \left(\frac{\partial S}{\partial T}\right)_p$$

gives $\left(\frac{\partial S}{\partial T}\right)_p = C_p/T$

Evaluate $\left(\frac{\partial S}{\partial p}\right)_T$?

p, T suggests using dG

$$dG = -SdT + Vdp$$

$$\left(\frac{\partial(-S)}{\partial p}\right)_T = \left(\frac{\partial V}{\partial T}\right)_p \quad (\text{Maxwell relation for } dG)$$

gives $\left(\frac{\partial S}{\partial p}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_p = -\beta V$

$c)$
all measurable
 C_p, T, β, V, p
convenient

$$ds = \left(\frac{\partial S}{\partial T}\right)_p dT + \left(\frac{\partial S}{\partial p}\right)_T dp \implies ds = \frac{C_p}{T} dT - \beta V dp$$

(Q1 cont.)

d) $ds = \frac{C_p}{T} dT - \beta v dp$ applies to any system of constant composition (no dn_1, dn_2, dn_3, \dots terms)
 $pV = nRT$ not assumed

Q2 a) $ds = \left(\frac{\partial s}{\partial T}\right)_v dT + \left(\frac{\partial s}{\partial v}\right)_T dv$

Not convenient for entropy calculations unless $(\partial s/\partial T)_v$ and $(\partial s/\partial v)_T$ can be calculated

b) Evaluate $(\partial s/\partial T)_v$? $dw = p_{ext} dv = 0$ at const. volume

$dU_v = dq_v - p_{ext} dv$

heat capacity at constant volume $C_v = \frac{dq_v}{dT} = \frac{dU_v}{dT} = \left(\frac{\partial U}{\partial T}\right)_v$

also: $dU_v = T ds_v - p_{ext} dv$ $\frac{dU_v}{dT} = T \frac{ds_v}{dT} = T \left(\frac{\partial s}{\partial T}\right)_v = C_v$

gives $\left(\frac{\partial s}{\partial T}\right)_v = \frac{C_v}{T}$

Evaluate $(\partial s/\partial v)_T$?

T, v suggest using $dA = -SdT - pdv$

$-\left(\frac{\partial s}{\partial v}\right)_T = -\left(\frac{\partial p}{\partial T}\right)_v$

from Chap. 3 (or Eq. Sheet!)

$\left(\frac{\partial s}{\partial v}\right)_T = \left(\frac{\partial p}{\partial T}\right)_v = -\left(\frac{\partial p}{\partial v}\right)_T \left(\frac{\partial v}{\partial T}\right)_p = -\frac{\left(\frac{\partial v}{\partial T}\right)_p}{\left(\frac{\partial v}{\partial p}\right)_T} = \frac{1/\alpha_p}{-1/\kappa_p} = \frac{\beta}{\kappa}$

$ds = \left(\frac{\partial s}{\partial T}\right)_v dT + \left(\frac{\partial s}{\partial v}\right)_T dv \Rightarrow$

$ds = \frac{C_v}{T} dT + \frac{\beta}{\kappa} dv$ C_v, T, β, κ, v convenient

applies to any constant-composition system ($pV = nRT$ not assumed)

Q3 a) Calculate $\left(\frac{\partial S}{\partial P}\right)_T = \beta V$ at 25°C, 1 bar

i) one mole of an ideal gas ($V = nRT/P$)

$$\beta \equiv \frac{1}{V} \left(\frac{\partial V}{\partial T}\right)_P = \frac{1}{V} \left(\frac{\partial}{\partial T} \frac{nRT}{P}\right)_P = \frac{1}{V} \frac{nR}{P} \left(\frac{\partial T}{\partial T}\right)_P = \frac{1}{T}$$

$$\left(\frac{\partial S}{\partial P}\right)_T = \beta V = \frac{1}{T} V = \frac{1}{T} \frac{nRT}{P} = \frac{nR}{P}$$

$$= \frac{(1.00 \text{ mol}) 8.314 \text{ J K}^{-1} \text{ mol}^{-1}}{100,000 \text{ Pa}} = 8.314 \times 10^{-5} \frac{\text{m}^3}{\text{K}}$$

$$= 0.08314 \frac{\text{L}}{\text{K}}$$

data:

ii) one mole of liquid water $\left(\begin{array}{l} \rho = 0.997 \frac{\text{g}}{\text{cm}^3} \\ \beta = 0.000204 \text{ K}^{-1} \end{array} \right)$

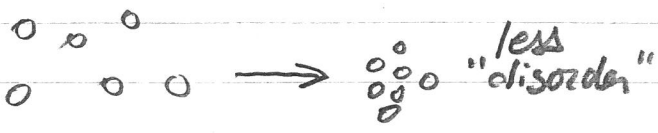
$$\text{volume} = \frac{\text{mass}}{\text{density}}$$

$$V = \frac{18.015 \text{ g}}{0.997 \text{ g cm}^{-3}} = 18.07 \text{ cm}^3 = 18.07 \times 10^{-6} \text{ m}^3$$


$$\left(\frac{\partial S}{\partial P}\right)_T = \beta V = (0.000204 \text{ K}^{-1})(18.07 \times 10^{-6} \text{ m}^3)$$

$$= 3.69 \times 10^{-9} \frac{\text{m}^3}{\text{K}} = 3.69 \times 10^{-6} \frac{\text{L}}{\text{K}}$$

b) pressurize a gas


 5 significantly decreased

pressurize a liquid


 almost no effect on S



$$q = \Delta H^\circ = -\Delta H_{\text{fus}}^\circ(H_2O) = -6010 \text{ J}$$

(pressure const.)

$$\Delta S^\circ = S_m^\circ(H_2O, s) - S_m^\circ(H_2O, l)$$

$$= (41.32 - 63.32) \frac{\text{J}}{\text{K}} = -22.00 \frac{\text{J}}{\text{K}}$$

$$\Delta G = \Delta(U + pV - TS) = \Delta(H - TS)$$

$$= \Delta H - \Delta(TS) \quad (T \text{ constant})$$

$$\Delta G = \Delta H - T\Delta S$$

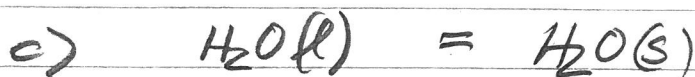
here $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ = -6010 \text{ J} - (273.15 \text{ K})(-22.00 \frac{\text{J}}{\text{K}})$

$$= (-6010 + 6010) \frac{\text{J}}{\text{K}}$$

$$= 0$$

b) $\Delta G = 0$ at fixed T, p ($0^\circ C, 1 \text{ bar}$)

$\Delta G_{T,p} \leq 0$	$\Delta G_{T,p} < 0$ spont.	$\Delta G_{T,p} > 0$ impossible	$\Delta G_{T,p} = 0$ reversible
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$\Delta G = 0$ at $0^\circ C, 1 \text{ bar}$

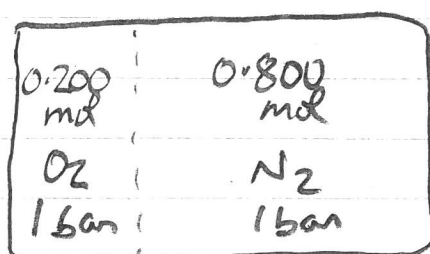
$$\left(\frac{\partial \Delta G}{\partial T}\right)_p = -\Delta S = -(-22.00 \frac{\text{J}}{\text{K}}) = +22.00 \frac{\text{J}}{\text{K}}$$

$\therefore \Delta G > 0$ at temperatures above $0^\circ C$ (non-spontaneous) positive

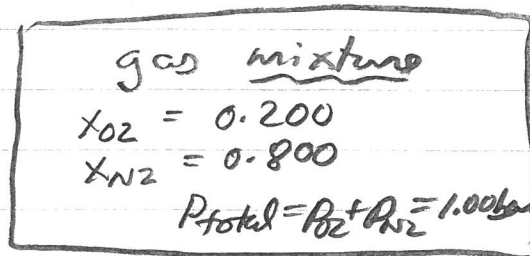
$\Delta G < 0$ at temperatures below $0^\circ C$
spontaneous freezing here

Q5

0.200 mol O_2 and 0.800 mol N_2
mix at 300 K and 1.00 bar



→



$$\Delta G = G_f - G_i$$

$$= n_{O_2} G_m(O_2)_f + n_{N_2} G_m(N_2)_f - [n_{O_2} G_m(O_2)_i + n_{N_2} G_m(N_2)_i]$$

$$= n_{O_2} \left[G_m^\circ(O_2) + RT \ln \left(\frac{P_{O_2f}}{P_0} \right) \right] + n_{N_2} \left[G_m^\circ(N_2) + RT \ln \left(\frac{P_{N_2f}}{P_0} \right) \right]$$

$$- \left\{ n_{O_2} \left[G_m^\circ(O_2) + RT \ln \left(\frac{P_{O_2i}}{P_0} \right) \right] + n_{N_2} \left[G_m^\circ(N_2) + RT \ln \left(\frac{P_{N_2i}}{P_0} \right) \right] \right\}$$

$$= n_{O_2} RT \left[\ln \left(\frac{P_{O_2f}}{P_0} \right) - \ln \left(\frac{P_{O_2i}}{P_0} \right) \right] + n_{N_2} RT \left[\ln \left(\frac{P_{N_2f}}{P_0} \right) - \ln \left(\frac{P_{N_2i}}{P_0} \right) \right]$$

$$= n_{O_2} RT \ln \left(\frac{P_{O_2f}}{P_{O_2i}} \right) + n_{N_2} RT \ln \left(\frac{P_{N_2f}}{P_{N_2i}} \right)$$

$$= \left(8.314 \frac{\text{J}}{\text{K mol}} \right) (300 \text{ K}) \left[0.200 \text{ mol} \ln \left(\frac{0.200}{1.00} \right) + 0.800 \ln \left(\frac{0.800}{1.00} \right) \right]$$

$$\Delta G = -1250 \text{ J}$$

$$\Delta G < 0 \text{ at fixed } T, P$$

⇒ the mixing process is spontaneous

(Q5 cont.)

b) at constant temperature:

$$\Delta S = \int \frac{dq_{rev}}{T} = \frac{1}{T} \int dq_{rev} = \frac{q_{rev}}{T}$$

but this mixing process is not reversible
($\Delta G_{T,P} < 0$)

here

$$q \neq q_{rev}$$

$$q = q_{irrev} = 0$$

$$\Delta S \neq \frac{q_{irrev}}{T} = 0$$

$$H \equiv U + PV$$

$$G \equiv U + PV - TS$$

$$\begin{aligned} c) \quad \Delta G &= \Delta(U + PV - TS) \quad (T_{const.}) \\ &= \Delta(U + PV) - \Delta(TS) \\ &= \Delta H - T\Delta S \\ &= 0 - T\Delta S \end{aligned}$$

$$\text{here } \Delta S = - \frac{\Delta G}{T} = - \frac{(-12500 \text{ J})}{300 \text{ K}}$$

$$\Delta S = +4.17 \frac{\text{J}}{\text{K}}$$

$$\Delta S > 0$$

for an isolated system

$$(\Delta U = 0 \quad q = 0 \quad w = 0)$$

\therefore mixing is spontaneous