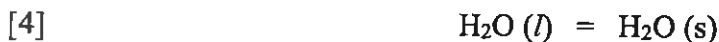


1. For freezing one mole of liquid water at 1.00 bar and  $-10\text{ }^\circ\text{C}$



we calculated  $q = -5618\text{ J}$  and  $\Delta S = -19.20\text{ J K}^{-1}$  in class.

a)  $\int \frac{dq}{T}$  is frequently used to calculate entropy changes, but for this process  $\Delta S \neq \int \frac{dq}{T}$ . Why?

b) Show  $dq < TdS$  (an important criterion for spontaneous processes).

c) Calculate  $\Delta G$ .

d) Use the value of  $\Delta G$  to prove that freezing water is spontaneous at 1.00 bar and  $-10\text{ }^\circ\text{C}$ .

2. The temperature can increase dramatically if a system is compressed adiabatically. For a reversible adiabatic compression, show

[2] 
$$\left(\frac{\partial T}{\partial p}\right)_s = \frac{T}{C_p} \left(\frac{\partial V}{\partial T}\right)_p = \frac{TV\beta}{C_p}$$

3. a) Calculate  $(\partial T/\partial p)_s$  at  $25\text{ }^\circ\text{C}$  and 1 bar for

i) water vapor (assumed to be an ideal gas,  $C_{pm} = 33.6\text{ J K}^{-1}\text{ mol}^{-1}$ )

[5]

ii) liquid water ( $C_{pm} = 75.3\text{ J K}^{-1}\text{ mol}^{-1}$ ,  $\beta = 0.000204\text{ K}^{-1}$ , density  $0.997\text{ g cm}^{-3}$ )

b) Can you suggest why  $(\partial T/\partial p)_s$  for liquid water is so much smaller than that for the vapor?

4. Use  $dA = -SdT - pdV$  for the Helmholtz energy (*not your equation sheet!*) to prove:

[3]

a)  $(\partial A/\partial T)_V = -S$

b)  $(\partial A/\partial V)_T = -p$

c)  $(\partial S/\partial V)_T = (\partial p/\partial T)_V$

5. 2.00 moles of pure oxygen and 8.00 moles of pure nitrogen mix at 300 K and 1.00 bar. Assuming ideal gas behavior:

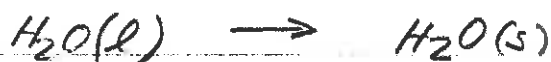
[6]

a) Calculate  $q$ ,  $w$ , and  $\Delta U$ . Is the system isolated?

b) Calculate  $\Delta S$ . Can the value of  $\Delta S$  be used to show the process is spontaneous?

c) Calculate  $\Delta G$ . Can the value of  $\Delta G$  be used to show the process is spontaneous?

(Q1) One mole of liquid water freezes at 1.00 bar and  $-10^\circ\text{C}$ .



$$q = -5618 \text{ J}$$

$$\Delta S = -19.20 \text{ J K}^{-1}$$

a) For this process  $\Delta S \neq \int \frac{dq}{T} = \frac{q}{T}$  (isothermal)

Why?  $\Delta S = \int \frac{dq_{\text{rev}}}{T}$  and this process is not reversible  
( $q \neq q_{\text{rev}}$ )

b) Proof:  $\int \frac{dq}{T}$  for freezing one mole of water at  $-10^\circ\text{C}$   
(isothermal)

$$= \frac{1}{T} \int dq = \frac{q}{T} = \frac{-5618 \text{ J}}{263 \text{ K}} = -21.36 \frac{\text{J}}{\text{K}}$$

$$\frac{q}{T} = -21.36 \frac{\text{J}}{\text{K}} < \Delta S = -19.20 \frac{\text{J}}{\text{K}}$$

c)  $\Delta G = \Delta(U + PV - TS) = \Delta(U + PV) - \overset{H}{\Delta(TS)}$  (isothermal)

$$\Delta G = \Delta H - T\Delta S \quad (\text{constant pressure, so } \Delta H = q)$$

$$\Delta G = q - T\Delta S = -5618 \text{ J} - (263 \text{ K})(-19.20 \text{ J K}^{-1})$$

$$\Delta G = -5618 \text{ J} + 5050 \text{ J} = -568 \text{ J}$$

d)  $\Delta G < 0$  at constant  $T, P$  (263 K, 1 bar)

$$\Delta G_{T,P} < 0$$

$\Rightarrow$  freezing water is spontaneous

or //  $ds = \frac{C_p}{T} dT - \beta V dp = 0$  at constant  $S$   
 given  $\frac{C_p}{T} dT_s = \beta V dp_s \div dp_s \Rightarrow \left(\frac{\partial T}{\partial P}\right)_S = \frac{\beta V T}{C_p}$

Q2

Reversible adiabatic process:  $\Delta S = \int \frac{dq_{rev}}{T} = 0$   
 (constant entropy)

Change in temperature with pressure at constant entropy:

all required equations on your trusty equation sheet!

$\left(\frac{\partial T}{\partial P}\right)_S = - \left(\frac{\partial T}{\partial S}\right)_P \left(\frac{\partial S}{\partial P}\right)_T$  (cyclic rule)

$= - \frac{\left(\frac{\partial S}{\partial P}\right)_T}{\left(\frac{\partial S}{\partial T}\right)_P}$  (inverse rule)

from  $dG = -SdT + Vdp$   
 get  $-\left(\frac{\partial S}{\partial P}\right)_T = \left(\frac{\partial V}{\partial T}\right)_P$

$= \frac{\left(\frac{\partial V}{\partial T}\right)_P}{\frac{C_p}{T}}$

from  $dH = TdS + Vdp$   
 get  $\left(\frac{\partial H}{\partial T}\right)_P = T \left(\frac{\partial S}{\partial T}\right)_P = \frac{dq_{rev}}{dT} = C_p$

$= \frac{T}{C_p} \left(\frac{\partial V}{\partial T}\right)_P$

volumetric thermal expansion coefficient  
 $\beta = \frac{1}{V} \left(\frac{\partial V}{\partial T}\right)_P$   
 so  $\beta V = \left(\frac{\partial V}{\partial T}\right)_P$

$= \frac{T}{C_p} \beta V$

for an ideal gas, recall

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

Q3 a)  $(\partial T/\partial P)_S$  at 25 °C and 1 bar for

i) water vapor (assumed to be an ideal gas,  $\beta = \frac{1}{T}$ )

$$\left(\frac{\partial T}{\partial P}\right)_S = \frac{\gamma V \beta}{C_p} = \frac{\gamma V \frac{1}{T}}{C_p} = \frac{\gamma}{C_p} = \frac{\frac{nRT}{P}}{C_p}$$

$$= \frac{\frac{RT}{P}}{C_p/n} = \frac{RT}{P C_p} = 0.08314 \text{ Lbar}$$

$$= \frac{(8.314 \text{ J K}^{-1} \text{ mol}^{-1})(298.15 \text{ K})}{(100,000 \text{ Pa})(33.6 \text{ J K}^{-1} \text{ mol}^{-1})}$$

$$\left(\frac{\partial T}{\partial P}\right)_S = 7.38 \times 10^{-4} \frac{\text{K}}{\text{Pa}}$$

watch the units!  
 $C_p$  is "SI"  
 $\Rightarrow$  don't use R  
 in  $\text{Lbar K}^{-1} \text{mol}^{-1}$   
 or p in bar

$$\left(\frac{\partial T}{\partial P}\right)_S = \left(7.38 \times 10^{-4} \frac{\text{K}}{\text{Pa}}\right) \left(\frac{100,000 \text{ Pa}}{\text{bar}}\right) = 73.8 \frac{\text{K}}{\text{bar}}$$

ii) liquid water with  $C_{p,m} = 75.3 \text{ J K}^{-1} \text{ mol}^{-1}$ ,  $\beta = 0.000204 \text{ K}^{-1}$   
 and molar volume  $V_m = \frac{M}{\rho} = \frac{18.02 \text{ g mol}^{-1}}{0.997 \text{ g cm}^{-3}} = 18.1 \frac{\text{cm}^3}{\text{mol}}$

$$\left(\frac{\partial T}{\partial P}\right)_S = \frac{\gamma V \beta}{C_p} = \frac{\gamma \left(\frac{V}{n}\right) \beta}{C_{p,m}} = \frac{\gamma V_m \beta}{C_{p,m}} \quad (\text{SI}) \rightarrow (= 18.1 \times 10^{-6} \frac{\text{m}^3}{\text{mol}})$$

$$= \frac{(298.15 \text{ K})(18.1 \times 10^{-6} \text{ m}^3 \text{ mol}^{-1})(0.000204 \text{ K}^{-1})}{75.3 \text{ J K}^{-1} \text{ mol}^{-1}} = 1.46 \times 10^{-8} \frac{\text{K}}{\text{Pa}}$$

$$\left(\frac{\partial T}{\partial P}\right)_S = 0.00146 \frac{\text{K}}{\text{bar}}$$

c)  $(\partial T/\partial P)_S$  for  $\text{H}_2\text{O}(l)$  is very small because  $\text{H}_2\text{O}(l)$  is almost incompressible so almost zero work is done compressing the liquid  $\Rightarrow$  very small  $T$  change

Q4  $dA = -SdT - PdV$   
 $= \left(\frac{\partial A}{\partial T}\right)_P dT + \left(\frac{\partial A}{\partial V}\right)_T dV$  shows  $\left(\frac{\partial A}{\partial T}\right)_P = -S$   
 $\left(\frac{\partial A}{\partial V}\right)_T = -P$

order of differentiation "doesn't matter":

$$\left[\frac{\partial}{\partial V} \left(\frac{\partial A}{\partial T}\right)_P\right]_T = \left(\frac{\partial (-S)}{\partial V}\right)_T = \left[\frac{\partial}{\partial T} \left(\frac{\partial A}{\partial V}\right)_T\right]_V = \left(\frac{\partial (-P)}{\partial T}\right)_V$$

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$$

(RS "easy" to measure)

Q5 a) 2.00 mol  $O_2(g)$  + 8.00 mol  $N_2(g)$   
 mix at 300 K and 1.00 bar.

$$\Delta U = 0$$

$$q = 0$$

$$w = 0$$

this is an isolated system

isothermal ideal gases ... means  $\Delta U = 0$   
 (U depends on T only)

$$V = (n_{O_2} + n_{N_2}) \frac{RT}{P}$$

$n_{O_2}, n_{N_2}, T, P$  all constant  
 $\therefore$  constant V ... means  $w = 0$

$$\Delta U = q + w \Rightarrow 0 = q + 0$$

$$q = 0 \text{ too!}$$

b)  $\Delta S = \Delta S_{mix} = -n_{O_2} R \ln x_{O_2} - n_{N_2} R \ln x_{N_2}$

$$= -(2.00 \text{ mol}) \left(8.314 \frac{\text{J}}{\text{K mol}}\right) \ln\left(\frac{2.00}{2.00+8.00}\right) - 8.00 (8.314) \ln\left(\frac{8.00}{2.00+8.00}\right)$$

$$\Delta S = (+26.8 + 14.8) \frac{\text{J}}{\text{K}} = 41.6 \text{ J K}^{-1}$$

spontaneous

WHY?  
 $\Delta S > 0$  for an isolated system

c)  $\Delta G = \Delta G_{mix} = n_{O_2} RT \ln x_{O_2} + n_{N_2} RT \ln x_{N_2} = -T \Delta S_{mix}$   
 $= -(300 \text{ K})(41.6 \text{ J K}^{-1}) = -12480 \text{ J}$

$\Delta G_{T,P} < 0$   
 $\Rightarrow$  spontaneous mixing

$\Delta G = \Delta(H-TS)$  (fixed T)

$\Delta H = 0$  for isothermal ideal gases

$$\Delta H - T \Delta S = 0 - T \Delta S$$