

## HW 2 KEY

E3.1a Assume the block is large, such that its temperature doesn't change significantly as a result of the heat transfer.

$$\Delta S = \int_i^f \frac{dq_{\text{rev}}}{T} = \frac{1}{T} \int_i^f dq_{\text{rev}} \text{ (if } T \text{ constant)} = \frac{q_{\text{rev}}}{T}$$

$$\text{a) } \Delta S = \frac{25 \times 10^3 \text{ J}}{273.15 \text{ K}} = 92 \text{ J K}^{-1}$$

$$\text{b) } \Delta S = \frac{25 \times 10^3 \text{ J}}{373.15 \text{ K}} = 67 \text{ J K}^{-1}$$

$$\text{E3.7a } \Delta S_{\text{vap}} = \frac{\Delta_{\text{vap}} H}{T_b} = \frac{29.4 \times 10^3 \text{ J mol}^{-1}}{334.88 \text{ K}} = 88 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$\text{E3.8a } \Delta_r S^\circ = \sum_{\text{prod.}} \nu S_m^\circ - \sum_{\text{react.}} \nu S_m^\circ$$

From tables in text - values

$$\text{a) } \Delta_r S^\circ = 2 S_m^\circ(\text{CH}_3\text{COOH}, \ell) - 2 S_m^\circ(\text{CH}_3\text{COOH}, \text{g}) - S_m^\circ(\text{O}_2, \text{g}) \\ = [2(159.8) - 2(250.3) - 205.14] \text{ J K}^{-1} \text{ mol}^{-1} = -386.1 \text{ J/K mol}$$

$$\text{b) } \Delta_r S^\circ = 2 S_m^\circ(\text{AgBr}, \text{s}) + S_m^\circ(\text{Cl}_2, \text{g}) - 2 S_m^\circ(\text{AgCl}, \text{s}) - S_m^\circ(\text{Br}_2, \ell) \\ \Delta_r S^\circ = [2(107.1) + 223.07 - 2(96.2) - 152.23] = 92.4 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$\text{c) Same method, } \Delta_r S^\circ = -153.1 \text{ J K}^{-1} \text{ mol}^{-1}$$

P3.4 Need to determine the final state in each section.

Section B: constant T,  $P_i V_i = P_f V_f$ ;  $P_{Bf} = 2 P_{Bi}$

Piston ensures pressures are equal in both chambers

$$2 P_{A,f} = 2 P_{B,i} = 2 P_{A,i} \quad \text{dm}^3 = 1 \text{ L}$$

$$\text{Thus, } \frac{T_{A,f}}{T_{A,i}} = \frac{P_{A,f} V_{A,f}}{P_{A,i} V_{A,i}} = \frac{(2 P_{A,i})(3 \text{ dm}^3)}{(P_{A,i})(2 \text{ dm}^3)} = 3$$

$$\therefore T_{A,f} = T_{A,i}(3) = 900 \text{ K}$$

P3.4 cont a)  $\Delta S_A = nC_{v,m} \ln\left(\frac{T_{Af}}{T_{Ai}}\right) + nR \ln\left(\frac{V_{Af}}{V_{Ai}}\right)$   
 $= 2 \text{ mol} (20 \text{ J K}^{-1} \text{ mol}^{-1}) \ln(3) + 2 \text{ mol} \left(\frac{8.314 \text{ J}}{\text{K mol}}\right) \ln\left(\frac{3}{2}\right)$

$$\Delta S_A = 50.7 \text{ J K}^{-1}$$

$$\Delta S_B = nR \ln\left(\frac{V_{Bf}}{V_{Bi}}\right) = 2 \text{ mol} (8.314 \text{ J K}^{-1} \text{ mol}^{-1}) \ln\left(\frac{1 \text{ dm}^3}{2 \text{ dm}^3}\right)$$

$$\Delta S_B = -11.5 \text{ J K}^{-1}$$

b)  $A \equiv U - TS$  (Helmholtz free energy)

Section B is isotherm,  $\Delta U = 0$  and  $\Delta(TS) = T\Delta S$

$$\Delta A_B = \Delta U - T\Delta S = (-300 \text{ K})(-11.5 \text{ J K}^{-1}) = 3.46 \text{ kJ}$$

Section A - cannot compute  $\Delta(TS)$ , and thus can't find  $\Delta U$ .

$\Delta A$  - indeterminate, in value and sign

However in a perfect gas,  $U$  depends only on temperature, and  $U(T)$  is an increasing function of  $T$  as  $\left(\frac{dU}{dT}\right) = C$  (heat capacity,  $\oplus$  value)  
 $\Delta T > 0$ ,  $\Delta U > 0$ ; But  $\Delta(TS) > 0$  too, since both  $T$  and  $S$  increase.

c) constant temperature  $G \equiv H - TS$

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

Section B,  $\Delta H_B = 0$  since  $\Delta T = 0$  and perfect gas, so

$$\Delta G_B = -T_B \Delta S_B = (-300 \text{ K})(-11.5 \text{ J K}^{-1}) = 3.46 \text{ kJ}$$

$\Delta G_A =$  indeterminate in magnitude and sign

$$d) \Delta S_{\text{total(system)}} = \Delta S_A + \Delta S_B = (50.7 + -11.5) \text{ J K}^{-1} = 39.2 \text{ J K}^{-1}$$

If reversible process,  $\Delta S(\text{system}) + \Delta S(\text{surrounding}) = 0$

$$\therefore \Delta S_{\text{surr}} = -39.2 \text{ J K}^{-1}$$

P3.14 ~~Patn A~~ Patn A:

$$w = -nRT \ln\left(\frac{V_f}{V_i}\right) = -nRT \ln\left(\frac{P_i}{P_f}\right) = (-1 \text{ mol}) \left(\frac{8.314 \text{ J}}{\text{K mol}}\right) (300 \text{ K}) \ln\left(\frac{3 \text{ atm}}{1 \text{ atm}}\right)$$

$$\underline{w} = -2.74 \text{ kJ}$$

$$\underline{\Delta H} = \underline{\Delta U} = 0 \text{ (isothermal process, perfect gas)}$$

$$U = q + w = 0; \underline{q} = -w \quad \underline{q} = 2.74 \text{ kJ}$$

$$\underline{\Delta S} = \frac{q_{\text{rev}}}{T} \text{ (isothermal)} = \frac{2.74 \text{ kJ}}{300 \text{ K}} = 9.13 \text{ J K}^{-1}$$

$$\underline{\Delta S_{\text{total}}} = 0 \text{ (reversible process)}$$

$$\underline{\Delta S_{\text{surr}}} = \Delta S_{\text{tot}} - \Delta S = 0 - 9.13 \text{ J K}^{-1} = -9.13 \text{ J K}^{-1}$$

Patn B

$$w = -P_{\text{ex}} \Delta V = -P_{\text{ex}} (V_f - V_i) = -P_{\text{ex}} \left( \frac{nRT}{P_f} - \frac{nRT}{P_i} \right) = -nRT \left( \frac{P_{\text{ex}}}{P_f} - \frac{P_{\text{ex}}}{P_i} \right)$$

$$\underline{w} = -1 \text{ mol} (8.314 \text{ J K}^{-1} \text{ mol}^{-1}) (300 \text{ K}) \left( \frac{1 \text{ atm}}{1 \text{ atm}} - \frac{1 \text{ atm}}{3 \text{ atm}} \right)$$

$$w = -1.666 \text{ kJ}$$

$$\underline{\Delta H} = \underline{\Delta U} = 0$$

$$\underline{q} = \Delta U - w = -w = 1.666 \text{ kJ}$$

Remember, path A is reversible path.

$$\underline{\Delta S} = \frac{q_{\text{rev}}}{T} = \frac{2.74 \times 10^3 \text{ J}}{300 \text{ K}} = 9.13 \text{ J K}^{-1} = \Delta S(\text{path a, entropy is state fn})$$

$$\underline{\Delta S_{\text{surr}}} = \frac{q_{\text{surr}}}{T_{\text{surr}}} = \frac{-q}{T_{\text{surr}}} = \frac{-1.666 \times 10^3 \text{ J}}{300 \text{ K}} = -5.53 \text{ J K}^{-1}$$

$$\underline{\Delta S_{\text{total}}} = \Delta S + \Delta S_{\text{surr}} = (9.13 + -5.53) \text{ J K}^{-1} = 3.6 \text{ J K}^{-1}$$

P3.28

$$\left(\frac{\partial H}{\partial P}\right)_T = \left(\frac{\partial H}{\partial S}\right)_P \left(\frac{\partial S}{\partial P}\right)_T = \left(\frac{\partial H}{\partial P}\right)_S$$

$$dH = dU + PdV + VdP = TdS - PdV + PdV + VdP$$

$$dH = TdS + VdP$$

$$dH = \left(\frac{\partial H}{\partial S}\right)_P dS + \left(\frac{\partial H}{\partial P}\right)_S dP \quad (\text{exact differential})$$

$$\text{Thus, } \left(\frac{\partial H}{\partial S}\right)_P = T \text{ and } \left(\frac{\partial H}{\partial P}\right)_S = V$$

Substitute:

$$\left(\frac{\partial H}{\partial P}\right)_T = T \left(\frac{\partial S}{\partial P}\right)_T + V = -T \left(\frac{\partial V}{\partial T}\right)_P + V \quad (\text{maxwell})$$

a)  $PV = nRT$

$$\left(\frac{\partial V}{\partial T}\right)_P = \frac{nR}{P} \quad \text{so } \left(\frac{\partial H}{\partial P}\right)_T = \frac{-nRT}{P} + V = 0$$

$$b) P = \frac{nRT}{V-nb} - \frac{an^2}{V^2}$$

$$T = \frac{P(V-nb)}{nR} + \frac{na(V-nb)}{RV^2}$$

$$\left(\frac{\partial T}{\partial V}\right)_P = \frac{P}{nR} + \frac{na}{RV^2} - \frac{2na(V-nb)}{RV^3}$$

$$\left(\frac{\partial H}{\partial P}\right)_T = \frac{-T}{\frac{P}{nR} + \frac{na}{RV^2} - \frac{2na(V-nb)}{RV^3}} + V$$

After algebra (you won't expect this much algebra on the exam)

$$\left(\frac{dH}{dP}\right)_T = \frac{nb - \frac{2na}{RT} \left(1 - \frac{nb}{V}\right)^2}{1 - \frac{2na}{RTV} \left(1 - \frac{nb}{V}\right)^2}$$

If  $b \ll V_m$ ,  $\left(1 - \frac{nb}{V}\right) \approx 1$

$$\frac{2na}{RTV} = \frac{2na}{RT} \left(\frac{1}{V}\right) \approx \frac{2na}{RT} \left(\frac{P}{nRT}\right) = \frac{2Pa}{R^2T^2}$$

$$\left(\frac{dH}{dP}\right)_T \approx \frac{nb - \left(\frac{2na}{RT}\right)}{1 - \left(\frac{2Pa}{R^2T^2}\right)}$$

Argon,  $a = 1.337 \text{ dm}^6 \text{ atm mol}^{-2}$ ,  $b = 3.2 \times 10^{-2} \text{ dm}^3 \text{ mol}^{-1}$

$$\frac{2na}{RT} = \frac{2(1 \text{ mol})(1.337 \text{ dm}^6 \text{ atm mol}^{-2})}{(0.08206 \text{ dm}^3 \text{ atm K}^{-1} \text{ mol}^{-1})(298 \text{ K})} = 0.11 \text{ dm}^3$$

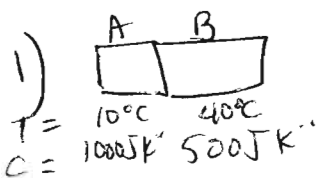
$$\frac{2Pa}{R^2T^2} = \frac{2(10 \text{ atm})(1.337 \text{ dm}^6 \text{ atm mol}^{-2})}{(0.08206)^2 (298)^2} = 0.045$$

$$\left(\frac{dH}{dP}\right)_T = \frac{(0.0320 - 0.11) \text{ dm}^3}{1 - 0.045} = -0.0817 \text{ dm}^3$$

$$\left(\frac{dH}{dP}\right)_T = -8.3 \text{ J atm}$$

$$\Delta H \approx \left(\frac{dH}{dP}\right)_T \Delta P \approx (-8.3 \text{ J atm})(1 \text{ atm}) = -8 \text{ J}$$

# HW2: Dr VDB's problems



a) Final temperature of block A and B

b)  $\Delta S_A$ ,  $\Delta S_B$ ,  $\Delta S_{\text{tot}}$

a)  $C_{p,A} = 1000\text{J/K}$     $T_A = 10^\circ\text{C} = 283\text{K}$

$C_{p,B} = 500\text{J/K}$     $T_B = 40^\circ\text{C} = 313\text{K}$

$\Delta H = C_p \Delta T$  Amount of heat from B block lost = heat gained by A

$$\Delta H_A + \Delta H_B = 0 \quad \Delta H_A = -\Delta H_B$$

$$\Delta H_A = 500\text{J/K} \cdot (T_f - 313\text{K}) \quad \Delta H_B = 1000\text{J/K} \cdot (T_f - 283\text{K})$$

$$500\text{J/K} \cdot T_f - 500(313)\text{J} = -1000\text{J/K} \cdot T_f + 1000(283)\text{J}$$

$$\text{Solve for } T_f = \frac{439500\text{J/K}}{1500\text{J}} = 293\text{K} = T_{f,A,B}$$

$$\Delta H_A = 10000\text{J} = -\Delta H_B$$

b)  $\Delta S = S(T_f) - S(T_i) = \frac{dq}{T} = \int_{T_i}^{T_f} \frac{C_p dT}{T} = C_p \ln\left(\frac{T_f}{T_i}\right)$

hot block:  $\Delta S_B(\text{block B}) = C_p \ln\left(\frac{293}{313}\right) = 500\text{J/K} \cdot \ln\left(\frac{293}{313}\right) = -33\text{J/K}$

cold block:  $\Delta S_A(\text{block A}) = C_p \ln\left(\frac{293}{283}\right) = 1000\text{J/K} \cdot \ln\left(\frac{293}{283}\right) = 34.7\text{J/K}$

$$\Delta S_{\text{tot}} = -33\text{J/K} + 34.7\text{J/K} = 1.7\text{J/K}$$

It should make qualitative sense that  $\Delta S_B$  is  $\ominus$ , since it is losing heat to block A.

2)  $n = 2 \text{ mol}$   $C_{v,m} = 1.5R$   $P_i = 1 \text{ bar}$ ,  $T = 300 \text{ K}$  IG.

one step,  $P_f = 10 \text{ bar}$ , temp bath  $T = 500 \text{ K}$

Find  $\Delta S_{\text{sys}}$ ,  $\Delta S_{\text{surr}}$ ,  $\Delta S_{\text{tot}}$

$$\Delta S_{\text{sys}} = -nR \ln\left(\frac{P_f}{P_i}\right) + C_p \ln\left(\frac{T_f}{T_i}\right); \quad C_v = 2(1.5) = 3R$$

$$\Delta S_{\text{sys}} = (-2 \text{ mol})(8.314 \text{ J/K mol}) \ln\left(\frac{10}{1}\right) + 5 \ln\left(\frac{500}{300}\right) \quad C_p = 5R = C_v + nR$$

$$\Delta S_{\text{sys}} = (-38.3 + 42.5) \text{ J K}^{-1} = 4.18 \text{ J K}^{-1}$$

$$\text{Step 2: } \Delta S_{\text{surr}} = -\frac{q}{T} \quad q = \Delta U - w$$

$$\Delta U = C_v \Delta T = (1.5R)(2 \text{ mol})(200 \text{ K}) = 4988 \text{ J}$$

$$\text{constant } P: \quad w = -P_{\text{ext}} \Delta V = -P_f (V_f - V_i) = -P_f \left( \frac{nRT_f}{P_f} - \frac{nRT_i}{P_i} \right)$$

$$w = -10 \text{ bar} (2 \text{ mol}) (8.314 \text{ J K}^{-1} \text{ mol}^{-1}) \left( \frac{500 \text{ K}}{10 \text{ bar}} - \frac{300 \text{ K}}{1 \text{ bar}} \right) = +41570 \text{ J}$$

$$q = (4988 - 41570) \text{ J} = -36582 \text{ J}$$

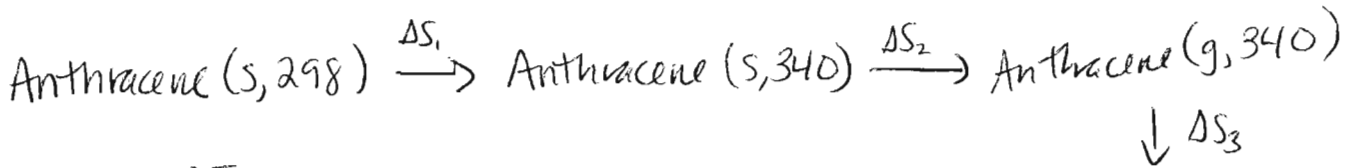
$$\Delta S_{\text{surr}} = \frac{36582 \text{ J}}{500 \text{ K}} = 73.2 \text{ J K}^{-1}$$

$$\Delta S_{\text{tot}} = (73.2 + 4.18) \text{ J K}^{-1} = 77.3 \text{ J K}^{-1}$$

3)  $T_{sub} = 340K$  ( $S \rightarrow G$ )

solid: Assume  $C_p$  temperature independent

gas:  $C_p$  varies linearly with temperature



$\Delta S_1 = \int_{T_i}^{T_f} \frac{C_p}{T} dT$  ; since  $C_p$  not fcn of  $T$  (solid) Anthracene (g, 500)

$\Delta S_1 = C_p \ln\left(\frac{T_f}{T_i}\right) = 210 JK^{-1} mol^{-1} = 27.7 JK^{-1} mol^{-1}$

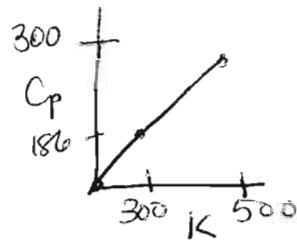
phase change  $\Delta S_2 = \frac{\Delta H}{T} = \frac{100 KJ}{mol} \left(\frac{1}{340}\right) = 294 JK^{-1} mol^{-1}$

$\Delta S_3 = \int_{T_i}^{T_f} \frac{C_p}{T} dT$   
g, 340  $\rightarrow$  500 K

Assume  $C_p$  linear with respect to  $T$

Force  $C_p(0K) = 0$ , since  $S = \int_{T=0}^{T_f} \frac{C_p}{T} dT$

would yield infinite entropy, which violates 3rd law.



thus,  $C_p(T) = \text{slope } T = \frac{(300 - 186) JK^{-1} mol^{-1}}{(500 - 300) K} = 0.57 JK^{-2} mol^{-1}$

$\Delta S_3 = \int_{340}^{500} \frac{0.57T}{T} dT = 0.57 \Delta T = 0.57 (160 K) = 91.2 JK^{-1} mol^{-1}$

$(208 + 91.2 + 294 + 27.7) JK^{-1} mol^{-1} = S_{absolute} (500K, anthracene(g))$   
 $S_{initial} \text{ solid, } 298K$   
 $S_{absolute} = 621 JK^{-1} mol^{-1}$



4)  $n = 3 \text{ mol}$   $C_{v,m} = \frac{7}{2} R$   $T_i = 300 \text{ K}$ , perfect gas

A to B: Isothermal expansion, reversible at 300 K  $q = \oplus 10.37 \text{ kJ}$   

$$\Delta S = \frac{q}{T} = \frac{10.37 \text{ kJ}}{300 \text{ K}} = 34.6 \text{ J K}^{-1}$$

B to C: Reversible expansion, adiabatically to  $V_2$  and  $T_2$   
 No heat  $dq = 0$   $dS = \frac{dq}{T}$   
 $\Delta S = 0$  for reversible, adiabatic process

C to A:  $\Delta S_{\text{surr}} = 40 \text{ J K}^{-1} (\text{C} \rightarrow \text{A})$

$$\Delta S_{\text{total}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}}$$

$$(\text{C} \rightarrow \text{A}) \Delta S_{\text{tot}} = -\Delta S(\text{A} \rightarrow \text{B}) - \Delta S(\text{B} \rightarrow \text{C}) + \Delta S_{\text{surr}}$$

$$\Delta S_{\text{tot}} = -34.6 \text{ J K}^{-1} + 40 \text{ J K}^{-1} = 5.4 \text{ J K}^{-1}$$

5)  $3 \text{ H}_2(\text{g}) + \text{N}_2(\text{g}) \rightarrow 2 \text{ NH}_3(\text{g})$  at 500 K

$$S_{\text{H}_2}(500 \text{ K}) = S(298) + \int_{T_i}^{T_f} \frac{C_p}{T} dT = \frac{131 \text{ J}}{\text{K mol}} + \frac{28.8 \text{ J}}{\text{K mol}} \ln\left(\frac{500}{298}\right)$$

$$\text{at } (500 \text{ K}) S_{\text{H}_2} = 131 \text{ J K}^{-1} \text{ mol}^{-1} + 28.8 \text{ J K}^{-1} \text{ mol}^{-1} (0.52) = 146 \text{ J K}^{-1} \text{ mol}^{-1}$$

Same for  $\text{N}_2(\text{g})$

$$\text{at } (500 \text{ K}) S_{\text{N}_2} = S_{\text{N}_2}(298 \text{ K}) + \int_{298}^{500} \frac{C_p}{T} dT = 191.6 \text{ J K}^{-1} \text{ mol}^{-1} + 29.13 \text{ J K}^{-1} \text{ mol}^{-1} \ln\left(\frac{500}{298}\right)$$

$$\text{at } (500 \text{ K}) S_{\text{N}_2} = 206.7 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$S_{\text{NH}_3}(500 \text{ K}) = \frac{192.45 \text{ J}}{\text{K mol}} + \frac{35.06 \text{ J}}{\text{K mol}} (0.52) = 211 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$\Delta_r S = [2(211) - 3(146) - 206.7] = -222 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$\Delta_r H^\circ(298) = \sum_{\text{prod}} \nu_i \Delta_f H_i^\circ - \sum_{\text{reactants}} \nu_i \Delta_f H_i^\circ$$

$$2 \Delta_f H_{\text{NH}_3}(500 \text{ K}) = \Delta_r H(500 \text{ K})$$

$$\Delta_r H_{\text{NH}_3}(500 \text{ K}) = 2 \left( H_{\text{NH}_3}(298 \text{ K}) \right) + \int C_p dT$$

$$\Delta_r C_p^\circ = 3(28.82) + -(2 \cdot 9.125) + 2(35.06) = -45.9 \text{ J K}^{-1} \text{ mol}^{-1}$$

$\text{H}_2$ 
 $\text{N}_2$ 
 $\text{NH}_3$

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$$\Delta_r H(298 \text{ K}) = 2 \Delta_f H(\text{NH}_3, 298) = 2(-46.11) \frac{\text{kJ}}{\text{mol}} = -92.2 \text{ kJ/mol}$$

$$\Delta_r H(500 \text{ K}) = -92.2 \text{ kJ/mol} + C_p^\circ \Delta T = -92.2 \frac{\text{kJ}}{\text{mol}} + (-45.9) 10^{-3} (202)$$

$$\Delta_r H(500 \text{ K}) = -92.2 + 9.27 = -101 \text{ kJ mol}^{-1}$$

①  $G \equiv H - TS$

$$\Delta_r G(500 \text{ K}) = \Delta_r H(500 \text{ K}) - T \Delta_r S(500 \text{ K})$$

$$\Delta_r G = -101 \text{ kJ/mol} - (500)(-222 \text{ J K}^{-1} \text{ mol}^{-1})(10^{-3})$$

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