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Homework Set 4

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Analytical Problems
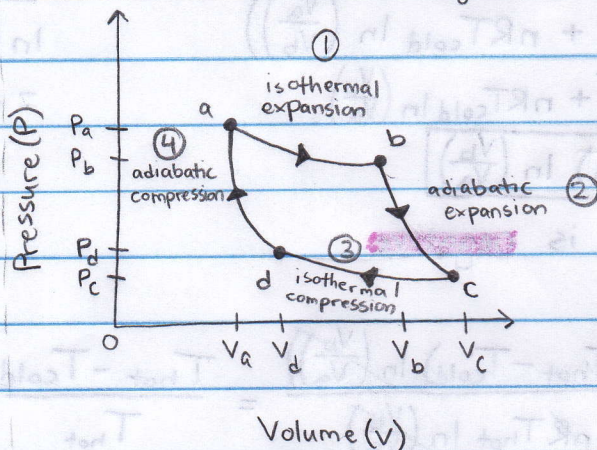
① $(V_i, T_i) \longrightarrow (V_f, T_f)$; Prove $\Delta S = 0$ for an ideal gas expanded reversibly and

↳ $V_i = V_f$

adiabatically

↳ $q_{rev} = 0$ $(T_i = T_f)$ → $dq_{rev} = 0$ for adiabatic

$$dS = \frac{dq_{rev}}{T} \rightarrow \Delta S = \int_i^f \frac{dq_{rev}}{T} = \int_i^f \frac{0}{T} = \boxed{0}$$

② Given reversible Carnot cycle,

a) $\Delta U_{cycle} = 0$

$\Delta H_{cycle} = 0$

$\Delta S_{cycle} = 0$

} because it's a cycle

b) $q_{ab} = -w_{ab} = \boxed{nRT_{hot} \ln \frac{V_b}{V_a}}$ ←

↳ $\int_{V_a}^{V_b} P dV \rightarrow \int_{V_a}^{V_b} \frac{nRT}{V} dV$

• Heat is absorbed in step 1, which

is isothermal expansion $(a \rightarrow b)$

c)   Over →

adiabatic $\rightarrow q = 0$

$w_{cycle} = -q_{cycle}$

c) $w_{cycle} = -(q_{ab} + \cancel{q_{bc}}^{0} + q_{cd} + \cancel{q_{da}}^{0})$

$= -(q_{ab} + q_{da}) = -\left(nRT_h \ln\left(\frac{V_b}{V_a}\right) + nRT_c \ln\left(\frac{V_d}{V_c}\right)\right)$

$T_{hot} V_b^{\gamma-1} = T_{cold} V_c^{\gamma-1}$ $T_{cold} V_d^{\gamma-1} = T_{hot} V_a^{\gamma-1}$

$V_c^{\gamma-1} = \dfrac{T_{hot} V_b^{\gamma-1}}{T_{cold}}$ $V_d^{\gamma-1} = \dfrac{T_{hot} V_a^{\gamma-1}}{T_{cold}}$

$\hookrightarrow \left(\dfrac{V_d}{V_c}\right)^{\gamma-1} = \left(\dfrac{T_{hot}}{T_{cold}} V_a^{\gamma-1}\right) \cdot \left(\dfrac{T_{cold}}{T_{hot} V_b^{\gamma-1}}\right)$

$\hookrightarrow \left(\dfrac{V_d}{V_c}\right)^{\gamma-1} = \left(\dfrac{V_a^{\gamma-1}}{V_b^{\gamma-1}}\right) \longrightarrow \dfrac{V_d}{V_c} = \dfrac{V_a}{V_b}$

Note:

$\ln\left(\dfrac{V_a}{V_b}\right)$

$= -\ln\left(\dfrac{V_b}{V_a}\right)$

$w_{cycle} = -\left(nRT_{hot} \ln\left(\frac{V_b}{V_a}\right) + nRT_{cold} \ln\left(\frac{V_a}{V_b}\right)\right)$

$= -nRT_{hot} \ln\left(\frac{V_b}{V_a}\right) + nRT_{cold} \ln\left(\frac{V_b}{V_a}\right)$

$= \boxed{-nR(T_{hot} - T_{cold}) \ln\left(\frac{V_b}{V_a}\right)}$

$\hookrightarrow$ Total work is **negative**

d) $\varepsilon = \dfrac{-w_{cycle}}{q_{ab}} = \dfrac{nR(T_{hot} - T_{cold}) \ln\left(\frac{V_b}{V_a}\right)}{nR T_{hot} \ln\left(\frac{V_b}{V_a}\right)} = \dfrac{T_{hot} - T_{cold}}{T_{hot}}$

$\hookrightarrow \dfrac{T_{hot} - T_{cold}}{T_{hot}} < 1$

$\hookrightarrow$ "ε" or efficiency is <u>less</u> than 1, since $(T_{hot} - T_{cold}) < T_{hot}$

so numerator always less than denominator.

T,P dependence (include only T, C_P, α, β)

③ A) $dU = \delta q + \delta w = dH - PdV - VdP$

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

$TdS - \cancel{PdV} = dH - \cancel{PdV} - VdP$

$\left(\dfrac{dH}{dT}\right)_P = C_P$
↳ constant P

$dH = TdS + VdP$

$C_P dT = TdS + \cancel{VdP} \rightarrow dP=0$

$\dfrac{TdS}{T} = \dfrac{C_P}{T}dT$

$\dfrac{dS}{dT} = \dfrac{C_P}{T}\dfrac{dT}{dT} \rightarrow \boxed{\left(\dfrac{\partial S}{\partial T}\right)_P = \dfrac{C_P}{T}}$

$\dfrac{dH}{dP} = \dfrac{TdS + VdP}{dP} \rightarrow \left(\dfrac{\partial H}{\partial P}\right)_T = T\left(\dfrac{\partial S}{\partial P}\right)_T + V$

$\dfrac{\cancel{V} - V\beta T}{\cancel{T}} = \dfrac{\cancel{T}\left(\dfrac{\partial S}{\partial P}\right)_T \cancel{+V}}{\cancel{T}} \rightarrow \left(\dfrac{\partial S}{\partial P}\right)_T = \boxed{-V\beta}$

B) Expression for dS in terms of dP and dT

$dS = \left(\dfrac{\partial S}{\partial T}\right)_P dT + \left(\dfrac{\partial S}{\partial P}\right)_T dP$
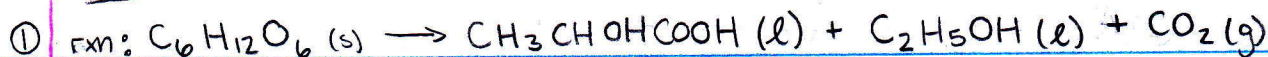
$\boxed{dS = \dfrac{C_P}{T}dT - V\beta\, dP}$

↳ parts taken from part A

→

Standard State Conditions
↳ 1 bar
→ 298.15 k

① rxn: $C_6H_{12}O_6 \, (s) \longrightarrow CH_3CHOHCOOH \, (\ell) + C_2H_5OH \, (\ell) + CO_2 \, (g)$

a) $\Delta H°_{rxn} = \left[\left(-1364 \frac{KJ}{mol}\right) + \left(-278 \frac{KJ}{mol}\right) + \left(-394 \frac{KJ}{mol}\right) \right] - \left[-1273 \frac{KJ}{mol}\right]$

$$\boxed{\Delta H°_{rxn} = -763 \text{ KJ/mol}}$$

b) $\Delta S°_{rxn} = \left[\left(192 \frac{J}{mol\,K}\right) + \left(161 \frac{J}{mol\,K}\right) + \left(213 \frac{J}{mol\,K}\right) \right] - \left[209 \frac{J}{mol\,K}\right]$

$$\boxed{\Delta S°_{rxn} = 357 \text{ J/mol K}}$$

c) $\Delta S_{surr} = \dfrac{-\Delta H_{rxn}}{T_{surr}} = \dfrac{763 \text{ KJ/mol}}{298.15 \text{ K}} = 2.56 \dfrac{KJ}{mol\,K} = \boxed{2,560 \dfrac{J}{mol\,K}}$

d) $\Delta S_{univ} = \Delta S_{rxn} - \dfrac{\Delta H_{rxn}}{T_{surr}} = 357 \dfrac{J}{mol\,K} - \dfrac{-763 \text{ KJ/mol}}{298.15 \text{ K}}$

$= 357 \dfrac{J}{mol\,K} + 2560 \dfrac{J}{mol\,K} = \boxed{2,917 \text{ J/mol K}}$

e) Under standard conditions, the reaction is **spontaneous** because ΔS_{univ} is greater than zero $(\Delta S > 0)$.

78.3°C → boils
↓
351.45 K

② **Molar enthalpy**

a)
$$\Delta H_{351.45K} = \Delta H°_{rxn} + \int_{T_i}^{T_f} C_p \, dT$$

$$C_p = \left[65.6 \frac{J}{mol\,K} + 2.38 \times 10^{-4} \, T \frac{J}{mol\,K} \right] - \left[112 \frac{J}{mol\,K} \right]$$

$$C_p = -46.4 \frac{J}{mol\,K} + 2.38 \times 10^{-4} \, T \frac{J}{mol\,K}$$

$$\Delta H_{351.45k} = 42.3 \text{ KJ/mol} + \int_{298.15K}^{351.45K} \left(-46.4 + 2.38 \times 10^{-4} T \right) \frac{J}{mol\,K} \, dT$$

→

Molar enthalpy cont'd...

a) $\Delta H_{351.45K} = 42,300 \frac{J}{mol} + \int_{298.15K}^{351.45K} -46.4 \left(\frac{J}{mol\,K}\right) dT + \int_{298.15K}^{351.45K} 2.38 \times 10^{-4} T \left(\frac{J}{mol\,K}\right) dT$

$= 42,300 \frac{J}{mol} + -46.4 T \frac{J}{mol\,K} \Big|_{298.15K}^{351.45K} + 2.38 \times 10^{-4} \frac{T^2}{2} \left(\frac{J}{mol\,K}\right) \Big|_{298.15K}^{351.45K}$

$= 42,300 \frac{J}{mol} + \left(-2473.12 \frac{J}{mol}\right) + \left(4.12 \frac{J}{mol}\right)$

$\boxed{\Delta H_{351.45K} = 39,831 \; J/mol \quad or \quad 39.831 \; kJ/mol}$

Molar entropy

b) $\Delta S_{vap} = \frac{\Delta H_{vap}}{T_{vap}} = \frac{39,831 \; J/mol}{351.45K} = \boxed{113.3 \; J/mol\,K}$

Graphical Problems

③ Equation: $S_m(T) = S_m(0K) + \int_0^{T_f} \frac{C_{p,m}^{solid} \; dT'}{T'} + \frac{\Delta H_{fus}}{T_f} + \int_{T_f}^{T_b} \frac{C_{p,m}^{liquid} \; dT'}{T'}$

$+ \frac{\Delta H_{vap}}{T_b} + \int_{T_b}^{T} \frac{C_{p,m}^{gas} \; dT'}{T'}$

$O_2 \quad S_m(0K) = 0$

a) $S_m(70K) = \int_{0K}^{23.66K} \frac{C_{p,m}^{solid\,III} \; dT}{T} + \frac{93,80J}{23.66K} + \int_{23.66}^{43.76} \frac{C_{p,m}^{solid\,II} \; dT}{T} + \frac{743\,J}{43.76K}$

$+ \int_{43.76}^{54.39} \frac{C_{p,m}^{solid\,I} \; dT}{T} + \frac{4450.0J}{54.39K} + \int_{54.39}^{70} \frac{C_{p,m}^{liquid} \; dT}{T}$

$= 8,182 \; J/K + 3.964 \; J/K + 19.61 \; J/K + 16.98 \; J/K$

$+ 10.13 \; J/K + 8.181 \; J/K + 13.434 \; J/K$

$= \boxed{80.482 \; J/mol\,K}$

b)

$$S_m(150\text{K}) = \int_0^{23.66} \frac{C_{p,m}^{\text{solid III}}}{T}\,dT + \frac{93.80\text{ J}}{23.66\text{K}} + \int_{23.66}^{43.76} \frac{C_{p,m}^{\text{solid II}}}{T}\,dT + \frac{743\text{ J}}{43.76\text{k}}$$

$$+ \int_{43.76}^{54.39} \frac{C_{p,m}^{\text{solid I}}}{T}\,dT + \frac{445.0\text{ J}}{54.39\text{k}} + \int_{54.39}^{90.20} \frac{C_{p,m}^{\text{liquid}}}{T}\,dT + \frac{6815\text{ J}}{90.20\text{k}}$$

$$+ \int_{90.20}^{150} \frac{C_{p,m}^{\text{gas}}}{T}\,dT$$

$$= 8.182 \text{ J/K} + 3.964 \text{ J/k} + 19.61 \text{ J/K} + 16.98 \text{ J/K}$$

$$+ 10.13 \text{ J/K} + 8.181 \text{ J/K} + 27.06 \text{ J/K} + 75.59 \text{ J/K}$$

$$+ 15.14 \text{ J/K}$$

$$S_m = \boxed{184.8 \text{ J/mol K}}$$

c) $\Delta S_{70\text{K} \to 150\text{K}} = 184.8 \text{ J/mol K} - 80.482 \text{ J/mol K}$

$$= \boxed{104.318 \text{ J/mol K}}$$

d) The process is spontaneous because ΔS is greater than 0.