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Problem set 4
Macroscopic Physical Chemistry
Analytical Problems:

1. ideal gas expanded reversibly, adiabatically $(V_i, T_i) \rightarrow (V_f, T_f)$ Prove $\Delta S = 0$?

Entropy Transfer takes place through reversible of heat

$$\Delta S = \frac{dq_{rev.}}{T}$$

Adiabatic Process means no heat can leave or enter the system

so, $dq_{rev} = 0$

So this means for a reversible adiabatic process $\Delta S = 0$

2. a. ΔU, ΔH, and ΔS for the entire cycle are going to be equal to zero because since they are state functions they are not path dependent, and only depend on final and initial states. For a cyclic process initial and final states are the same, therefore the change in state is zero, so all ΔU, ΔH, and $\Delta S = 0$.

b. steps: $a \rightarrow b$, Temperature is constant so $\Delta U = 0$
steps: $b \rightarrow c$ and $d \rightarrow a$ are adiabatic so $q = 0$
work done by system is carried out from heat supplied to the system

$$w = -nRT_h \ln\left(\frac{V_b}{V_a}\right) ; \Delta U = q + w = 0$$

$$q = -w = -nRT_h \ln\left(\frac{V_b}{V_a}\right) \Rightarrow q = nRT_h \ln\left(\frac{V_b}{V_a}\right)$$

Heat absorbed from step $a \rightarrow b$

c. $W_{total} = W_{ab} + \cancel{W_{bc}}^{0} + W_{cd} + \cancel{W_{da}}^{0}$

$W_{total} = -nRT_h \ln\left(\frac{V_b}{V_a}\right) - nRT_i \ln\left(\frac{V_a}{V_b}\right)$

$W_{total} = -(T_h - T_i) nR \ln\left(\frac{V_b}{V_a}\right)$

Total work is negative = system does work on surroundings

d. Efficiency (ε) $= \frac{\text{net work done by heat engine}}{\text{heat absorbed by heat engine}}$

$\varepsilon = \frac{-w}{q} = -\frac{[-(T_h - T_c) nRT \ln V_b/V_a)]}{nRT_h \ln(V_b/V_a)}$

$\varepsilon = \frac{T_h - T_c}{T_h} = 1 - \frac{T_c}{T_h}$, therefore $\varepsilon < 1$

3. a. (T, C_p, α, β), and no derivatives

$\left(\frac{\partial S}{\partial T}\right)_p$, $\left(\frac{\partial S}{\partial P}\right)_T$

$S(T, P)$

$dS = \left(\frac{\partial S}{\partial T}\right)_T dP + \left(\frac{\partial S}{\partial T}\right)_p dT$

$\left(\frac{\partial S}{\partial P}\right)_p = \frac{C_p}{T}$ and $\left(\frac{\partial S}{\partial T}\right)_p = \frac{1}{T}\left[\left(\frac{\partial H}{\partial P}\right)_T - V\right]$

Maxwell's relation: $\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_p = -V\beta$

$dS = \frac{C_p}{T} dT - \left(\frac{\partial V}{\partial T}\right)_p dP$

b. $ds = \left(\frac{\partial s}{\partial T}\right)_p dT + \left(\frac{\partial s}{\partial p}\right)_T dp$

$du = Tds - pdv = dH - pdv - vdp$

$ds = \frac{1}{T} dH - \frac{v}{T} dp$

$dH = \left(\frac{\partial H}{\partial T}\right)_p dT + \left(\frac{\partial H}{\partial p}\right)_T dp = C_p dT + \left(\frac{\partial H}{\partial p}\right)_T dp$

$ds = \frac{C_p}{T} dT + \frac{1}{T}\left[\left(\frac{\partial H}{\partial p}\right)_T - v\right] dp = \left(\frac{\partial s}{\partial T}\right)_p dT + \left(\frac{\partial s}{\partial p}\right)_T dp$

$\left(\frac{\partial s}{\partial T}\right)_p = \frac{C_p}{T}$ and $\left(\frac{\partial s}{\partial p}\right)_T = \frac{1}{T}\left[\left(\frac{\partial H}{\partial p}\right)_T - v\right]$

$\left(\frac{\partial}{\partial T}\left(\frac{\partial s}{\partial p}\right)_T\right)_p = \left(\frac{\partial}{\partial p}\left(\frac{\partial s}{\partial T}\right)_p\right)_T$

$\left(\frac{\partial}{\partial p}\left(\frac{\partial s}{\partial T}\right)_p\right)_T = \frac{1}{T}\left(\frac{\partial C_p}{\partial p}\right)_T = \frac{1}{T}\left(\frac{\partial}{\partial p}\left(\frac{\partial H}{\partial T}\right)_p\right)_T$

$\left(\frac{\partial}{\partial T}\left(\frac{\partial s}{\partial p}\right)_T\right)_p = \frac{1}{T}\left[\left(\frac{\partial}{\partial T}\left(\frac{\partial H}{\partial p}\right)_T\right)_p - \left(\frac{\partial v}{\partial T}\right)_p\right]$
$- \frac{1}{T^2}\left[\left(\frac{\partial H}{\partial p}\right)_T - v\right]$

$\frac{1}{T}\left(\frac{\partial}{\partial T}\left(\frac{\partial H}{\partial p}\right)_T\right)_p = \frac{1}{T}\left[\left(\frac{\partial}{\partial T}\left(\frac{\partial H}{\partial p}\right)_T\right)_p - \left(\frac{\partial v}{\partial T}\right)_p\right]$
$- \frac{1}{T^2}\left[\left(\frac{\partial H}{\partial p}\right)_T - v\right]$

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

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

$ds = \frac{C_p}{T} dT - v\beta dp$

$\Delta S = \int_{T_i}^{T_f} \frac{C_p}{T} dT - \int_{p_i}^{p_f} v\beta dp$

Numerical Problems:

1. $\Delta H°_{reaction} = \sum \Delta H°_f \text{ products} - \sum H°_f \text{ reactants}$

$= [(-1364 - 278 - 394) - (-1273)]$ kJ/mol

$\boxed{\Delta H°_{reaction} = -763 \text{ kJ/m}}$

$\Delta S_{reaction} = \sum S°_{products} - \sum S°_{reactants}$

$= [(192 + 161 + 213) - (209)]$ J/mol·K

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

$\Delta S_{surroundings} = \frac{-\Delta H_{reaction}}{T} = \frac{-(-763 \text{ kJ/mol})}{298 \text{ K}} = 2.56 \times 10^3 \frac{\text{J}}{\text{mol·K}}$

$\boxed{\Delta S_{surrounding} = 2.56 \times 10^3 \text{ J/mol·K}}$

$\Delta S_{universe} = \Delta S_{reaction} + \Delta S_{surroundings} = 357 \text{ J/mol·K} + 2.56 \times 10^3 \text{ J/mol·K}$

$\boxed{\Delta S_{universe} = 2,917 \text{ J/mol·K}}$

This reaction is spontaneous because $\Delta S_{universe} > 0$

2. $\Delta_{vap} H_m(25.0°C) = 42.3 \text{ kJ/mol}$

$C°_p = 65.6 \text{ J/mol·K} + 2.38 \times 10^{-4} \text{ T J mol}^{-1} \text{K}^{-2}$

$C'_p = 112. \text{ J/mol·K}$

$\Delta H_m(78.3°C) = \Delta_{vap} H_m(25°C) + \int_{298 \text{ K}}^{351.3 \text{ K}} \Delta C_p dT$ -1

$\Delta C_p = C_{p,product} - C_{p,reac} = C_p^{(prod)} - C_p^{reac}$

$= (65.6 \text{ J/mol·K} + 2.38 \times 10^{-4} \text{ T·J/mol/K}) - 112 \text{ J/mol·K}$

$= -46.4 \text{ J/mol·K} + 2.38 \times 10^{-4} \text{ J·T/mol/K}$

$\int_{298 \text{ K}}^{351.3 \text{ K}} C_p dT = \int_{298 \text{ K}}^{351.3 \text{ K}} (-46.4 \text{ J/mol·K} + 2.38 \text{ T·J/mol/K}) dT$

$$= -46.4[T]\Big|_{298K}^{351.3K} + \frac{2.38\times10^{-4}}{2}[T^2]\Big|_{298K}^{351.3K}$$

$$= -46.4(351.3-298) + 1.19\times10^{-4}(351.3^2 - 298^2)$$

$$= -2473.12\ J/mol + 4.1183\ J/mol$$

$$= -2469\ J/mol = -2.469\ kJ/mol$$

$$\boxed{\Delta H_m = -2.469\ kJ/mol}$$

$$\Delta_{vap}H_m(78.3^\circ C) = \Delta_{vap}H_m(25^\circ C) + \int_{298K}^{351.3K} C_p\,dT$$

$$= 42.3\ kJ/mol - 2.469\ \frac{kJ}{mol}$$

$$\boxed{\Delta_{vap}H_m = 39.831\ kJ/mol}$$

$$\Delta_{vap}S_m(78.3^\circ C) = \frac{\Delta_{vap}H_m(78.3^\circ C)}{T\ln(K)} = \frac{39.831\ kJ/mol}{351.3\ K}$$

$$\boxed{\Delta_{vap}S_m = 113.38\ J/mol/K}$$

Graphical Problems:

3. $S_m(70K)$, calculate $S_m(150K)$, $\Delta S_{70K\to150K}$

$$S_m^\circ(70K) = \int_0^{23.66} \frac{C_{p_m}^{solid\ III}}{T}dT + \frac{93.80\ J}{23.66\ K} + \int_{23.66}^{43.76} \frac{C_{p_m}^{solid\ II}}{T}dT + \frac{743\ J}{43.76\ K}$$

$$+ \int_{43.76}^{54.39} \frac{C_{p,m}^{solid\ I}}{T}dT + \frac{445.0\ J}{54.39\ K} + \int_{54.39}^{70.0K} \frac{C_{p_m}^{liquid}}{T}dT$$

$\frac{204.9}{298.15} = \frac{x}{70K}$

$$= 8.182\ J/K + 3.964\ J/K + 19.61\ J/K + 16.98\ J/K + 10.13\ J/K + 8.181\ J/K + 13.323$$

$$= 180.37\ J/mol\,K$$

70K → 298
80.37 → 205

$$S_m^\circ(150K) = \int_0^{23.66} \frac{C_{p,m}^{\text{solid II}}}{T}dT + \frac{93.80\,J}{23.66K} + \int_{23.76}^{43.76} \frac{C_{p,m}^{\text{solid II}}}{T} + \frac{743\,J}{43.76K}$$

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

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

$= 8.182\,J/K + 3.964\,J/K + 19.61\,J/K + 16.98\,J/K + 10.13\,J/K$
$+ 8.181\,J/K + 27.06\,J/K + 75.59\,J/K + 14.973$

$S_m^\circ(150K) = 184.67\,J/mol\,K$

$\Delta S_{70K \to 150K} = 184.67\,J/mol\,K - 80.37\,J/mol\,K$
$= 104.3\,J/mol\,K$