Problem Set 4

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Analytical Problems:

1. An ideal gas is expanded reversibly & adiabatically from $(V_i, T_i) \to (V_f, T_f)$. Prove that $\Delta S = 0$ for the expansion process.

($V_i = V_f$; $P = P_{ext}$)

$dU = dq + dw$

$= dq - P_{ext}\,dV$

for rev. path: $dU = dq_{rev} - P\,dV$

$= T\,dS - P\,dV$

$dU = dU$

$P = P_{ext}$

$dq - P_{ext}\,dV = T\,dS - P\,dV$

$dq - P\,dV = T\,dS - P\,dV$

$dS = \frac{dq}{T}$

$dq = 0 \Rightarrow \Delta S = 0$ for adiabatic

2. Given the following reversible Carnot cycle:

a) $\Delta U = 0$

$\Delta H = 0$ $\to$ it is a cycle

$\Delta S = 0$

b) Write an expression for the heat absorbed during the cycle. During which step does this occur? from a to b

$q_{cycle} = q_{ab} + q_{bc} + q_{cd} + q_{da}$

adiabatic, adiabatic

$q_{ab} = -w_{ab} = -nRT_{hot}\ln\left(\frac{V_b}{V_a}\right)$

q_{ab}: isothermal expansion; q_{cd}: isothermal compression

c) Derive an expression for the total work done by the cycle that does not include V_c & V_d using the following relationships:

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

$w_{cycle} = -(q_{cycle}) = -(q_{ab} + q_{bc}^{0} + q_{cd} + q_{da}^{0}) = -(q_{ab} + q_{cd}) = -\left(nRT_{hot}\ln\frac{V_b}{V_a} + nRT_{cold}\ln\frac{V_d}{V_c}\right)$

(q_{ab}: +, q_{cd}: −)

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

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

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

$T_{cold} < T_{hot}$

$\Rightarrow w_{cycle} = -nRT_{hot}\ln\frac{V_a}{V_b} + nRT_{cold}\ln\frac{V_a}{V_b} = nR\ln\frac{V_a}{V_b}\left(T_{cold} - T_{hot}\right) < 0$

d) Derive an expression for efficiency, $\mathcal{E}$, using answers from above. Is the $\mathcal{E}$ greater than, equal to, or less than 1? Justify your answer.

$$\mathcal{E} = \frac{-w_{cycle}}{q_{absorbed}} = \frac{-nRT_{hot}\ln\frac{V_b}{V_a}\left(T_{cold}-T_{hot}\right)}{nRT_{hot}\ln\frac{V_b}{V_a}} = \frac{T_{hot}-T_{cold}}{T_{hot}} < 1$$

as $T_{hot} > T_{cold}$, so $T_{hot} - T_{cold} < T_{hot}$

3. A) Derive expressions for the T, P dependence of entropy that only includes experimentally available measurable quantities T, C_p, α, β, & no derivatives

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

$dH = TdS + VdP$

$C_p dT = TdS + VdP^{0}$

$$\frac{dS}{dT} = \frac{C_p}{T} \rightarrow \left(\frac{\partial S}{\partial T}\right)_P = \frac{C_p}{T}$$

$$\frac{dH}{dP} = T\frac{dS}{dP} + V$$

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

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

$$\left(\frac{\partial S}{\partial P}\right)_T = -V\beta$$

B) Write an expression for dS in terms of T, C_p, α, β, & dT & dP

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

$dH = C_p dT + V(1-\beta T)dP$

$$dS = \frac{dH}{T} - \frac{V}{T}dP$$

$$dS = \frac{1}{T}\left[C_p dT + VdP - V\beta T dP\right] - \frac{V}{T}dP$$

$$dS = \frac{C_p}{T}dT - V\beta dP$$

Numerical Problems:

1. ΔH°_{rxn}, ΔS°_{rxn}, ΔS_{surr}, ΔS_{univ}, spontaneous?

$$\Delta H^{\circ}_{rxn} = (-394 - 278 - 1364) - (-1273)\ \frac{kJ}{mol} = -763\ \frac{kJ}{mol}$$

$$\Delta S^{\circ}_{rxn} = (213 + 161 + 192) - (209)\ \frac{J}{mol\,K} = 357\ \frac{J}{mol\,K}$$

$$\Delta S_{surr} = \frac{\Delta H_{rxn}}{T_{surr}} = \frac{+763\ kJ/mol}{298\ K} = 2.56\ \frac{kJ}{mol\,K} = 2560\ \frac{J}{mol\,K}$$

$$\Delta S_{univ} = \Delta S_{rxn} + \Delta S_{surr} = 357\ \frac{J}{mol\,K} - 2560\ \frac{J}{mol\,K} = 2917\ \frac{J}{mol\,K}$$

→ the reaction is spontaneous under standard conditions as $\Delta S_{univ} > 0$

2. $T_b = 78.3°C = 351.45K$

$\Delta_{vap}H_m = ?$

$\Delta_{vap}S_m = ?$

$\Delta_{vap}H_m(25.0°C) = 42.3 \frac{kJ}{mol}$

$C_p^g = 65.6 \frac{J}{molK} + 2.38 \cdot 10^{-4} T \frac{J}{molK}$

$C_p^l = 112 \frac{J}{molK}$

$\Delta H_m(78.3) = \Delta H_{298}^\circ + \int_{298}^{351.4} \Delta C_p' \, dT + C_p^g T_b =$

$= 42.3 \frac{kJ}{mol} + 112 \frac{J}{molK} \cdot (351.45 - 298)K + (65.6 \frac{J}{mol} + 2.38 \cdot 10^{-4} \cdot 351.4) 351.4$

$= 42300 \frac{J}{mol} + 5986.4 \frac{J}{mol} + 23084.5 \frac{J}{mol}$

$\Delta H = 71371 \frac{J}{mol} = 71.4 \frac{kJ}{mol}$

$\Delta_{vap}S = \frac{\Delta H_{vap}}{T_{vap}} = \frac{71.4 kJ/mol}{351.45K} = 203. \frac{J}{molK}$

Graphical problems

3. $S_m(70K)$

$S_m(150K)$

$\Delta S_{70K \to 150K}$

→ textbook p. 103 has $\int \frac{C_p}{T} dT$ values

$S_m(70K) = S_m(0K) + \int_0^{23.66} \frac{C_{p,m}}{T'} dT' + \frac{\Delta H_{fusion}}{23.66K} + \int_{23.66}^{43.76} \frac{C_{p,m}}{T'} dT' + \frac{\Delta H_{vap}}{43.76K} +$

$+ \int_{43.76}^{54.39} \frac{C_{p,m}}{T'} dT' + \frac{\Delta H_{fusion}}{54.39K} + \int_{54.39}^{70} \frac{C_{p,m}}{T'} dT' =$

$= 0 + (8.182 + 3.964 + 19.61 + 16.98) \frac{J}{K} + 10.13 \frac{J}{K} + 8.181 \frac{J}{K} +$

$+ \int_{54.39}^{70} \frac{81.268 - 1.1467 \frac{T}{K} + 6.0156 \frac{T^2}{K^2} - 6.407 \times 10^{-5} \frac{T^3}{K^3}}{T} dT =$

$= 67.047 \frac{J}{K} + 13.43 \frac{J}{K} = 80.5 \frac{J}{molK}$

$S_m(150K) = S_m(70K) + \int_{70}^{90.2} \frac{C_{p,m}}{T} dT + \frac{\Delta H_{vap}}{T_{vap}} + \int_{90.2}^{150} \frac{C_p'}{T} dT' = 94.04 + 75.59 +$

$+ \int_{90.2}^{150} \frac{32.71 - 0.04093T + 1.545 \cdot 10^{-4} T^2 - 1.819 \cdot 10^{-7} \cdot T^3}{T} dT = 169.63 + 15.14 = 184.77 \frac{J}{molK}$

$\Delta S_{70K \to 150K} = (184.8 - 80.5) \frac{J}{K} = 104.3 \frac{J}{molK}$

→ it is spontaneous as $\Delta S > 0$