

Analytical Problems:

- 1.) An ideal gas (not monoatomic) is expanded reversibly and adiabatically from $(V_i, T_i) \rightarrow (V_f, T_f)$. Prove that $\Delta S = 0$ for the expansion process.

By definition entropy change: $\int ds = \int \frac{dq}{T}$

now as the process is a reversible adiabatic process, expansion of an ideal gas from volume $V_i \rightarrow V_f$ and temperature $T_i \rightarrow T_f$

Since adiabatic system doesn't allow any transfer of heat from surrounding, so $dq = 0 \therefore \Delta S = 0$

- 2.) a) What is ΔU , ΔH , and ΔS for the entire cycle?

H (enthalpy), U (internal energy) and S (entropy) are all state functions.

For cyclic processes, the change of initial to final is 0.

$$\therefore \Delta H = 0, \Delta U = 0, \Delta S = 0$$

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

For processes $b \rightarrow c$ and $d \rightarrow a$, they are adiabatic processes, so heat is not absorbed
 $\therefore q = 0$. During the process $a \rightarrow b$, temperature is constant $\therefore \Delta U = 0$

The work done by the system is being carried out by the heat supplied to the system.

Work done by the system in reversible isothermal process = w

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

for isothermal expansion $\Delta U = q + w = 0$

$$\therefore q = -w = -\left(-nRT_{\text{hot}} \ln\left(\frac{V_b}{V_a}\right)\right) = nRT_{\text{hot}} \ln\left(\frac{V_b}{V_a}\right)$$

for isothermal compression, heat is released.

- c) Derive an expression for the total work done by system.

isothermal expansion: $w_{ab} = -nRT_{\text{hot}} \ln\left(\frac{V_b}{V_a}\right)$

adiabatic expansion: $w_{bc} = nC_V(T_{\text{cold}} - T_{\text{hot}})$

isothermal compression: $w_{cd} = -nRT_{\text{cold}} \ln\left(\frac{V_d}{V_a}\right)$

adiabatic compression: $w_{da} = nC_V(T_{\text{hot}} - T_{\text{cold}})$

Total work: $w_{\text{net}} = -nRT_{\text{hot}} \ln\left(\frac{V_b}{V_a}\right) - nRT_{\text{cold}} \ln\left(\frac{V_d}{V_c}\right)$

$$\text{Now: } T_{\text{hot}} V_a^{\gamma-1} = T_{\text{cold}} V_d^{\gamma-1} \quad T_{\text{hot}} V_B^{\gamma-1} = T_{\text{cold}} V_c^{\gamma-1}$$

$$\therefore \left(\frac{V_a}{V_b}\right)^{\gamma-1} = \left(\frac{V_d}{V_c}\right)^{\gamma-1}$$

$$\therefore \frac{V_a}{V_b} = \frac{V_d}{V_c}$$

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

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

$$T_{\text{cold}} < T_{\text{hot}} \text{ and } V_b > V_a$$

So the total work done by the system is negative.

(d) Derive an expression for the efficiency, ϵ . Is it greater than, equal, or less than 1?

$$\text{efficiency } (\epsilon) = \frac{\text{net work done by heat engine}}{\text{heat absorbed by heat engine}} = \frac{-W_{\text{sys}}}{Q}$$

$$\epsilon = \frac{nR(T_{\text{hot}} - T_{\text{cold}}) \ln \left(\frac{V_B}{V_A} \right)}{nRT_{\text{hot}} \ln \left(\frac{V_B}{V_A} \right)}$$

$$\epsilon = \frac{T_{\text{hot}} - T_{\text{cold}}}{T_{\text{hot}}} = 1 - \frac{T_{\text{cold}}}{T_{\text{hot}}} \quad \therefore T_{\text{cold}} < T_{\text{hot}} \\ \therefore \epsilon < 1$$

3) (a) Derive expressions for the T, P dependence of entropy

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

$$\text{Since } U = H - PV$$

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

$$dS = \frac{1}{T} dH - \frac{V}{T} dP$$

$$dH = \left(\frac{\partial H}{\partial T} \right)_P dT + \left(\frac{\partial H}{\partial P} \right)_T dP = C_P dT + \left(\frac{\partial H}{\partial P} \right)_T dP$$

$$dS = \frac{C_P}{T} dT + \frac{1}{T} \left[\left(\frac{\partial H}{\partial P} \right)_T - V \right] dP = \left(\frac{\partial S}{\partial T} \right)_P dT + \left(\frac{\partial S}{\partial P} \right)_T dP$$

$$\left(\frac{\partial S}{\partial T} \right)_P = \frac{C_P}{T} \quad \text{and} \quad \left(\frac{\partial S}{\partial P} \right)_T = \frac{1}{T} \left[\left(\frac{\partial H}{\partial P} \right)_T - V \right]$$

$$\text{where } \beta = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_P \quad \text{and} \quad \alpha = -\frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_T$$

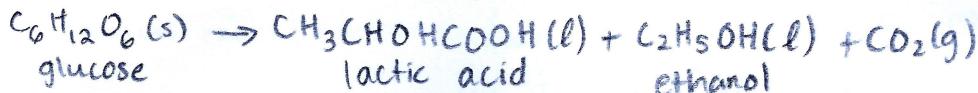
(b) Write an expression for ds

$$ds = \frac{C_P}{T} dT - \beta V dP$$

$$\Delta S = \int_{T_1}^{T_2} \frac{C_P}{T} dT - \int_{P_1}^{P_2} \beta V dP$$

Numerical Problems

1) (a) Calculate ΔH_{rxn}° , ΔS_{rxn}° , ΔS_{surr} , ΔS_{univ} . Is the reaction spontaneous?



$$\begin{aligned} \Delta H_{rxn}^\circ &= \Delta H_f^\circ(\text{lactic acid}) + \Delta H_f^\circ(\text{ethanol}) + \Delta H_f^\circ(\text{CO}_2(g)) - \Delta H_f^\circ(\text{glucose}) \\ &= -1364 \frac{\text{kJ}}{\text{mol}} + (-278 \frac{\text{kJ}}{\text{mol}}) + (-394 \frac{\text{kJ}}{\text{mol}}) - (-1273 \frac{\text{kJ}}{\text{mol}}) = -763 \frac{\text{kJ}}{\text{mol}} \end{aligned}$$

$$\begin{aligned} \Delta S_{rxn}^\circ &= \sum S_{\text{products}}^\circ - \sum S_{\text{reactants}}^\circ \\ &= \left(192 \frac{\text{J}}{\text{mol K}} + 161 \frac{\text{J}}{\text{mol K}} + 213 \frac{\text{J}}{\text{mol K}} \right) - 209 \frac{\text{J}}{\text{mol K}} = 357 \frac{\text{J}}{\text{mol K}} \end{aligned}$$

$$\Delta S_{\text{surr}} = \frac{-\Delta H_{rxn}^\circ}{T} = \frac{-(-763 \frac{\text{kJ}}{\text{mol}})}{298 \text{K}} = 2560.4 \frac{\text{J}}{\text{mol K}}$$

$$\Delta S_{\text{univ}} = \Delta S_{rxn}^\circ + \Delta S_{\text{surr}} = 357 \frac{\text{J}}{\text{mol K}} + 2560.4 \frac{\text{J}}{\text{mol K}} = 2917.4 \frac{\text{J}}{\text{mol K}}$$

The rxn is spontaneous at standard state conditions b/c $\Delta H_{rxn}^\circ < 0$ (exothermic rxn) and $\Delta S_{rxn}^\circ > 0$ (entropy inc.) $\therefore \Delta S_{\text{univ}} > 0$ and is spontaneous

2) Calculate the molar enthalpy and molar entropy of vaporization.

Given: $\Delta_{\text{vap}} H_m(25^\circ\text{C}) = 42.3 \text{ kJ/mol}$

$$C_p^g = 65.6 \frac{\text{J}}{\text{mol K}} + 2.38 \times 10^{-4} T \frac{\text{J}}{\text{mol K}^2}$$

$$C_p^l = 112 \frac{\text{J}}{\text{mol K}}$$

$$T_1 = 25^\circ\text{C} + 273 = 300 \text{ K}$$

$$T_2 = 78.3^\circ\text{C} + 273 = 351.3 \text{ K}$$

For molar enthalpy: $dH = C_p dP$

$$\text{Integrate both sides: } \int_{H_1}^{H_2} dH = \int_{T_1}^{T_2} C_p dP$$

$$= \int_{300}^{351.3} 65.6 + 2.38 \times 10^{-4} T dP$$

$$H_2 - H_1 = 65.6(T) \Big|_{300 \text{ K}}^{351.3 \text{ K}} + 2.38 \times 10^{-4} (T^2) \Big|_{300 \text{ K}}^{351.3 \text{ K}}$$

$$H_2 - 42.3 \frac{\text{kJ}}{\text{mol}} = 65.6 (351.3 - 300) \text{ K} + 2.38 \times 10^{-4} (186645 - 90000) \text{ K}^2$$

$$= 65.6 \frac{\text{J}}{\text{mol K}} (51.3 \text{ K}) + 2.38 \times 10^{-4} \frac{\text{J}}{\text{mol K}^2} (96645 \text{ K}^2)$$

$$= 3.36 \frac{\text{kJ}}{\text{mol}} + 0.023 \frac{\text{kJ}}{\text{mol}}$$

$$H_2 - 42.3 \frac{\text{kJ}}{\text{mol}} = 3.383 \frac{\text{kJ}}{\text{mol}}$$

$$H_2 = 3.383 \frac{\text{kJ}}{\text{mol}} + 42.3 \frac{\text{kJ}}{\text{mol}} = 45 \frac{\text{kJ}}{\text{mol}}$$

$$\Delta_{\text{vap}} H_m(78.3^\circ\text{C}) = 45 \frac{\text{kJ}}{\text{mol}}$$

molar entropy during the phase change: liquid \rightarrow vapour

$$\Delta S_{\text{vap}} = \frac{\Delta H_{\text{vap}}}{T_b}$$

ΔH_{vap} = molar heat of vaporization

T_b = boiling point of ethanol

$$\Delta S_{\text{vap}} = \frac{42.3 \frac{\text{kJ}}{\text{mol}}}{(78.3^\circ\text{C} + 273)} = \frac{42.3 \frac{\text{kJ}}{\text{mol}}}{351.3 \text{ K}} = 0.1204 \frac{\text{kJ}}{\text{mol K}}$$

$$\Delta_{\text{vap}} S_m(78.3^\circ\text{C}) = 120.4 \frac{\text{J}}{\text{mol K}}$$

Graphical Problems

3) Calculate $S_m(70 \text{ K})$, $S_m(150 \text{ K})$ and $\Delta S_{70 \text{ K} \rightarrow 150 \text{ K}}$. Is this process spontaneous?

$$\Delta H = T \Delta S$$

$$\Delta S_{70 \text{ K} - 150 \text{ K}} = \frac{(\Delta H)_2}{T_2} - \frac{(\Delta H)_1}{T_1} = \frac{4450}{54.39} - \frac{6815}{90.2}$$

$$= (81.81 - 75.55) \frac{\text{J}}{\text{K}}$$

$$= 6.26 \frac{\text{J}}{\text{K}}$$

$$\Delta S_{70 \text{ K} - 150 \text{ K}} = 6.26 \frac{\text{J}}{\text{K}}$$

The process is spontaneous because $\Delta S > 0$ (positive)