

$$2. \Delta H_m(78.3^\circ\text{C}) = \Delta_{\text{vap}}H_m(25^\circ\text{C}) + \int_{298\text{K}}^{351.3\text{K}} \Delta C_p dT - 1$$

$$\Delta C_p = C_{p,\text{prod}} - C_{p,\text{react}} = C_{p,\text{prod}} - C_{p,\text{react}}$$

$$= (66.6 \text{ J/mol}\cdot\text{K} + 2.38 \times 10^{-4} \text{ J/mol}\cdot\text{K}) - 112 \text{ J/mol}\cdot\text{K}$$

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

$$\int_{298\text{K}}^{351.3\text{K}} C_p dT = \int_{298\text{K}}^{351.3\text{K}} (-46.4 \text{ J/mol}\cdot\text{K} + 2.38 \times 10^{-4} \text{ J/mol}\cdot\text{K}) dT$$

$$= -46.4 [T] \Big|_{298\text{K}}^{351.3\text{K}} + \frac{2.38 \times 10^{-4}}{2} [T^2] \Big|_{298\text{K}}^{351.3\text{K}}$$

$$= -46.4 (351.3 - 298) + 1.19 \times 10^{-4} (351.3^2 - 298^2)$$

$$= -2.469 \text{ kJ/mol}$$

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

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

$$= 42.2 \text{ kJ/mol} - 2.469 \text{ kJ/mol}$$

$$\boxed{\Delta_{\text{vap}}H_m = 39.731 \text{ kJ/mol}}$$

$$\Delta_{\text{vap}}S_m(78.3^\circ\text{C}) = \frac{\Delta_{\text{vap}}H_m(78.3^\circ\text{C})}{T_b \ln(K)} = \frac{39.731 \text{ kJ/mol}}{351.3\text{K}}$$

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

Graph problem

$$\Delta H = T \Delta S \quad \Delta S_{70\text{K} \rightarrow 150\text{K}} = \frac{(\Delta H_2)}{T_2} - \frac{(\Delta H_1)}{T_1}$$

$$\frac{4450.0}{54.39} - \frac{6815.0}{90.26} = 6.26 \text{ J/K}$$

$$\boxed{\Delta S_{70\text{K} \rightarrow 150\text{K}} = 6.26 \text{ J/K}}$$

The process is spontaneous.

$$3. (a) dS = \left(\frac{\partial S}{\partial P}\right)_T dP + \left(\frac{\partial S}{\partial T}\right)_P dT$$

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

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

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

$$(b) dS = \frac{C_P}{T} dT - V\beta dP$$

$$\Delta S = \int_{T_i}^{T_f} \frac{C_P}{T} dT - \int_{P_i}^{P_f} V\beta dP$$

Numerical problems

$$1. \Delta H^\circ_{\text{rxn}} = \sum \Delta H^\circ_{F, \text{prod}} - \sum \Delta H^\circ_{F, \text{react}} \\ = (-1364 - 218 - 394) - (-1273) \quad \text{kJ/mol} \\ = -763 \text{ kJ/mol}$$

$$\Delta S^\circ_{\text{rxn}} = \sum S^\circ_{\text{prod}} - \sum S^\circ_{\text{react}} \\ = (192 + 161 + 213) - (209) \quad \text{J/mol K} \\ = 357 \text{ J/mol K}$$

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

$$\Delta S_{\text{univ}} = \Delta S_{\text{rxn}} + \Delta S_{\text{sur}} = 357 \frac{\text{J}}{\text{mol K}} + 2.56 \times 10^3 \frac{\text{J}}{\text{mol K}} \\ = 2917 \text{ J/mol K}$$

the reaction is spontaneous because $\Delta S_{\text{univ}} > 0$

problem set 4

Kylee McDonald

Analytical problems

1. Reversible: entropy transfers through heat interactions

$$\Delta S = \frac{dq_{\text{reversible}}}{T}$$

adiabatic: no heat enters or leaves the system
so $q = 0$

thus, for a reversible adiabatic process: $\Delta S = 0$

2. (a) $\Delta U = 0$
 $\Delta H = 0$
 $\Delta S = 0$ } all three are state functions and in a cyclic process initial and final states are the same. Thus, all state functions are 0

(b) $a \rightarrow b$ $T = \text{constant}$. $\Delta U = 0$
 $b \rightarrow c$ and $d \rightarrow a$ adiabatic: $q = 0$

$$W = -nRT_h \ln\left(\frac{V_b}{V_a}\right) \quad \Delta U = q$$

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

from $a \rightarrow b$ heat is absorbed

$$(c) W_{\text{tot}} = W_{ab} + W_{cd} + W_{da} + W_{bc}$$

$$W_{\text{tot}} = -nRT_h \ln\left(\frac{V_b}{V_a}\right) - nRT_c \ln\left(\frac{V_a}{V_b}\right)$$

$$W_{\text{tot}} = -(T_h - T_c) nR \ln\left(\frac{V_b}{V_a}\right)$$

total work is negative

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

$$\epsilon = \frac{W}{q} = \frac{-[(T_h - T_c) nR \ln\left(\frac{V_b}{V_a}\right)]}{nRT_h \ln\left(\frac{V_b}{V_a}\right)}$$

$$\Rightarrow \epsilon = \frac{T_h - T_c}{T_h} = 1 - \frac{T_c}{T_h}$$