Homework 4 Solutions

1. $U = U(0) + (3/2)nRT$ $\quad$ U is independent of V, p $\quad$ $(\partial U/\partial V)_T = 0$ and $(\partial U/\partial p)_T = 0$
$H = U + pV = U + nRT = U(0) + (5/2)nRT$ $\quad$ $(\partial H/\partial V)_T = 0$ and $(\partial H/\partial p)_T = 0$

2. The isothermal Joule-Thompson coefficient is
$\mu_T = (\partial H/\partial p)_T = -\mu C_p = (-1.11 \text{ K atm}^{-1}) \times (37.11 \text{ J K}^{-1} \text{ mol}^{-1}) = -41.2 \text{ J atm}^{-1} \text{ mol}^{-1}$
If this coefficient is constant in an isothermal Joule-Thompson experiment, then the heat which must be supplied to maintain constant temperature is ΔH:
$(\Delta H/n) / \Delta p = -41.2 \text{ J atm}^{-1} \text{ mol}^{-1}$ $\quad$ $\Delta H = (-41.2 \text{ J atm}^{-1} \text{ mol}^{-1})n\Delta p$
$\Delta H = (-41.2 \text{ J atm}^{-1} \text{ mol}^{-1}) \times (12.0 \text{ mol}) \times (-55 \text{ atm}) = 27.2 \text{ kJ}$

3. $V_f = 2\ V_i$ $\quad$ $(T_f/T_i)^c = (V_i/V_f)$ $\quad$ $c \ln(T_f/T_i) = \ln(V_i/V_f)$ $\quad$ $c = \ln(V_i/V_f) / \ln(T_f/T_i)$
$c = \ln(0.5) / \ln(248.44 \text{ K} / 298.15 \text{ K}) = 3.800$
$c = C_{V,m} / R$ $\quad$ $C_{V,m} = c\times R = 3.800 \times (8.314 \text{ J K}^{-1} \text{ mol}^{-1}) = 31.595 \text{ J K}^{-1} \text{ mol}^{-1}$
$p_i V_i^{\gamma} = p_f V_f^{\gamma}$ $\quad$ $\ln(p_i/p_f) = \gamma \ln(V_f/V_i)$ $\quad$ $\gamma = \ln(p_i/p_f) / \ln(V_f/V_i)$
$\gamma = \ln(1522.2 \text{ Torr} / 613.85 \text{ Torr}) / \ln(2) = 1.3102$
$\gamma = C_{p,m}/C_{V,m}$ $\quad$ $C_{p,m} = \gamma\times C_{V,m} = 1.3102\times(31.595 \text{ J K}^{-1} \text{ mol}^{-1}) = 41.396 \text{ J K}^{-1} \text{ mol}^{-1}$

4. (a) We assume that the ice melts reversibly under the conditions described, therefore
$\Delta S_{\text{ice}} = q_{\text{rev}}/T = 33 \text{ kJ} / 273 \text{ K} = +0.12 \text{ kJ K}^{-1}$
(b) $\Delta S_{\text{water}} = \Delta S_{\text{sur}} = q_{\text{sur}}/T = -33 \text{ kJ} / 273 \text{ K} = -0.12 \text{ kJ K}^{-1}$

5. $q = nC_{p,m}\Delta T$
$q = (1.25\times10^3 \text{ g} / 26.98 \text{ g mol}^{-1})\times(24.35 \text{ J K}^{-1} \text{ mol}^{-1})\times(-40 \text{ K}) = -45.1 \text{ kJ}$
$\Delta S = C_p\ln(T_2/T_1) = nC_{p,m}\ln(T_2/T_1) = (1.25\times10^3 \text{ g} / 26.98 \text{ g mol}^{-1})\times(24.35 \text{ J K}^{-1} \text{ mol}^{-1})\times\ln(260 \text{ K} / 300 \text{ K}) = -161.4 \text{ J K}^{-1}$

6. $\Delta S = nR \ln(V_f/V_i)$ (Assuming gas is perfect)
$\Delta S = 8.31 \text{ J K}^{-1} \text{ mol}^{-1} \times \ln(4.5 \text{ L}/1.5 \text{ L}) = +9.1 \text{ J K}^{-1} \text{ mol}^{-1}$

7. (a) According to Trouton's rule, which applies well to hydrocarbons, such as octane,
$\Delta_{\text{vap}}S = +85 \text{ J K}^{-1} \text{ mol}^{-1}$
(b) $\Delta_{\text{vap}}S = \Delta_{\text{vap}}H / T_b = +85 \text{ J K}^{-1} \text{ mol}^{-1}$
$\Delta_{\text{vap}}H = \Delta_{\text{vap}}S\times T_b = (+85 \text{ J K}^{-1} \text{ mol}^{-1})\times(399 \text{ K}) = +33.9 \text{ kJ K}^{-1} \text{ mol}^{-1}$

8. (a) $\Delta_r S^{\varnothing} = 2\ S_m^{\varnothing}(\text{CH}_3\text{COOH, l}) - 2\ S_m^{\varnothing}(\text{CH}_3\text{CHO, g}) - S_m^{\varnothing}(\text{O}_2\text{, g}) = [(2\times159.8) - (2\times250.3) - 205.14] \text{ J K}^{-1} \text{ mol}^{-1} = -386.1 \text{ J K}^{-1} \text{ mol}^{-1}$
(b) $\Delta_r S^{\varnothing} = 2\ S_m^{\varnothing}(\text{AgBr, s}) + S_m^{\varnothing}(\text{Cl}_2\text{, g}) - 2\ S_m^{\varnothing}(\text{AgCl, s}) - S_m^{\varnothing}(\text{Br}_2\text{, l}) = [(2\times107.1) + 223.07 - (2\times96.2) - 152.23] \text{ J K}^{-1} \text{ mol}^{-1} = +92.6 \text{ J K}^{-1} \text{ mol}^{-1}$
(c) $\Delta_r S^{\varnothing} = S_m^{\varnothing}(\text{HgCl}_2\text{, l}) - S_m^{\varnothing}(\text{Hg, l}) - S_m^{\varnothing}(\text{Cl}_2\text{, g}) = [146.0 - 76.02 - 223.07] \text{ J K}^{-1} \text{ mol}^{-1} = -153.1 \text{ J K}^{-1} \text{ mol}^{-1}$
(d) $\Delta_r S^{\varnothing} = S_m^{\varnothing}(\text{Zn}^{2+}\text{, aq}) + S_m^{\varnothing}(\text{Cu, s}) - S_m^{\varnothing}(\text{Zn, s}) - S_m^{\varnothing}(\text{Cu}^{2+}\text{, aq}) = [-112.1 + 33.15 - 41.63 - (-99.6)] \text{ J K}^{-1} \text{ mol}^{-1} = -21.0 \text{ J K}^{-1} \text{ mol}^{-1}$

(e) $\Delta_r S^{\varnothing} = 12\, S_m^{\varnothing}(CO_2, s) + 11\, S_m^{\varnothing}(H_2O, l) - S_m^{\varnothing}(C_{12}H_{22}O_{11}, s) - 12\, S_m^{\varnothing}(O_2, g) =$ $[(12\times213.74) + (11\times69.91) - 360.2 - (12\times205.14)]$ J K^{-1} mol^{-1} = +512.0 J K^{-1} mol^{-1}

9. $$\Delta S_m = \int_{T_1}^{T_2} \frac{C_{p,m}dT}{T} = \int_{T_1}^{T_2} \frac{(a+bT)dT}{T} = a\ln\left(\frac{T_2}{T_1}\right) + b(T_2 - T_1)$$

$a = 91.47$ J K^{-1} mol^{-1} $\qquad$ $b = 7.5\times10^{-2}$ J K^{-2} mol^{-1}

$\Delta S_m = (91.47$ J K^{-1} $mol^{-1}) \times \ln(330$ K $/273$ K$) + (7.5\times10^{-2}$ J K^{-2} $mol^{-1}) \times (330$ K $-$ 273 K$) = 10.7$ J K^{-1} mol^{-1}