

Anas Saleh

Homework Set 4

Thermodynamics

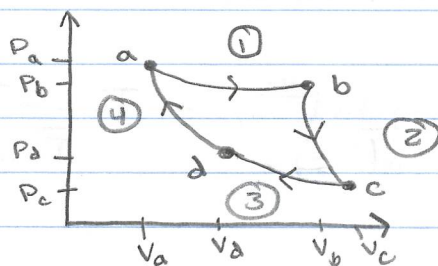
Due: 24-Mar-2020

Analytical Problems

- ① $(V_i, T_i) \rightarrow (V_f, T_f)$; Prove $\Delta S = 0$ for an ideal gas expanded reversibly and adiabatically.

$$dS = \frac{\delta q_{rev}}{T} \rightarrow \Delta S = \int_i^f \frac{\delta q_{rev}}{T} = \int_i^f \frac{0}{T} = 0$$

- ② Given Reversible Carnot cycle,



- 1) Isothermal Expansion
- 2) Adiabatic Expansion
- 3) Isothermal Compression
- 4) Adiabatic Compression

2a) $\Delta U_{cycle} = 0$

$\Delta H_{cycle} = 0$

$\Delta S_{cycle} = 0$

Derived from $\int_{V_a}^{V_b} P dV \rightarrow \int_{V_a}^{V_b} \frac{nRT}{V} dV$

2b) $q_{ab} = -w_{ab} = nRT_{hot} \ln \frac{V_b}{V_a}$

• Heat is absorbed in step 1, which is isothermal expansion (a → b)

2c) $W_{cycle} = -(q_{ab} + q_{bc} + q_{cd} + q_{da})$

$= -(q_{ab} + q_{da}) = -(nRT_{hot} \ln \frac{V_b}{V_a} + nRT_{cold} \ln \frac{V_d}{V_c})$

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

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

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

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

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

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

$$W_{cycle} = -(nRT_{hot} \ln\left(\frac{V_b}{V_a}\right) + nRT_{cold} \ln\left(\frac{V_a}{V_b}\right))$$

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

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

→ Total work is negative

d) $\epsilon = \frac{-W_{cycle}}{Q_{ab}} = \frac{nR(T_{hot} - T_{cold}) \ln\left(\frac{V_a}{V_b}\right)}{nRT_{hot} \ln\left(\frac{V_b}{V_a}\right)} = \frac{T_{hot} - T_{cold}}{T_{hot}}$

is always less than 1 because the numerator is always less than denominator.

→ $\frac{T_{hot} - T_{cold}}{T_{hot}} < 1$

3A) $du = dq + dw = dH - PdV - VdP$

$$du = Tds - PdV = dH - PdV - VdP$$

$$Tds - PdV = dH - PdV - VdP$$

$$dH = Tds + VdP$$

$$C_p dT = Tds + VdP \rightarrow dP = 0$$

$$\frac{Tds}{T} = \frac{C_p}{T} dT$$

$$\frac{ds}{dT} = \frac{C_p}{T} \frac{dT}{dT} \rightarrow \left(\frac{ds}{dT}\right)_P = \frac{C_p}{T}$$

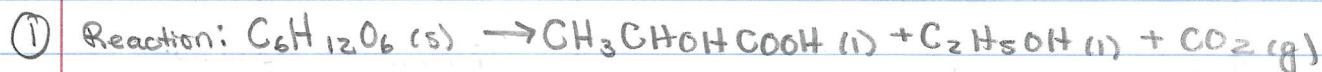
$$dH = \frac{Tds + VdP}{dP} \rightarrow \left(\frac{dH}{dP} \right)_T = T \left(\frac{ds}{dP} \right)_T + V$$

$$V - \frac{V\beta T}{T} = \frac{T \left(\frac{ds}{dP} \right)_T}{T} + V \rightarrow \left(\frac{ds}{dP} \right)_T = -V\beta$$

$$3B) ds = \left(\frac{ds}{dT} \right)_P dT + \left(\frac{ds}{dP} \right)_T dP$$

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

Numerical Problems



$$1a) \Delta H^\circ_{rxn} = \left[(-1364 \frac{kJ}{mol}) + (-278 \frac{kJ}{mol}) + (-394 \frac{kJ}{mol}) \right] - \left[-1273 \frac{kJ}{mol} \right]$$

$$\Delta H^\circ_{rxn} = -763 \text{ kJ/mol}$$

$$1b) \Delta S^\circ_{rxn} = \left[(192 \frac{J}{mol \cdot K}) + (161 \frac{J}{mol \cdot K}) + (213 \frac{J}{mol \cdot K}) \right] - \left[269 \frac{J}{mol \cdot K} \right]$$

$$\Delta S^\circ_{rxn} = 357 \text{ J/mol} \cdot K$$

$$1c) \Delta S_{surr} = -\frac{\Delta H_{rxn}}{T_{surr}} = \frac{763 \text{ kJ/mol}}{298.15 \text{ K}} = \frac{2.36 \text{ kJ}}{\text{mol} \cdot K} = 2360 \text{ J/mol} \cdot K$$

$$1d) \Delta S_{univ} = \Delta S_{rxn} - \frac{\Delta H_{rxn}}{T_{surr}} = 357 \text{ J/mol} \cdot K - \frac{-763 \text{ kJ/mol}}{298.15 \text{ K}}$$

$$\Delta S_{univ} = 2917 \text{ J/mol} \cdot K$$

1e) The rxn is spontaneous because ΔS_{univ} is greater than zero.

$$2a) \Delta H_{351.45K} = \Delta H_{rxn}^{\circ} + \int_{T_i}^{T_f} C_p dT$$

$$C_p = \left[65.6 \frac{J}{mol \cdot K} + 2.38 \times 10^{-4} T \frac{J}{mol \cdot K} \right] - \left[112 \frac{J}{mol \cdot K} \right]$$

$$C_p = -46.4 \frac{J}{mol \cdot K} + 2.38 \times 10^{-4} T \frac{J}{mol \cdot K}$$

$$\Delta H_{351.45K} = 42.3 \text{ kJ/mol} + \int_{298.15K}^{351.45K} (-46.4 + 2.38 \times 10^{-4} T) \frac{J}{mol \cdot K} dT$$

$$\begin{aligned} \Delta H_{351.45K} &= 42,300 \frac{J}{mol} + \int_{298.15K}^{351.45K} -46.4 \left(\frac{J}{mol \cdot K} \right) dT + \int_{298.15K}^{351.45K} 2.38 \times 10^{-4} T \left(\frac{J}{mol \cdot K} \right) dT \\ &= 42,300 \frac{J}{mol} + -46.4 T \frac{J}{mol \cdot K} \Big|_{298.15K}^{351.45K} + 2.38 \times 10^{-4} \frac{T^2}{2} \left(\frac{J}{mol \cdot K} \right) \Big|_{298.15K}^{351.45K} \\ &= 42,300 \frac{J}{mol} + (-2473.12 \frac{J}{mol}) + (4.12 \frac{J}{mol}) \end{aligned}$$

$$\Delta H_{351.45K} = 39831 \text{ J/mol}$$

$$2b) \Delta S_{vap} = \frac{\Delta H_{vap}}{T_{vap}} = \frac{39,831 \text{ J/mol}}{351.45K} = 113.3 \text{ J/mol} \cdot K$$

Graphical Problems

$$\textcircled{3} S_m(T) = S_m(0K) + \int_0^{T_f} \frac{C_{p,m}^{\text{solid}} dT}{T} + \frac{\Delta H_{fus}}{T_f} + \int_{T_f}^{T_b} \frac{C_{p,m}^{\text{liquid}} dT}{T}$$

$$+ \frac{\Delta H_{vap}}{T_b} + \int_{T_b}^T \frac{C_{p,m}^{\text{gas}} dT}{T}$$

$$O_2 S_m(0K) = 0$$

$$\begin{aligned} 3a) S_m(70K) &= \int_{0K}^{23.66K} \frac{C_{p,m}^{\text{Solid III}} dT}{T} + \frac{93.80 \text{ J}}{23.66K} + \int_{23.66K}^{43.76K} \frac{C_{p,m}^{\text{Solid II}} dT}{T} + \frac{743 \text{ J}}{43.76K} \\ &\quad + \int_{43.76K}^{54.39K} \frac{C_{p,m}^{\text{Solid I}} dT}{T} + \frac{4450.0 \text{ J}}{54.39K} + \int_{54.39K}^{70K} \frac{C_{p,m}^{\text{liquid}} dT}{T} \end{aligned}$$

$$= 8.182 \text{ J/K} + 3.964 \text{ J/K} + 19.61 \text{ J/K} + 16.98 \text{ J/K}$$

$$+ 10.13 \text{ J/K} + 8.181 \text{ J/K} + 13.434 \text{ J/K}$$

$$= 80.482 \text{ J/mol} \cdot K$$

$$\begin{aligned}
 3b) S_m(150\text{ K}) &= \int_0^{23.66} \frac{C_{p,m}^{\text{Solid III}}}{T} dT + \frac{93.80\text{ J}}{23.66\text{ K}} + \int_{23.66}^{43.76} \frac{C_{p,m}^{\text{Solid II}}}{T} dT + \frac{743\text{ J}}{43.76\text{ K}} \\
 &+ \int_{43.76}^{54.39} \frac{C_{p,m}^{\text{Solid I}}}{T} dT + \frac{445.0\text{ J}}{54.39\text{ K}} + \int_{54.39}^{90.20} \frac{C_{p,m}^{\text{Liquid}}}{T} dT + \frac{6815\text{ J}}{90.20\text{ K}} \\
 &+ \int_{90.20}^{150} \frac{C_{p,m}}{T} dT \\
 &= (8.182 + 3.964 + 19.61 + 16.98 + 10.13 + 8.181 + 27.06 + 75.59 + 1514) \text{ J/K} \\
 &= 184.8 \text{ J/mol K}
 \end{aligned}$$

$$3c) \Delta S_{70\text{ K} \rightarrow 150\text{ K}} = 184.8 \text{ J/mol K} - 80.482 \text{ J/mol K} = 104.318 \text{ J/mol K}$$

3d) ΔS is greater than 0 so must be spontaneous,