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Problem set 4

Due: 03-2~~4~~-20
Physical chemistry

Analytical Problems:

1. For any reversible adiabatic process $q_{reversible} = 0$ so...

$$\Delta S = \int (dq_{reversible}/T) = 0$$

for cyclic $\left(\Delta S = \oint (dq_{reversible}/T) = 0 \right)$

$\Delta U = 0$

$$q_{reversible} = -w_{reversible} = nRT \ln \frac{V_f}{V_i} \text{ and}$$

$$\Delta S = \int \frac{dq_{reversible}}{T} = \frac{1}{T} \times q_{reversible} = nR \ln \frac{V_f}{V_i}$$

2. (a) $\left.\begin{array}{l} \Delta U = 0 \\ \Delta H = 0 \\ \Delta S = 0 \end{array}\right\}$ since it is cyclic state function!

(b) $$\varepsilon = -\frac{w_{cycle}}{q_{ab}} = \frac{q_{ab} + q_{cd}}{q_{ab}}$$

$$= 1 - \frac{|q_{cd}|}{|q_{ab}|} < 1 \text{ b/c } |q_{ab}| > |q_{cd}|, q_{ab} > 0, \text{ and } q_{cd} < 0$$

in step a—b heat is absorbed

(c) $T_{hot} V_b^{\gamma-1} = T_{cold} V_c^{\gamma-1}$ and $T_{cold} V_d^{\gamma-1} = T_{hot} V_a^{\gamma-1}$

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

the total work is (−)

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

$$\varepsilon = \frac{|w_{cycle}|}{q_{ab}} = \frac{T_{hot} - T_{cold}}{T_{hot}} = 1 - \frac{T_{cold}}{T_{hot}} < 1$$

$$\varepsilon_{irreversible} < \varepsilon_{reversible} < 1$$

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

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

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

Clausius ineq $dS > \frac{dq}{T}$

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

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