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Macro. P. Chem.

March 24th, 2020
HW #4

1.) $\Delta U = q + w$

$\partial U = \partial q + \partial w$

$\partial q = \partial U + PdV$

$\partial q = nC_v dT + nRT \frac{dV}{V}$

$\partial q/T = nC_v \, dT/T + nR \, dV/V$

$\int dS = \int_{T_i}^{T_f} nC_v \, dT/T + \int_{V_i}^{V_f} nR \, dV/V$

$\Delta S = nC_v \ln\left[\frac{T_f}{T_i}\right] + nR \ln\left[\frac{V_f}{V_i}\right]$

* $\partial U = nC_v dT$

* $PV = nRT$

* $dS = \frac{dq}{T}$

Adiabatic change
$dq = 0$

$dU = dw$

$C_v dT = -PdV$

*Again $PV = nRT$

$\int_{T_i}^{T_f} C_v \, dT/T = \int_{V_i}^{V_f} -R \, dV/V$

$C_v \ln\left[\frac{T_f}{T_i}\right] = -R \ln\left[\frac{V_f}{V_i}\right]$

* $\ln\left[\frac{T_f}{T_i}\right] = \ln\left[\frac{V_f}{V_i}\right](-R/C_v)$

$\Delta S = nC_v \ln\left[\frac{T_f}{T_i}\right] + nR \ln\left[\frac{V_f}{V_i}\right]$

$\Delta S = n\cancel{C_v} \ln\left[\frac{V_f}{V_i}\right](-R/\cancel{C_v}) + nR \ln\left[\frac{V_f}{V_i}\right]$

$\Delta S = -nR \ln\left[\frac{V_f}{V_i}\right] + nR \ln[V_f/V_i]$

$\Delta S = 0$

2.) a.) $\Delta U = 0$ All state functions
$\Delta H = 0$ in a cyclic process
$\Delta S = 0$

b.) $\Delta U = q + w$

$\Delta U = \emptyset$ isothermal (expansion) state

$q = -w$

$w_{ab} = -nRT_{hot} \ln V_b/V_a$

From $a \to b$
(isothermal expansion)
heat is absorbed

Not including V_c & V_d

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

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

c.) isothermal expansion $-w_{ab} = -nRT_{hot}\ln V_b/V_a$

adiabatic expansion $-w_{bc} = nC_{v,m}(T_{cold} - T_{hot})$

isothermal compression $-w_{cd} = -nRT_{cold}\ln V_d/V_c$

adiabatic compression $-w_{da} = nC_{v,m}(T_{hot} - T_{cold})$

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

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

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

$W = -nRT_{hot}\ln(V_b/V_a) - nRT_{cold}(V_a/V_b)$

$W = -nRT_{hot}\ln(V_b/V_a) + nRT_{cold}(V_b/V_a)$

$W = nR(T_{cold} - T_{hot})\ln(V_b/V_a)$

where $T_{cold} < T_{hot}$ and $V_b > V_a$

therefore total work is negative

d.) $\varepsilon = |w_{cycle}|/q_{ab}$

$$\varepsilon = \frac{\cancel{nR}(T_{cold} - T_{hot})\cancel{\ln(V_b/V_a)}}{\cancel{nR}T_{hot}\cancel{\ln(V_b/V_a)}}$$

$$\varepsilon = \frac{T_{cold} - T_{hot}}{T_{hot}} = 1 - \frac{T_{cold}}{T_{hot}}$$

$\varepsilon < 1$ b/c $T_{hot} > T_{cold}$

$$\beta = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P$$

$$\alpha = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T$$

3.) A.)

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

Maxwell's Relation:

$$\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P = \beta V \quad \& \left(\frac{\partial S}{\partial T}\right)_P = \frac{C_P}{T}$$

$$dS = C_P/T \, dT - \left(\frac{\partial V}{\partial T}\right)_P dP$$

B.) $dS = C_P/T \, dT - \beta V \, dP$

$$\Delta S = \int_{T_i}^{T_f} C_P/T \, dT - \int_{V_i}^{P_f} \beta V \, dP$$

1.) $\Delta H^\circ_{rxn} = [\Delta H_f^\circ(\text{lactic acid}) + \Delta H_f^\circ(\text{ethanol}) + \Delta H_f^\circ(CO_2)] - \Delta H_f^\circ(\text{glucose})$

$\Delta H^\circ_{rxn} = [-1364\ kJ/mol + -278\ kJ/mol + -394\ kJ/mol] + +1273\ kJ/mol$

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

ΔS°_{rxn} = same formula Σ products − reactants

$192\ J/mol\,K + 161\ J/mol\,K + 213\ J/mol\,K - 209\ J/mol\,K$

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

$\Delta S_{surr} = \frac{-\Delta H_{rxn}}{T} = \left(\frac{763\ kJ/mol \times 1000\ J/kJ}{298.15K}\right)$

$\Delta S_{surr} = 2559\ J/mol\,K$

$\Delta S_{univ} = \Delta S_{rxn} + \Delta S_{surr}$

$= 357\ J/mol\,K + 2559\ J/mol\,K$

$= 2916\ J/mol\,K$

* The reaction is spontaneous at standard conditions b/c Δenthalpy rxn is negative → meaning exothermic reaction and entropy change rxn is positive (increasing)

$\Delta H(-)$
$\Delta S(+)$

2.) $\int_{H_i}^{H_f} dH = \int_{T_i}^{T_f} C_P dT$

$$\int dH = \int_{300K}^{351.3K} 65.6\ J/mol\,K + 2.38\times10^{-4}\ T\ J/mol\,K\ dT$$

molar enthalpy $H_2 - 42.3\ kJ/mol = 65.6(351.3-300) + 2.38\times10^{-4}(186645 - 90000)$

$H_2 - 42.3\ kJ/mol = 3.38\ kJ/mol$

$H_2 = 45.68\ kJ/mol$

$l \to g$

Boiling Temp

Molar entropy

$\Delta S_{vap} = \Delta H_{vap} / T_b$

$\Delta S_{vap} = 42.3 \text{ kJ/mol} / 351.3 \text{ K}$

$\Delta S_{vap} = 120.4 \text{ J/mol K}$

3.) $\Delta S_m (70K)$

$\Delta S_m (150K)$

70K 150K

$$\Delta S_{70K \to 150K} = \left(\frac{\Delta H_2}{T_2}\right) - \left(\frac{\Delta H_1}{T_1}\right)$$

$$6.26 \text{ J/mol K} \quad \left(\frac{4450}{54.39}\right) - \left(\frac{6815.0}{90.2}\right)$$

$$81.81 - 75.55$$