Kevin Harry

3-24-20

5.12 Using the fact that S is a state function to Determine the Dependence of S on V and T

$dS = \left(\frac{\partial S}{\partial T}\right)_V dT + \left(\frac{\partial S}{\partial V}\right)_T dV$ S=entropy T=temperature V=volume

where $\left(\frac{\partial S}{\partial T}\right)_V = \frac{C_V}{T}$ and $\left(\frac{\partial S}{\partial V}\right)_T = \frac{1}{T}\left[P + \left(\frac{\partial U}{\partial V}\right)_T\right] = \left(\frac{\partial P}{\partial T}\right)_V = \frac{\beta}{\kappa}$

C_V = heat capacity (constant volume) P=pressure U=energy

The second law of thermodynamics is applied here.

5.13 The Dependence of S on T and P

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

C_P = heat capacity (constant pressure)

The second law of thermodynamics is applied here.

6.1 The Gibbs Energy and the Helmholtz Energy

$\Delta G = \Delta H - T\Delta S$ G=Gibbs energy H=enthalpy

$\Delta A = \Delta U - T\Delta S$ A=Helmholtz energy

Both equations involve reactions

The second law of thermodynamics is applied here.

6.2 The Differential Forms of U, H, A, G

$H = U + PV \quad A = U - TS \quad G = H - TS$

$dU = TdS - PdV$

$dH = TdS + VdP$

$dA = -SdT - PdV$

$dG = -SdT + VdP$

$\left(\frac{\partial U}{\partial S}\right)_V = T \quad \left(\frac{\partial U}{\partial V}\right)_S = -P \quad \left(\frac{\partial A}{\partial T}\right)_V = -S \quad \left(\frac{\partial A}{\partial V}\right)_T = -P$

$\left(\frac{\partial H}{\partial S}\right)_P = T \quad \left(\frac{\partial H}{\partial P}\right)_S = V \quad \left(\frac{\partial G}{\partial T}\right)_P = -S \quad \left(\frac{\partial G}{\partial P}\right)_T = V$

The second law of thermodynamics is applied here.

6.3 The Dependence of the Gibbs and Helmholtz Energies on P, V, and T

$\left(\frac{\partial A}{\partial T}\right)_V = -S \quad \left(\frac{\partial A}{\partial V}\right)_T = -P \quad \left(\frac{\partial G}{\partial T}\right)_P = -S \quad \left(\frac{\partial G}{\partial P}\right)_T = V$

Gibbs-Helmholtz equation $\frac{d\left(\frac{1}{T}\right)}{dT} = -\frac{1}{T^2}$

$\left(\frac{\partial (G/T)}{\partial (1/T)}\right)_P = H$

The second law of thermodynamics is applied here.

Reading HW 6

Kevin Murcy

3-23-20

① $\frac{q_{ab}}{T_a} + \frac{q_{cd}}{T_c} = \oint \frac{dq_{rev}}{T} = 0$ $\qquad \oint \frac{dq_{rev}}{T} = \int_i^f \frac{dq_{rev}}{T} = \Delta S$

② $ab \rightarrow q^+$
$bc \rightarrow q = 0$
$cd \rightarrow q^-$
$ad \rightarrow q = 0$

$q_{ab} = -q_{cd}$

$\Delta U = 0, \Delta H = 0, \Delta S = 0$

ⓑ That $V_b \neq$ This occurs at step ab.

ⓒ $w_{cycle} = -(q_{ab} + q_{cd})$ The total work is 0.

ⓓ $\varepsilon = -\left(\frac{w_{cycle}}{q_{ab}}\right)$ The efficiency has to be less than 1 because a cyclic process can't convert heat to work with 100% efficiency.

③ $\left(\frac{\partial S}{\partial T}\right)_P = \frac{C_P}{T}$ $\qquad \left(\frac{\partial S}{\partial P}\right)_T = -V\beta$

ⓑ $dS = \frac{C_P}{T} dT - V\beta dP$

④ $\Delta H°_{rxn} = (-1{,}364\ kJ/mol + (-278\ kJ/mol) + (-394\ kJ/mol)) - (-1{,}273\ kJ/mol) = -763\ kJ/mol$

$\Delta S°_{rxn} = (192\ J/mol\ K + (161\ J/mol\ K) + (213\ J/mol\ K)) - (209\ J/mol\ K) = 357\ J/mol\ K$

$\Delta S_{sur} = -\left(\frac{-763\ kJ/mol}{298\ K}\right) \approx 2.56\ kJ/mol\ K$ $\qquad \Delta S_{uni} = 357\ J/mol\ K - 2.56\ kJ/mol\ K$
$= -2{,}203\ J/mol\ K$

The reaction isn't spontaneous because in the equation $\Delta G = \Delta H - T\Delta S$, since ΔS is negative, and $|\Delta S| > |\Delta H|$, ΔG will be positive.

⑤ $\Delta H = (65.6\ J\ mol^{-1}K^{-1} + 2.38\times10^{-1}T\ J\ mol^{-1}K^{-2})(T_f - 58.3K) + (112\ J\ mol^{-1}K^{-1})(58.3K) \approx -1.4\ kJ\ mol^{-1}$

$\Delta S = \frac{-1.4\ kJ/mol}{78.3K} \approx -17.6\ kJ/molK$

⑥ $S_m(70K) = 0 + \int_0^{23.66} 0.83\,dT + \frac{93.8\ J/mol}{23.66\ K} + \int_{23.66}^{43.76} 0.19\,dT + \frac{7.43\ J/mol}{93.76K} + \int_{43.76}^{54.39} -0.20\,dT + \frac{4,450\ J/mol}{54.39K} + \int_{54.39}^{90.2} -0.6\,dT + \frac{6,815\ J/mol}{35.81\ K} + \int_{90.2}^{70} 0.5\,dT = 282.8\ J/molK$

$S_m(150\ K) = 322.8\ J/molK$ same process, replace 70 with 150

$S_{m\ 70\to150}$ $(322.8\ J/molK - 282.8\ J/molK) = 40\ J/molK$

Questions