

Effect of Temperature on the Heat of Reaction and Gibbs free energy

$$\Delta H^{\circ}_{298} = \sum (v_i \Delta H_{fi})_p - \sum (v_i \Delta H_{fi})_R \quad \text{-----18}$$

$$\Delta G^{\circ}_{298} = \left(\sum v_i \Delta G^{\circ}_f \right)_p - \left(\sum v_i \Delta G^{\circ}_f \right)_R \quad \text{-----19}$$

From Eq. 6a where the heat of the reaction

$$\Delta H_r(T) = \Delta H_r(T_R) + \int_{T_1}^{T_2} C_p .dT \quad \text{.....6a}$$

Since the heat capacity of each component is frequently given as:

$$C_p = a + bT + cT^2 \quad \text{and ;}$$

$$\Delta H_r(T) = \Delta H_r(T_R) + \int_{T_1}^{T_2} \sum [v_i C_{pi}]_p .dt - \int_{T_1}^{T_2} \sum [v_i C_{pi}]_R .dt$$

The term $\sum [v_i C_{pi}]_p .dt - \int_{T_1}^{T_2} \sum [v_i C_{pi}]_R$ may be expressed as;

$$\Delta H_r(T) = \Delta H_r(T_R) + \int_{T_1}^{T_2} (\Delta a + \Delta bT + \Delta cT^2) .dT$$

Integrating gives

$$\Delta H^{\circ}_T = \Delta H^{\circ}_{T_R} - \Delta a(T - T_R) - \frac{\Delta b}{2}(T^2 - T_R^2) - \frac{\Delta c}{3}(T^3 - T_R^3) \quad \text{----20}$$

$$\Delta H^{\circ}_T = \left[\Delta H^{\circ}_{T_R} - \Delta a T_R - \frac{\Delta b}{2} T_R^2 - \frac{\Delta c}{3} T_R^3 \right] + \Delta a T - \frac{\Delta b}{2} T^2 - \frac{\Delta c}{3} T^3$$

The term $\left[\Delta H^{\circ}_{T_R} - \Delta a T_R - \frac{\Delta b}{2} T_R^2 - \frac{\Delta c}{3} T_R^3 \right]$ is a constant usually denoted as J and it is a hypothetical value of ΔH at 0 K.

$$\Delta H^{\circ}_T = J + \Delta aT + \frac{\Delta b}{2}T^2 + \frac{\Delta c}{3}T^3 \quad \text{-----21}$$

If ΔH_r° is dependent on temperature then by integration of Eq.7 Eq. 8 will be

$$\frac{d}{dT}(\ln K_{eq}) = \frac{\Delta H_r^{\circ}}{RT^2} \quad \text{-----7} \quad \ln K_{eq} = \ln K_{298} + \int_{298}^T \frac{\Delta H_r^{\circ}}{RT^2} dT \quad \text{-----8}$$

Using Eq.21

$$\ln K_{eq} = \int_{298}^T \left(\frac{J}{RT^2} + \frac{\Delta a}{RT} + \frac{\Delta b}{2R} + \frac{\Delta c}{3R} \right) dT \quad \text{-----22}$$

$$\ln K_{eq} = \frac{-J}{RT} + \frac{\Delta a}{R} \ln T + \frac{\Delta b}{2R}T + \frac{\Delta c}{6R}T^2 + I \quad \text{-----23}$$

$$\Delta G^{\circ}_T = J - \Delta aT \ln T - \frac{\Delta b}{2}T^2 - \frac{\Delta c}{6}T^3 - IT \quad \text{-----24}$$

Effect of pressure on heat of reaction

The effect of pressure on the heat of reaction depends upon the degree of deviation from ideal gases behavior. If the reactants & products behave as ideal gases there is no effect. Even for non ideal behavior, the effect of pressure is generally small.

Chemical equilibrium

The change in the free energy between the products and reactants is expressed by Eq.11:

$$\Delta G^{\circ} = -RT \ln K_{eq} \quad \text{.....11 ; T absolute temp.}$$

R = gas constant = 8.314kJ/mol.K or 1.987 cal/mol.K where , cal=4.18J and 252cal=Btu.

Equilibrium constant for the reaction

$$K = \frac{a_c^c \cdot a_D^d}{a_A^a \cdot a_B^b} \quad \text{where a's are the activities of equilibrium}$$

1- If ideal gas law applies then a is expressed as partial pressure,

$$K = \frac{P_C^c \cdot P_D^d}{P_A^a \cdot P_B^b} = K_P \quad \text{since } P_A = y_A P_T$$

$$K = \frac{y_C^c \cdot y_D^d}{y_A^a \cdot y_B^b} \cdot P_T^{\Delta n} \quad \text{where } \Delta n = (c+d) - (a+b)$$

$K = K_y \cdot P_T^{\Delta n}$ since $P_A = n_A RT/V = CRT$ then

$$K = \frac{C_C^c \cdot C_D^d}{C_A^a \cdot C_B^b} (RT)^{\Delta n} = K_c (RT)^{\Delta n}$$

2- For non ideal gases the activity is expressed as fugacity

$$K = \frac{f_C^c \cdot f_D^d}{f_A^a \cdot f_B^b} \quad \text{since } \alpha_i = \frac{f_i}{p_i} \quad \text{or} \quad f_i = \alpha_i P_i$$

$$K = \frac{P_C^c \cdot P_D^d}{P_A^a \cdot P_B^b} \cdot \frac{\alpha_C^c \cdot \alpha_D^d}{\alpha_A^a \cdot \alpha_B^b} = K_P \cdot K_\alpha$$

For Lewis Randall rule $\alpha_i = \frac{f'_i}{p_i}$ where f'_i is the fugacity of pure component available in plots as a function of T_r & P_r . or,

$$K = K_y \cdot K_\alpha P_T^{\Delta n} \quad \text{and} \quad K = K_c K_\alpha (RT)^{\Delta n}$$

3- For liquids the activity is expressed as mole fraction x_i

a- for ideal solution

$$K = \frac{X_C^c \cdot X_D^d}{X_A^a \cdot X_B^b}$$

b- for non-ideal solution

$$K = \frac{X_C^c \cdot X_D^d}{X_A^a \cdot X_B^b} \cdot \frac{\gamma_C^c \cdot \gamma_D^d}{\gamma_A^a \cdot \gamma_B^b}$$

$$K = K_x K_\gamma$$

Example

Calculate ΔG° and ΔH° at 500K for the ammonia oxidation reaction
 $4\text{NH}_3 + 5\text{O}_2 \longrightarrow 4\text{NO} + 6\text{H}_2\text{O}_{(g)}$

use data from tables and take into account the variation of specific heat with temperature. $\Delta H^\circ_{298} = -216348 \text{ cal}$, $\Delta G^\circ_{298} = -229146 \text{ cal}$

Cp cal/gmol.°C	
NH _{3(g)}	$8.4 + 0.7 \cdot 10^{-2}T + 0.105 \cdot 10^{-5}T^2$
O ₂	$6.95 + 0.27 \cdot 10^{-3}T - 0.145 \cdot 10^{-5}T^2$
NO	$7.05 + 0.195 \cdot 10^{-2}T - 0.07 \cdot 10^{-5}T^2$
H _{2O(g)}	$7.99 + 0.164 \cdot 10^{-2}T + 0.18 \cdot 10^{-5}T^2$

Solution:

Calculate Δa , Δb , Δc

$$\Delta a = [4(7.05) + 6(7.99)] - [4(8.4) + 5(6.95)] = 7.79$$

$$\Delta b = 0.01764 - 0.02938 = -2.416 \cdot 10^{-2}$$

$$\Delta c = [4 \cdot (-0.07 \cdot 10^{-5}) + 6(0.18 \cdot 10^{-5})] - [4 \cdot 0.105 \cdot 10^{-5} - 5 \cdot 0.145 \cdot 10^{-5}] = [-0.0000028 + 0.0000108] - [0.0000042 - 0.00000725] = 0.000008 + 0.00000305 = 0.00001105 = 1.105 \cdot 10^{-5}$$

Given $\Delta H^\circ_{298} = -216348 \text{ cal}$ or can be calculated using Eq.18

$$\Delta H^\circ_{298} = 6 \Delta H^\circ_{f\text{H}_2\text{O}} + 4(\Delta H^\circ_{f\text{NO}}) - 4(\Delta H^\circ_{f\text{NH}_3})$$

then calculate J from Eq. 20

$$\Delta H^\circ_T = J + \Delta aT + \frac{\Delta b}{2}T^2 + \frac{\Delta c}{3}T^3$$

$$J = \Delta H^{\circ}_{298} - \Delta a T_o - \frac{\Delta b}{2} T_o^2 - \frac{\Delta C}{3} T_o^3$$

$$J = -216348 - 7.79(298) + \frac{2.416 \cdot 10^{-2}}{2} (298)^2 - \frac{1.105 \cdot 10^{-5}}{3} (298)^3$$

$$J = -217694 \text{ cal}$$

Calculate I from Eq. 22

$$\Delta G^{\circ}_T = J - \Delta a T \ln T - \frac{\Delta b}{2} T^2 - \frac{\Delta C}{6} T^3$$

$$-229146 = -218698 - 7.79(298) \ln 298 - \frac{2.416 \cdot 10^{-2}}{2} 298^2 - \frac{1.105 \cdot 10^{-5}}{6} 298^3 - I(298)$$

$$17338.79 = I(298)$$

$$I = -2.5 \text{ cal/K}$$

$$\Delta G^{\circ}_{500} = 218698 - 7.79(500) \ln 500 - \frac{1.174 \cdot 10^{-2}}{2} 298^2 - \frac{1.105 \cdot 10^{-5}}{6} 298^3 + 2.5(500)$$

$$= \Delta G^{\circ}_{500} = -237860 \text{ cal}$$

Note: You can calculate the equilibrium constant K from

$$\Delta G^{\circ}_{500} = -RT \ln K$$

$$-237860 = -1.984(500) \ln K$$

$$\ln K = 240$$

$$-229146 = -1.987(298) \ln K$$

$$\ln K = 386$$

$$\ln K_{eq} = \ln K_{298} - \frac{\Delta H_{r,298}^{\circ}}{R} \left(\frac{1}{T} - \frac{1}{298} \right)$$

$$\ln K_{eq} = -\frac{\Delta H_r^{\circ}}{RT} + \frac{\Delta S^{\circ}}{R}$$

