Lecture 7.2

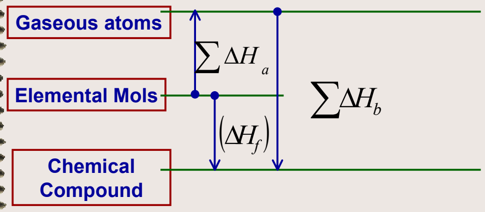
Bond energies +
Second Law Analysis of
Chemical Reactions

RECAP-Reactive mixtures

- Mass balance -balancing the no of atoms of each clement in the reactants & products
- First Law analysis : Need for absolute enthalpies
- Concept of enthalpy of formation- enthalpy of all stable elements at ref conditions = 0
- Adiabatic flame temperature

Bond Energies & Enthalpy of formation

The process of formation of a compound =>



Gaseous atoms

Elemental Mols

Chemical Compound

$\sum \Delta H_a$

(ΔH_f)

$\sum \Delta H_b$

Bond Energies & Enthalpy of formation

from above :

$$(\Delta H_f) = \sum \Delta H_a - \sum \Delta H_b$$

In reality

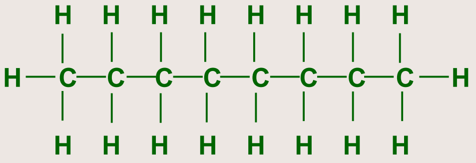
$$\Delta H_f = \sum \Delta H_a - \sum \Delta H_b - \sum \Delta H_{res} - \sum \Delta H_{latent}$$

Example

EXAMPLE

Find the enthalpy of formation of octane using bond energy approach

Sol : Structure of Octane



7 C – C bonds & 18 C – H bonds

SOLUTION

Chemical Equation

$$8C + 9H_2 \rightarrow C_8H_{18}$$

$$\therefore \Delta h_f = \{8 \times \Delta h_a[C] + 9 \times \Delta h_a[H-H]\} - \{7 \times \Delta h_b[C-C] + 18 \times \Delta h_b[C-H]\}$$

$$= 8 \times 717.2 + 9 \times 435.4 - 7 \times 347.5 - 18 \times 414.5$$

$$= -237.3 \; MJ/k\,mol$$

Tabulated value : - 208.45 MJ / kmol

SECOND LAW ANALYSIS OF CHEMICAL REACTIONS

Purpose :

Extent & direction of reaction

Basis :

Criterion of equilibrium

Const T&V => Helmhotz fn. minima

Const T&P => Min Gibbs fn.

SECOND LAW ANALYSIS OF CHEMICAL REACTIONS

Implications of eqlbm. Conditions :

T,P const. $\upsilon_1 R_1 + \upsilon_2 R_2 \Leftrightarrow \upsilon_3 P_3 + \upsilon_4 P_4$

From def. of Gibb's fn.; at const T & P

$$dG_{T,P} = \mu_1 dn_1 + \mu_2 dn_2 + \mu_3 dn_3 + \mu_4 dn_4$$

n_1, n_2, n_3, n_4 => no. of moles of constituents actually present

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SECOND LAW ANALYSIS OF CHEMICAL REACTIONS

In chem. reaction, the changes in no. of moles of various constituents present are related :

$$\frac{-dn_1}{\upsilon_1} = \frac{-dn_2}{\upsilon_2} = \frac{dn_3}{\upsilon_3} = \frac{dn_4}{\upsilon_4} = d\xi$$

Where ξ is called the extent of reaction. Using it in the equilibrium condition we get

$$dG_{T,P} = -(\mu_1\upsilon_1 + \mu_2\upsilon_2 - \mu_3\upsilon_3 - \mu_4\upsilon_4)d\xi \le 0$$

$dG_{T,P} = -A d\xi \le 0$ A : Affinity

SECOND LAW ANALYSIS OF CHEMICAL REACTIONS

Therefore a reaction would occur only if

This implies $A d\xi \ge 0$

$$If\ A > 0, i.e. \sum_{reac} \mu_i \nu_i > \sum_{prod} \mu_i \nu_i, d\xi > 0$$

$$If\ A < 0, i.e. \sum_{reac} \mu_i \nu_i < \sum_{prod} \mu_i \nu_i, d\xi < 0$$

thus the affinity A determines the direction of the reaction

SECOND LAW ANALYSIS OF CHEMICAL REACTIONS

Condition of eqlbm. at const T & P

$A=0 \Rightarrow \mu_1\upsilon_1 + \mu_2\upsilon_2 = \mu_3\upsilon_3 + \mu_4\upsilon_4$

To make this result more useful :

$$(d\mu_i)_T = RT\ d\ \ln\ f_i$$

Integrating between a std. state designated by superscript ^{0} {corresp. to Press P_{ref} & pure substance i) & the eqlbm. state

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SECOND LAW ANALYSIS OF CHEMICAL REACTIONS

$$\mu_i = \mu_i^0 + RT\ \ln\ f_i / f_i^0$$

$$= \mu_i^0 + RT\ \ln\ a_i$$

$$a_i = \frac{f_i}{f_i^0} = activity$$

Using this expression in the equilibrium condition we get:

$$(\mu_1^0\upsilon_1 + \mu_2^0\upsilon_2 - \mu_3^0\upsilon_3 - \mu_4^0\upsilon_4) + RT(\upsilon_1 \ln\ a_1 +$$

$$\upsilon_2 \ln a_2 - \upsilon_3 \ln a_3 - \upsilon_4 \ln\ a_4) = 0$$

SECOND LAW ANALYSIS OF CHEMICAL REACTIONS

Now for pure substance $\mu_i^0 = g_i^0$

& defining Gibb's free energy change of reaction

$$\Delta G_r = g_3^0\upsilon_3 + g_4^0\upsilon_4 - g_1^0\upsilon_1 - g_2^0\upsilon_2$$

Above equation becomes

$$\Delta G_r + RT\ln\left(\frac{a_3^{\upsilon_3}\, a_4^{\upsilon_4}}{a_1^{\upsilon_1}\, a_2^{\upsilon_2}}\right) = 0$$

SECOND LAW ANALYSIS OF CHEMICAL REACTIONS

We define

$$\frac{a_3^{\upsilon_3}\, a_4^{\upsilon_4}}{a_1^{\upsilon_1}\, a_2^{\upsilon_2}} \equiv \frac{\left(\Pi a_i^{\upsilon_i}\right)_{prod}}{\left(\Pi a_i^{\upsilon_i}\right)_{reac}} = K,\ the\ eqlbm.\ Const.$$

The eq. for chem. eqlbm. becomes

$$\Delta G_r + RT\ln K = 0$$

$$or\ K = \exp\left(-\frac{\Delta G_r}{RT}\right)$$

SECOND LAW ANALYSIS OF CHEMICAL REACTIONS

For reactions involving Ideal Gases

$$f_i = P\cdot x_i$$

$$f_i^0 = P_{ref},\ the\ std.\ press.$$

$$\therefore K = \left(\frac{P}{P_{ref}}\right)^{\upsilon_3+\upsilon_4-\upsilon_1-\upsilon_2}\left(\frac{x_3^{\upsilon_3}\, x_4^{\upsilon_4}}{x_1^{\upsilon_1}\, x_2^{\upsilon_2}}\right)$$

=> Examples

EXAMPLE

Gaseous propane C_3H_8 is burned with 80% theoretical air in a steady flow process at 1 atm. Both the fuel and air are supplied at 25^0 C. The products which consist of CO_2, CO, H_2O, H_2 and N_2 in equilibrium, leave the combustion chamber at 1500 K. Determine the composition of the products and the amt of heat transfer / kg of propane. [Hsieh p412]

End of Lecture

Lecture 7.3

Reaction Equilibrium

Recap…..

- Second law analysis –reaction equilibrium
- For ideal gas reactive mixtures

$$\therefore K = \left(\frac{P}{P_{ref}}\right)^{\upsilon_3+\upsilon_4-\upsilon_1-\upsilon_2} \left(\frac{x_3^{\upsilon_3} x_4^{\upsilon_4}}{x_1^{\upsilon_1} x_2^{\upsilon_2}}\right)$$

EXAMPLE

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SOLUTION

Let y & Z be the moles of CO_2 & H_2O in the products. The chemical eq. can then be written

$$C_3H_8 + 0.8\times5(O_2 + 3.76N_2) \rightarrow yCO_2 + (3-y)CO$$
$$+ zH_2O + (4-z)H_2 + 0.8\times5\times3.76N_2$$

Where the coeffs of CO & H_2 are obtained by mass balance on C and H_2.

SOLUTION

A mass balance for O_2 then gives

$$0.8\times5\times2 = 2y + 3 - y + z$$

or

$$y + z = 8 - 3 = 5 \qquad ------- \; (i)$$

SOLUTION

Another relation between y & z can be obtained from the equilibrium condition for the reaction

$CO_2 + H_2 \leftrightarrow CO + H_2O$ --------- (ii)

SOLUTION

$$K(T) = \frac{x_3x_4}{x_1x_2} \qquad [\upsilon_1 = \upsilon_2 = \upsilon_3 = \upsilon_4 = 1]$$

$$= \frac{p_{co} \; p_{H_2O}}{p_{co_2} \; p_{H_2}}$$

{mole fraction = partial pr ratio}

SOLUTION

Constitution of products :

y moles of CO_2
(3-y) moles of CO
Z moles of H_2O
4 - Z moles of H_2
15.04 moles of N_2

Σ : 22.04

SOLUTION

$\therefore$ for a total pressure of 1atm, the values of partial pressure in atm are

$$p_{co} = \frac{3-y}{22.04};\ p_{H_2O} = \frac{Z}{22.04};\ p_{co_2} = \frac{y}{22.04}$$

$$p_{H_2} = \frac{4-z}{22.04}$$

SOLUTION

Thus $K(T) = \dfrac{(3-y)z}{y(4-z)}$

From the std tables, for this reaction (ii), at 1500^0K we have

$$\log_{10}[K(T)] = 0.409 \quad or \quad K(T) = 2.56$$

SOLUTION

Therefore $\dfrac{(3-y)z}{y(4-z)} = 2.56 \quad -------(iii)$

Solving eqs (I) & (iii) simultaneously yields

$$y = 1.81 \ \ and \ \ z = 3.19$$

The chemical equation for the combustion process is then

SOLUTION

$$C_eH_8 + 4O_2 + 15.04N_2 \rightarrow 1.81CO_2 + 1.19CO$$
$$+ 3.19H_2O + 0.81H_2 + 15.04N_2$$

And the eqlbm mole fractions of the products are

SOLUTION

$$x_{co_2} = \frac{y}{22.04} = \frac{1.81}{22.04} = 8.21\% \qquad x_{H_2} = 3.68\%$$

$$x_{co} = \frac{1.19}{22.04} = 5.4\% \qquad x_{N_2} = 68.24\%$$

$$x_{H_2O} = 14.47\%$$

First Law analysis => Q= -13483 kJ / kg of fuel

Calculating K from Thermodynamic Data

$$K(T) = \exp\left(-\frac{\Delta G_r}{RT}\right)$$

$$\Delta G_r\left(T, P_{ref}\right) = \upsilon_3\left(h_3 - Ts_3\right) + \upsilon_4\left(h_4 - Ts_4\right)$$

$$-\upsilon_1\left(h_1 - Ts_1\right) + \upsilon_2\left(h_2 - Ts_2\right)$$

$$= \Delta H_R\left(T, P_{ref}\right) - T\Delta S_R\left(T, P_{ref}\right)$$

Calculating K from Thermodynamic Data

Where

$$\Delta H_R\left(T, P_0\right) = \upsilon_3 h_3 + \upsilon_4 h_4 - \upsilon_1 h_1 - \upsilon_2 h_2$$

$$\Delta S_R\left(T, P_0\right) = \upsilon_3 s_3 + \upsilon_4 s_4 - \upsilon_1 s_1 - \upsilon_2 s_2$$

Need for absolute entropy values

Calculating K from Thermodynamic Data

Third Law As T→0

S→0 for all substances

∴ **In principle we can find abs. entropies from above law using basic thermodynamics**

$$ds = \frac{C_p}{T}dT - \frac{v}{T}d\mathrm{P} = \frac{C_v}{T}dT + \frac{\mathrm{P}}{T}dv$$

Calculating K from Thermodynamic Data
EXAMPLE

Find eqlb constant for

$$H_2 0_{(g)} \leftrightarrow H_2 + \frac{1}{2} 0_2$$

at 298 K & 2000 K

SOLUTION

$$\ln K = \exp\left(-\frac{\Delta G_r}{RT}\right)$$

$$H_2 0_{(g)} \leftrightarrow H_2 + \frac{1}{2} 0_2$$

$$\Delta G_r = \Delta H_r - T\Delta S_r = \left(h_{H2} + \frac{1}{2} h_{0_2} - h_{H_2 0}\right)$$

$$-T\left(S_{H_2} + \frac{1}{2} S_{0_2} - S_{H_2 0}\right)$$

SOLUTION

at 298 K

$$= +241827 - 298\left(130.684 + \left(\frac{205.142}{2}\right) - 188.833\right)$$

$$= 228591$$

at 298 K from tables

$$\Delta G = g_{f_{H_2}} + \frac{1}{2} g_f\, 0_2 - g_{f_{H_2 0}}$$

$$= 0 + 0 - (-228583)$$

$$\therefore \ln K = \frac{-228583}{8.314 \times 298}$$

$$= -92.2$$

SOLUTION

at 2000 K $\Delta G = \Delta H - T\Delta S$

$$\Delta H = \left(h_{2000} - h_{298}\right)_{H_2} + \frac{1}{2}\left(h_{2000} - h_{298}\right)_{\partial_2}$$

$$-\left(h_f + h_{2000} - h_{298}\right)_{H_2 0}$$

$$= 52932 + \frac{1}{2}(59199) - (-241827 + 72689)$$

$$= 251670\, kJ$$

SOLUTION

$$\Delta S^0 = \left(S_{2000}\right)_{H_2} + \frac{1}{2}\left(S_{2000}\right)_{0_2} - \left(S_{2000}\right)_{H_2 0}$$

$$= 188.406 + \frac{1}{2} \times 268.764 - 264.681$$

$$= 58.107\ kJ/K$$

$$\therefore \Delta G = 251670 - 2.000 \times 58.107 = 135455\, kJ$$

$$(\ln K)_{2000} = -\frac{135455}{8.314 \times 2000} = -8.146$$

Dependence of K on Temperature

$$RT\ \ln K = -\Delta G_r = -(\nu_3 h_3 + \nu_4 h_4 - \nu_1 h_1 - \nu_2 h_2) +$$

$$+ T(\nu_3 s_3 + \nu_4 s_4 - \nu_1 s_1 - \nu_2 s_2)$$

Differentiating w r t Temperature at const P, we get

$$RT\frac{d\ln K}{dT} + R\ln K = \nu_3\left(T\frac{ds_3}{dT} - \frac{dh_3}{dT}\right) + \ldots similar\ terms$$

$$+(\nu_3 s_3 + \nu_4 s_4 - \nu_2 s_2 - \nu_1 s_1)$$

Dependence of K on Temperature

Simplifying the above equation we get

$$\frac{d\ln K}{dT} = \frac{\Delta h_r}{RT^2}$$

van't Hoff Equation

Δh_r is a weak function of T,therefore we can integrate above equation to get

$$\ln(K_2/K_1) = -\frac{\Delta h_r}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

End of Lecture