Lecture 26

Thermodynamics of Reactive Systems
Thermochemistry and The Chemical Equilibrium

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Today's Topics

● Thermochemistry

● The Chemical Equilibrium

    ☐ **The driving force for chemical reactions**

The Variance of Chemical Reaction

● If a reactive system consists of **E** elements and **C** components, some of which are molecules, then the number of independent chemical reactions, or variance **V**, can be written as

$$\mathbf{V = C - E} \tag{8.1}$$

Example 1

System contains the element C and O **(E = 2)** and is made up of the molecule species O_2, CO and CO_2 **(C = 3)**. The variance, **V** $= 3 - 2 = 1$.

This type of system is known as **univariant** system and exhibits one independent chemical reaction. In this case, $2CO + O_2 = 2CO_2$.

Example 2

System with elements C and O and molecule species C, O_2, CO and CO_2.

The variance, **V** $= 4 - 2 = 2$. This type of system is known as **multivariant** system and exhibits more than one independent chemical reaction.

In this case the two reactions can be: $C + O_2 = CO_2$, $2C + O_2 = 2CO$.

Thermochemistry

● The part of thermodynamics that is concerned with the heat changes accompanying chemical reactions, formation of solutions and changes in the state of matter such as melting or vaporisation, and other physico-chemical processes is known as **thermochemistry**.

● Metallurgical processes are usually carried out at constant pressure, so that we will consider the **heat evolved by the system at constant pressure, Q_P,** which we have seen is equal to the **change in enthalpy ΔH**.

Endothermic and Exothermic Reactions

Endothermic: $ZnO + C = Zn + CO$; $\Delta H = +349$ kJ

Exothermic: $2Al + 3/2 O_2 = Al_2O_3$; $\Delta H = -1674$ kJ
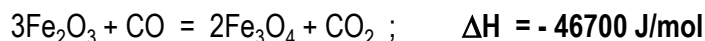
2 moles of aluminium react with 1.5 moles of oxygen to produce 1 mole of alumina and, during the process, 1674 kJ of energy is liberated.

Heat of Reactions

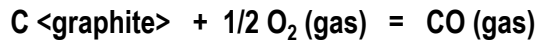**Change in Enthalpy = $\sum$ Enthalpy of Products – $\sum$ Enthalpy of Reactants**

$$x\,A \;+\; y\,B \;=\; A_xB_y$$

$$\Delta H \;=\; H(A_xB_y) \;-\; x\,H(A) \;-\; y\,H(B)$$

$$3Fe_2O_3 + CO = 2Fe_3O_4 + CO_2 \; ; \qquad \mathbf{\Delta H = -46700 \; J/mol}$$

(Standard) Heat of Formation

- **The heat of formation** of a compound is the enthalpy change associated with the formation of 1 mole of the compound from its constituent elements.

- Its value depends upon the temperature, pressure and the chemical state of the reactants and products.

- The state of the system must be specified while mentioning the heat of formation.

- The heat of formation of a compound from its elements in their standard states is called **the standard heat of formation, ΔH^o.**

- Generally, 25 C temperature and 1 atm pressure is chosen as the standard condition and enthalpy change in this state is written as ΔH^o_{298}.

- As a convention, **a value of zero is assigned to the standard heat content of a pure element** at 25 C and 1 atm pressure.

C <graphite> + 1/2 O_2 (gas) =   CO (gas)

ΔH^o_{298} (CO)   = ΔH^o_{298}

ZERO   ZERO

= H^o_{298} (CO) – H^o_{298}<C> – 1/2 H^o_{298} (O_2)

= H^o_{298} (CO)

ΔH^o_{298} (CO)   = ΔH^o_{298} = H^o_{298} (CO)

| standard heat of | standard heat | standard enthalpy |
| formation of CO | of reaction | of CO |

**The heat content of a compound or alloy in the standard state
is equal to its standard heat of formation.**

Example 8.1

Calculate the standard heat of reaction at 25 C and at 1 atm pressure of the reaction

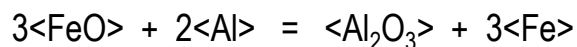**3<FeO> + 2<Al> = <Al_2O_3> + 3<Fe>**
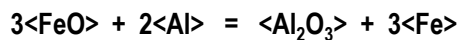
in terms of per mole of Al_2O_3 formed, per mole of Fe formed, per mole of FeO reacted, per mole of Al reacted and per g of Fe formed.

Given date: ΔH^o_{298}<FeO> = -63.3 kcal/mol; ΔH^o_{298}<Al_2O_3> = -400.0.

ANSWER

ΔH^o_{298} = Σ H^o_{298} (product) – Σ H^o_{298} (reactant)

= H^o_{298}< Al_2O_3> + 3H^o_{298}<Fe> – 3H^o_{298}<FeO> – 2H^o_{298}<Al>

= H^o_{298}< Al_2O_3>   + 0 – 3H^o_{298}<FeO> – 0

=   (-400.0 kcal) – 3(-63.3 kcal) = **–210.1 kcal**

$$3\langle FeO \rangle + 2\langle Al \rangle = \langle Al_2O_3 \rangle + 3\langle Fe \rangle$$

Thus, the standard heat of reaction

= (-210.1 kcal) /1 mol of Al_2O_3 formed = **-210.1 kcal/mol Al_2O_3**

= (-210.1 kcal) /3 mol of Fe formed = **- 70.03 kcal/mol Fe**

= (-210.1 kcal) /3 mol of FeO reacted = **- 70.03 kcal/mol FeO**

= (-210.1 kcal) /2 mol of Al reacted = **- 105.05 kcal/mol Al**

= (-210.1 kcal) /(3 x 56) g of Fe formed = **- 1.26 kcal/g Fe**


Heat of Combustion

Heat of Transformation

Hess's Law

The change in heat content in a chemical reaction is the same whether it takes place in one or several stages, provided that the temperature and either pressure or volume remain constant.

$Fe_2O_3 + 3C + 3/2O_2 = 2Fe + 3CO_2$,	$\Delta H = -425.7$ kJ (in single step)
$3/2C + 3/2O_2 = 3/2CO_2$,	$\Delta H = - 591.6$ kJ
$3/2CO_2 + 3/2C = 3CO$,	$\Delta H = + 258.6$ kJ
$Fe_2O_3 + 1/3CO = 2/3Fe_3O_4 + 1/3CO_2$,	$\Delta H = -17.6$ kJ
$2/3Fe_3O_4 + 8/3CO = 2Fe + 8/3CO_2$,	$\Delta H = -10.5$ kJ
$Fe_2O_3 + 3C + 3/2O_2 = 2Fe + 3CO_2$,	$\Delta H = -361.1$ kJ
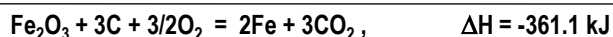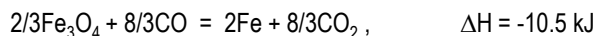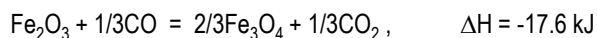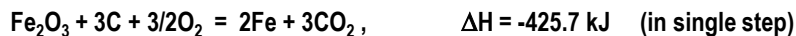
A large cumulative error can quickly build up this way from the summation of experimental errors of individual heat of formation. So Hess's law must be applied with caution.

Enthalpy Change of Reaction at Higher T

$$mM + nN = xX + yY$$

$$\Delta H^o = (xH^o_X + yH^o_Y) - (mH^o_M + nH^o_N)$$
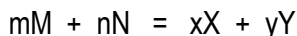
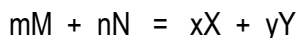$$d(\Delta H^o) = \Delta C_P \, dT \qquad \Delta C_P = C_P(P) - C_P(R)$$

$$\Delta H^o_2 = \Delta H^o_1 + \int_{T_1}^{T_2} \Delta C_P \, dT \qquad \textit{The Kirchhoff's equation}$$

● If the change in temperature from T_1 to T_2 involves a phase transition of reactant and/or product

$$\Delta H^o_2 = \Delta H^o_1 + \int_{T_1}^{T_t} \Delta C'_P \, dT \pm \Delta H^o_t + \int_{T_t}^{T_2} \Delta C''_P \, dT$$

If a product undergoes a physical change, ΔH^o_t will be positive, and if the reactant changes, ΔH^o_t will be -ve.

Entropy Change of Reaction at Higher T

$$mM + nN = xX + yY$$

$$\Delta S^o = (xS^o_X + yS^o_Y) - (mS^o_M + nS^o_N)$$

$$d(\Delta S^o) = (\Delta C_P/T) \, dT \qquad \Delta C_P = C_P(P) - C_P(R)$$

$$\Delta S^o_2 = \Delta S^o_1 + \int_{T_1}^{T_2} \frac{\Delta C_P}{T} \, dT$$

● If the change in temperature from T_1 to T_2 involves a phase transition of reactant and/or product

$$\Delta S^o_2 = \Delta S^o_1 + \int_{T_1}^{T_t} \frac{\Delta C'_P}{T} \, dT \pm \frac{\Delta H^o_T}{T_t} + \int_{T_t}^{T_2} \frac{\Delta C''_P}{T} \, dT$$

If a product undergoes a physical change, ΔS^o_t will be positive, and if the reactant changes, ΔS^o_t will be -ve.

Example 8.4

Calculate the standard entropy change for the reaction $\langle Pb \rangle + 1/2(O_2) = \langle PbO \rangle$ at 800 K from the following data:

$S^o_{298} \langle PbO \rangle = 16.20$ cal/deg/mol, $S^o_{298} \langle Pb \rangle = 15.50$, $S^o_{298}(O_2) = 49.02$

$T_m, Pb = 600$ K , $L_f, Pb = 1150$ cal/mol

$C_P \langle PbO \rangle = 10.60 + 4.0 \times 10^{-3}\, T$ cal/deg/mol

$C_P \langle Pb \rangle = 5.63 + 2.33 \times 10^{-3}\, T$, $C_P \{Pb\} = 7.75 - 0.74 \times 10^{-3}\, T$

$C_P (O_2) = 7.16 + 1.0 \times 10^{-3}\, T - 0.4 \times 10^5\, T^{-2}$

ANSWER

$$\Delta S^o_{800} = \Delta S^o_{298} + \int_{298}^{600} (\Delta C'_P/T)\, dT - (L_f/600) + \int_{600}^{800} (\Delta C''_P/T)\, dT$$

$$\Delta S^o_{298} = \sum S^o_{298}(\text{products}) - \sum S^o_{298}(\text{reactants})$$
$$= S^o_{298} \langle PbO \rangle - S^o_{298} \langle Pb \rangle - 1/2\, S^o_{298}(O_2)$$
$$= 16.20 - 15.50 - 1/2\,(49.02) = \textbf{–23.81 cal/deg}$$

$$\Delta C'_P = C_P \langle PbO \rangle - C_P \langle Pb \rangle - 1/2 C_P(O_2)$$
$$= 1.39 + 1.17 \times 10^{-3}\, T + 0.2 \times 10^5\, T^{-2} \quad \text{cal/deg/mol}$$

$$\int_{298}^{600} \frac{\Delta C'_P}{T}\, dT = \int_{298}^{600} (1.39 + 1.17 \times 10^{-3}\, T + 0.2 \times 10^5\, T^{-2})\, \frac{dT}{T} = \textbf{1.41 cal/mol}$$

$$\Delta C''_P = C_P \langle PbO \rangle - C_P \{Pb\} - 1/2 C_P(O_2)$$
$$= -0.73 + 4.24 \times 10^{-3}\, T + 0.2 \times 10^5\, T^{-2} \quad \text{cal/deg/mol}$$

$$\int_{600}^{800} \frac{\Delta C''_P}{T}\, dT = \int_{600}^{800} (-0.73 + 4.24 \times 10^{-3}\, T + 0.2 \times 10^5\, T^{-2})\, \frac{dT}{T} = \textbf{0.65 cal/mol}$$

$$\Delta S^o_{800} = -23.81 + 1.41 - (1150/600) + 0.65 = \textbf{– 23.67 cal/mol}$$

The Chemical Equilibrium

● Most of the materials and metallurgical process are chemically reactive processes where one or more chemical reactions has occurred.

- ☐ **the extraction and refining of metals,**
- ☐ **the production of alloys,**
- ☐ **the productions of plastics and polymers, etc.**

● The maximum extent of a certain chemical reaction is governed by thermodynamic equilibrium

- ☐ **the maximum conversion of the reactants to products is calculable at a given temperature, pressure and feed composition according to the law of thermodynamics.**
- ☐ **it is impossible at a given set of conditions to obtain a greater conversion than that predicted by chemical equilibrium calculations.**

● Thus such calculations serve as a screening device to determine if a certain reaction has any potential industrial use.

The Driving Force Behind a Chemical Reaction

● The basic criterion for equilibrium in a chemically reactive system is identical to that for equilibrium among phases.

> dU = negative at constant S and V
> dH = negative at constant S and P
> dF = negative at constant T and V
> dG = negative at constant T and P
> dS = positive at constant U and V

● Since most of the chemical reactions are carried out at constant pressures and, in some cases, at constant temperatures, the conditions for spontaneity or equilibrium for the chemical process can be determined by the equation

$$dG_{T,P} = \sum \mu_k \, dn_k \leq 0$$

● The free energy change of a chemical reaction can be written as

$$\Delta G \ = \ \sum n_j \, \mu_j - \sum n_k \, \mu_k$$

where **j** denotes the products species while **k** denotes the reactant species.

● **If ΔG is negative, the reaction will proceed "forward"**
(i.e., more of the products will be formed).
The more negative the value, the greater will be the driving force.

● **If ΔG is positive, the reaction will proceed "backward"**
(product will dissociate to form more reactants).

● The fundamental idea of chemical equilibrium denies the possibility of a "complete" reaction unless one or all of the products is completely removed from the system.

☐ **If one of the products is continuously removed, the reaction never reaches equilibrium - and will, in fact, progress to completion.**

2<MgO> + <Si> = 2(Mg) + <SiO$_2$>   **The Pidgeon Process**
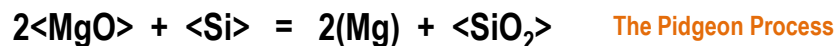
● This reaction is carried out above the boiling point of Mg (1105 C)

☐ **the magnesium vapour can be pumped off until virtually all the MgO has been reduced.**

☐ **the activity of SiO$_2$ is reduced by adding dolomite (CaO.SiO$_2$) into the charge.**

Next Class

Lecture 27

Thermodynamics of Reactive Systems
The Equilibrium Constant