S Y N O P S I S

INTRODUCTION :

Non-catalytic gas-solid reactions cover an important field in chemical and metallurgical industries. Many workers have taken up the investigations on those reactions and developed various reaction models. Some of the gas-solid reactions with high exothermic or endothermic heats of reaction, show isothermal behaviour at comparatively lower temperatures and become non-isothermal at higher temperatures. A brief review of important reaction models for both isothermal and non-isothermal conditions has been made and presented.

In Section - A, a reaction (Carboxylation of Sodium phenate) with small exothermic heat of reaction (ΔH^{o}_{298} = - 16.032 Kcals/gm.mole of CO_2 reacted) has been studied and treated under isothermal conditions. In Section - B, another reaction (Thermal decomposition of Sodium bicarbonate) with endothermic heat of reaction (ΔH^{o}_{298} = + 30.85 Kcals/gm.mole of CO_2 or H_2O formed) has been investigated under both isothermal and non-isothermal conditions. Two sections are dealt separately in details.

SECTION - A

CARBOXYLATION OF SODIUM PHENATE UNDER ISOTHERMAL CONDITION

Chapter I : Chapter one includes a survey of literature on industrial methods of carboxylation of sodium phenate leading to the commercial product, salicylic acid.

Chapter II : From thermochemical data, heat of reaction has been given as a function of temperature.

Considering all three resistances, namely, gas-film diffusion, chemical reaction and product (or ash) diffusion, a generalized reaction model has been developed for this type of reactions under isothermal conditions, and can be given as :

$$t = A_k \xi(r') + A_M \phi(r') + A_M B_M \psi(r') \quad ..(1)$$

For mass transport controlled reaction equation(1) may be modified as :

$$\frac{t}{\psi(r')} = A_M \frac{\phi(r')}{(r')} + A_M B_M \quad ..(2)$$

On the basis of the concept given by Ishida and Wen, equations for the effectiveness factor have been deduced for different shapes of particles under isothermal and non-isothermal conditions. For a cylindrical pellet and at isothermal condition, this may be given as :

$$\eta_s = \frac{1}{1 + \dfrac{\phi_c\, r'\,(b'+r')(1-r')\ln r'}{r'\ln r' - b'\,(1-r')} + \phi_c B_M r'(b'+r')} \quad ..(3)$$

Chapter III : The experimental set-up consists of a bomb - like reactor made of mild steel, with screwed cap, which is fitted with a thermocouple probe and with inlet and outlet valves. The reactor is heated in a glycerine bath. The reactant sample is suspended inside the bomb with a hook hanging from the top of the reactor. The reacted sample is analysed chemically by the standard method given by K.G.Stone.

Chapter IV : The experimental data on the carboxylation of sodium phenate fitted well the mass transport model and the different parameters have been evaluated. The reaction time predicted from the model using the evaluated parameters has been found to be comparable with the experimental reaction time.

From the plots of effectiveness factor versus conversion, the predominance of mass transport can be visualised. The relatively large magnitude of the mass transport resistance confirms the validity of the model.

NOMENCLATURE :

a	Stoichiometric coefficient
A	reactant gas, CO_2
A_k	model parameter for chemical reaction, $\frac{r_o}{a}\frac{\rho_M}{k_s C_{Ag}}$
A_M	model parameter for product-diffusion model, $\frac{r_o^2 \rho_M}{a D_e (C_{Ag}-C_{Ac})}$
b	the ratio of length to diameter of a reacting cylindrical pellet
b'	a constant, $= \frac{2}{3}(b-1)$
B	reactant solid
B_M	modified Biot modulus for mass transfer, $\frac{3}{(2b+1)}\cdot\frac{D_e}{r_o k_g}$, and b = 1.0 for spheres and cylinders of l/d = 1.0
C_{Ag}	bulk concentration of the reactant gas A, gm.moles of A/cm^3
C_{Ac}	interface concentration of the reactant gas A, gm.moles of A/cm^3
d	diameter of cylindrical pellet
D_e	effective diffusivity through the pores, $cm^2/sec.$
k_g	gas-film diffusion coefficient, cm/sec
k_s	reaction rate constant, cm/sec.

l length of the cylindrical pellet

r' r_c/r_o

r_o initial radius of a reacting pellet, cm

r_c core radius of a reacting pellet, cm

t reaction time, hour

Greek symbols

ρ_M density of the solid reactant B, gm.moles/cm^3

$\xi(r')$ a function of r', = (1-r')

$\phi(r')$ a function of r' $= \int_1^{r'} - \frac{r' \ln r' (b'+r')(1-r') dr'}{r' \ln r' - b'(1-r')}$ } for a cylindrical pellet of l/d = b

$\Psi(r')$ a function of r' $= [\frac{b'}{2}(1-r'^2) + \frac{1}{3}(1-r'^3)]$

η_s effectiveness factor

ϕ_c modified Thiele parameter, $r_o k_s / D_e$

REFERENCES :

1. Ishida, M., Wen, C.Y., Chem.Engg.Sci., 23, 125 (1968)

2. Stone, K.G., "Determination of organic compounds", McGraw-Hill Co. Inc., N.Y., 1956.