

On the other hand, the plots of F and Bt against time (t) at a concentration $0.01 M$ for irradiated and unirradiated samples overlap, indicating similar rates of exchange on the two samples. Moreover, the linear Bt versus t plots at $0.10M$ concentration reveal that the rate of exchange is controlled by the particle diffusion mechanism and since it is associated with the diffusion of ions inside the exchanger particles it can be inferred that no damage is imparted to the interior of the material.

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Effect of Precipitation Conditions upon Physico-chemical Properties of Iron Oxide Catalyst

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Physico-chemical properties of two hydrated iron oxide samples obtained by precipitation (i) with ammonium hydroxide and (ii) with ammonium carbonate have been explained on the basis of acid-base and redox equilibria prevailing during precipitation from ferrous salt solution.

THE major component of the catalyst for water gas shift reaction is iron oxide which is prepared by adding a base such as ammonium hydroxide or carbonate to a solution of iron salt. The composition of the precipitate and hence its structure obviously depend upon the method of precipitation. This is reflected in the variation of properties such as texture, catalytic activity, mechanical strength, etc. among catalysts manufactured by different processes. The present investigation deals with the physico-chemical studies using X-ray, TG, DTA and magnetic measurement and the study of the acid-base and redox equilibria prevailing during precipitation of two iron oxide catalysts prepared by two different precipitation methods. It is felt that these data will be very helpful in quality control during catalyst production.

Ferrous sulphate, ammonia solution and ammonium carbonate used were all BDH (LR) grade chemicals. Nitrogen (M/s Indian Oxygen Limited)

was used as such. Ferrous sulphate solution was prepared by dissolving the salt (50 g) in 1% sulphuric acid (500 ml). Ammonium carbonate and a concentrated solution of ammonia (sp. gr. 0.91) were used as precipitating reagents.

Precipitation titration was carried out in a beaker covered with a snugly fitting rubber stopper having holes for introducing the glass electrode (for pH measurement) or platinum electrode and salt bridge (for emf measurement), burette tip and the gas inlet tube. Nitrogen was bubbled through the solution vigorously to ensure good stirring. A Toshniwal pH-meter model CL-41 was used along with a Toshniwal calomel electrode and a Philips glass electrode type GAT 130 for pH measurement. For emf measurement a Philips DC microvoltmeter GM 6020 was used. X-ray photographs were taken with a Guinier camera using FeK_{α} radiation. TG and DTA measurements were done with a Stanton Thermograv and a Gallenkamp DTA unit respectively. A Gouy type magnetic balance was used for magnetic measurements.

About 100 ml of the iron solution were used for titration which was carried out at room temperature in presence of nitrogen. After precipitation was complete, the precipitate was washed free from sulphate and dried in air at $110^{\circ}C$. TG, DTA, X-ray and magnetic measurements were carried out with the dried sample. The dried sample was finally cured in air at $500^{\circ}C$ for 4 hr and characterized by X-ray and magnetic measurements.

It is seen that during precipitation both the pH and half-cell emf change very sharply. However, the nature of the change depends upon the precipitant used. In the presence of ammonium hydroxide the pH increases from <1 to 10 whereas when ammonium carbonate is used the pH remains steady ~ 6.5 even after complete precipitation. Similarly the half-cell potential changes from $+0.56$ to -0.64 volts upon addition of excess ammonium hydroxide but upto -0.13 volts if ammonium carbonate is used. Moreover after an equivalent amount of ammonium carbonate has been added, the half-cell potential decreases sharply.

The above phenomenon can be discussed on the basis of the E versus pH diagram (Fig. 1) from which a probable composition of the precipitate can be suggested. In a solution of iron salt the following equilibria can be considered along with their published E and K values¹.

- (a) $Fe^{2+} + 2e^{-} \rightleftharpoons Fe^{\circ}$; $E^{\circ} = -0.44 V$
- (b) $Fe^{3+} + e^{-} \rightleftharpoons Fe^{2+}$; $E^{\circ} = 0.771 V$
- (c) $Fe(OH)_2 + e^{-} \rightleftharpoons Fe^{\circ} + 2OH^{-}$; $E^{\circ} = -0.057 - 0.059 pH$
- (d) $Fe(OH)_2 \rightleftharpoons Fe^{2+} + 2OH^{-}$; $K^{\circ}_{s_0} = [Fe^{2+}][OH^{-}] = 10^{-15.1}$
- (e) $Fe(OH)_3 + e^{-} \rightleftharpoons Fe(OH)_2 + OH^{-}$; $E = 0.305 - 0.059 pH$
- (f) $Fe(OH)_3 + e^{-} \rightleftharpoons Fe^{2+} + 3OH^{-}$; $E = 1.20 - 0.059 (3) pH$
- (g) $Fe(OH)_3 \rightleftharpoons Fe^{3+} + 3OH^{-}$; $K^{\circ}_{s_0} = [Fe^{3+}][OH^{-}]^3 = 10^{-37}$

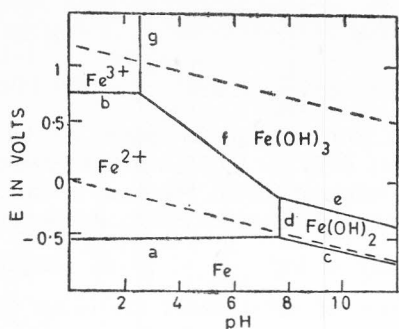


Fig. 1 — Relationship between half-cell potential (E) and pH of the Fe^{3+}/Fe^{2+} system.

TABLE 1 — PRESENCE OF VARIOUS PHASES IN OVEN-DRIED SAMPLES AS REVEALED BY X-RAY METHOD

Sample No.	Method of preparation	Crystalline phases present	Remarks
I	$FeSO_4 + NH_4OH$ dried in air at $110^\circ C$	Goethite (major) $\gamma-Fe_2O_3$ (minor) $Fe_3(SO_4)_2(OH)_5 \cdot 2H_2O$ (trace)	
IC	do; cured in air at $500^\circ C$	$\alpha-Fe_2O_3$ (major) $\gamma-Fe_2O_3$ (minor)	Crystallinity in Sample I is more than Sample II
II	$FeSO_4 + (NH_4)_2CO_3$ dried in air at $110^\circ C$	Goethite (major) $\gamma-Fe_2O_3$ (trace)	
IIC	do; cured in air at $500^\circ C$	$\alpha-Fe_2O_3$	

For the present discussion only three equilibria (b), (f) and (e) need be considered. In the presence of ammonia the final value of pH and half-cell potential are 9.5 and -0.65 volts respectively. From Fig. 1 it can be concluded that under these conditions only equilibrium (e) need be considered. In other words this means that the precipitate will consist of both $Fe(OH)_3$ and $Fe(OH)_2$. When ammonium carbonate is used as a precipitant the final value of pH and half-cell potential correspond to the presence of $Fe(OH)_3$ only in the solid phase (Equilibrium-f).

As the nitrogen used as purge gas contains trace of oxygen the $Fe(OH)_2$ formed during precipitation with ammonia undergoes slow oxidation in the presence of excess alkali to a mixed oxide phase which corresponds to the formula Fe_3O_4 (ref. 2). On drying in air $\gamma-Fe_2O_3$ is formed from this mixed oxide due to stronger oxidation⁴. X-ray analysis of the oven dried sample (Table 1) indicates the presence of more $\gamma-Fe_2O_3$ in ammonia precipitated sample as compared to ammonium carbonate precipitated variety. The presence of $\gamma-Fe_2O_3$ imparts strong ferromagnetism to both the oven dried samples. The $Fe(OH)_3$ phase in equilibria (e), (f) and (g) will actually exist as goethite and has been detected by X-ray.

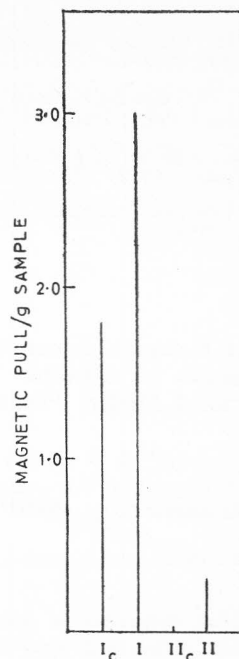


Fig. 2 — Magnetic measurements of dried (I and II) and cured (I_c and I_{ic}) samples [I, prepared from $FeSO_4 + NH_4OH$; and II, prepared from $FeSO_4 + (NH_4)_2CO_3$].

Since the phase composition of the two precipitates obtained by adding ammonium hydroxide and ammonium carbonate respectively, are different, they are expected to behave differently during thermal treatment. That they indeed do so is supported by their thermal behaviour. During thermal decomposition the sample prepared by ammonium hydroxide precipitation loses water in two steps whereas the sample prepared by ammonium carbonate precipitation shows only a single decomposition step. The DTA also indicates that there is difference in the location of peaks although the distinction between the two samples is not so remarkable as in TG.

The samples after curing at $500^\circ C$ show completely opposite magnetic behaviour as can be seen from Fig. 2. The ammonium hydroxide precipitated sample exhibits strong ferromagnetism but the other sample becomes non-magnetic. This is due to the fact that thermal decomposition of goethite gives antiferromagnetic $\alpha-Fe_2O_3$.

It has been reported³ that transformation of $\gamma-Fe_2O_3$ to $\alpha-Fe_2O_3$ takes place at temperature around $400^\circ C$. It is therefore surprising to find the presence of appreciable amount of $\gamma-Fe_2O_3$ in ammonia precipitated sample even after curing at $500^\circ C$. This sample undergoes complete dehydration at $600^\circ C$ and above. Probably the presence of H^+ ions from residual water helps in stabilizing the $\gamma-Fe_2O_3$ structure as suggested by Wells³. Besides, the transformation temperature is also enhanced by increasing the degree of crystallinity⁴. This can also account for better thermal stability of $\gamma-Fe_2O_3$ phase in ammonium hydroxide precipitated sample.

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Applicability of Hammett Equation to Insulated Systems — Kinetics of Alkaline Hydrolysis of *ortho*-Substituted Methyl Phenoxyacetates

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Kinetics of alkaline hydrolysis of some *ortho*-substituted methyl phenoxyacetates in methanol-water (85% wt/wt) at 10°, 15° and 20° are reported. The application of Taft's steric energy relationship shows that the reaction is not susceptible to the steric effect of *ortho*-substituents. Good correlation is obtained using σ_o^* values and better correlation is obtained using σ_p values for *ortho*-substituents.

IN continuation of our investigation¹ on the applicability of linear free energy relationships to some reactions involving some insulated systems, we report in this note the kinetics of saponification of some *ortho*-substituted methyl phenoxyacetates. The investigation is designed to see if the steric or polar effects of the *ortho*-substituents are important in the saponification of esters. The *ortho*-substituents are sufficiently away from the reaction centre and they may, therefore, be expected to behave like *meta*- and *para*-substituted acids in respect of the applicability of free energy relationships.

All the phenoxyacetic acids, were prepared by literature methods¹. Methyl esters were prepared by MeOH-H₂SO₄ method (3 hr reflux). Methanol was purified by the method of Bjerrum and Lund². The method of Evans *et al.*³ was employed for kinetic runs with equal concentration of ester and base. The equation used to calculate the specific reaction rate was the second-order expression, i.e., $k = x/ta(a-x)$, where k = the specific reaction rate, x = concentration of the ester reacted in time t , and a = initial concentration of the reactants.

The rates of alkaline hydrolysis of methyl phenoxyacetates were determined at 10°, 15° and 20° and the enthalpies and entropies of activation were calculated. These specific reaction rates for *ortho*-substituted methyl phenoxyacetates are much lower than those observed for *meta*- and *para*-substituted esters⁴.

A plot of $\log k/k_{Me}$ against E_s values (steric substituent constants⁵) gave only poor correlation (at 10°, $r = 0.795$) indicating that the steric effects are not important in this reaction

$$\log \frac{k}{k_{Me}} = \rho^* \sigma_o^* \quad \dots (1)$$

The plots of $\log \frac{k}{k_{Me}}$ against σ_o^* values (Taft equation)^{6,7} at 10°, 15° and 20° gave good correlation ($r = 0.979$; S. D. = 0.075) with the reaction constant (ρ^*) value of 0.563. Since σ_o^* values are the true measures of the polar effect, applicability of the Taft's equation $\log \frac{k}{k_{Me}} = \rho^* \sigma_o^*$ implies that steric effects of substituents are either completely absent or are approximately the same as the steric effect of the methyl group (the standard) within the range considered.

The general order of σ_o^* values corresponds very closely to that of σ_p values. When σ_o^* values are changed to σ_o with hydrogen as standard by assuming $\sigma_o = \sigma_p$ for methyl, it is seen that for other substituents $\sigma_o \approx \sigma_p$. A good linear plot was obtained (at 10°, $r = 0.976^\circ$; S. D. = 0.066) when σ_o was plotted against $\log k$ at 10°, 15° and 20°C, indicating a constant steric or resonance effect in the *ortho*-substituted compounds of that series.

The approximate equality of σ_p and Taft's σ_o values for several *ortho*-substituents and the applicability of the present results to the equation $\log k = \rho_o \sigma_o + \log k_H$ led us to use σ_p values⁸ as a measure of direct resonance and polar effects. In fact, the correlation was much improved using σ_p values (at 10°, $r = 0.987$; S.D. = 0.049), indicating that, apart from the constant bulk effect of the *ortho*-substituents, they behave in a manner similar to the *para*-substituents.

It may be stated in this connection that the corresponding *ortho*-substituted ethyl benzoates⁸ gave only poor correlation with σ_p -substituent constants ($r = 0.614$), indicating the importance of steric effects in this series in which the reaction centre is close to the *ortho* substituent. Baliah and Gurumurthy¹ also have noted the absence of any steric influence of *ortho* substituents in the esterification of phenoxyacetic acids.

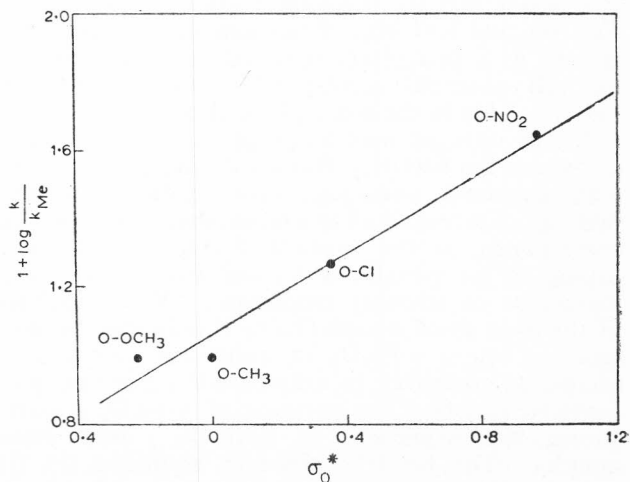


Fig. 1 — Plot of $\log k/k_{Me}$ versus σ_o^* constants for the alkaline hydrolysis of *ortho*-substituted methyl phenoxyacetates