

LETTERS TO THE EDITOR

KINETICS OF CHEMISORPTION OF
HYDROGEN ON IRON-KIESELGUHR:
APPLICATION OF THE EQUATION
OF KODAMA ET AL.

KODAMA *et al.*¹ assumed the surface of a catalyst to be heterogeneous and a molecule of hydrogen to be adsorbed on such a surface after dissociating into atoms, in which case equations of the following type could be written for various sites:

$$\frac{dX}{dt} = k_a P (A - X)^2 - k_d X^2 \quad (1)$$

where 'X' is the amount of hydrogen adsorbed by sites of a particular activity. Neglecting the desorption velocity, equation (1) can be transformed into the form

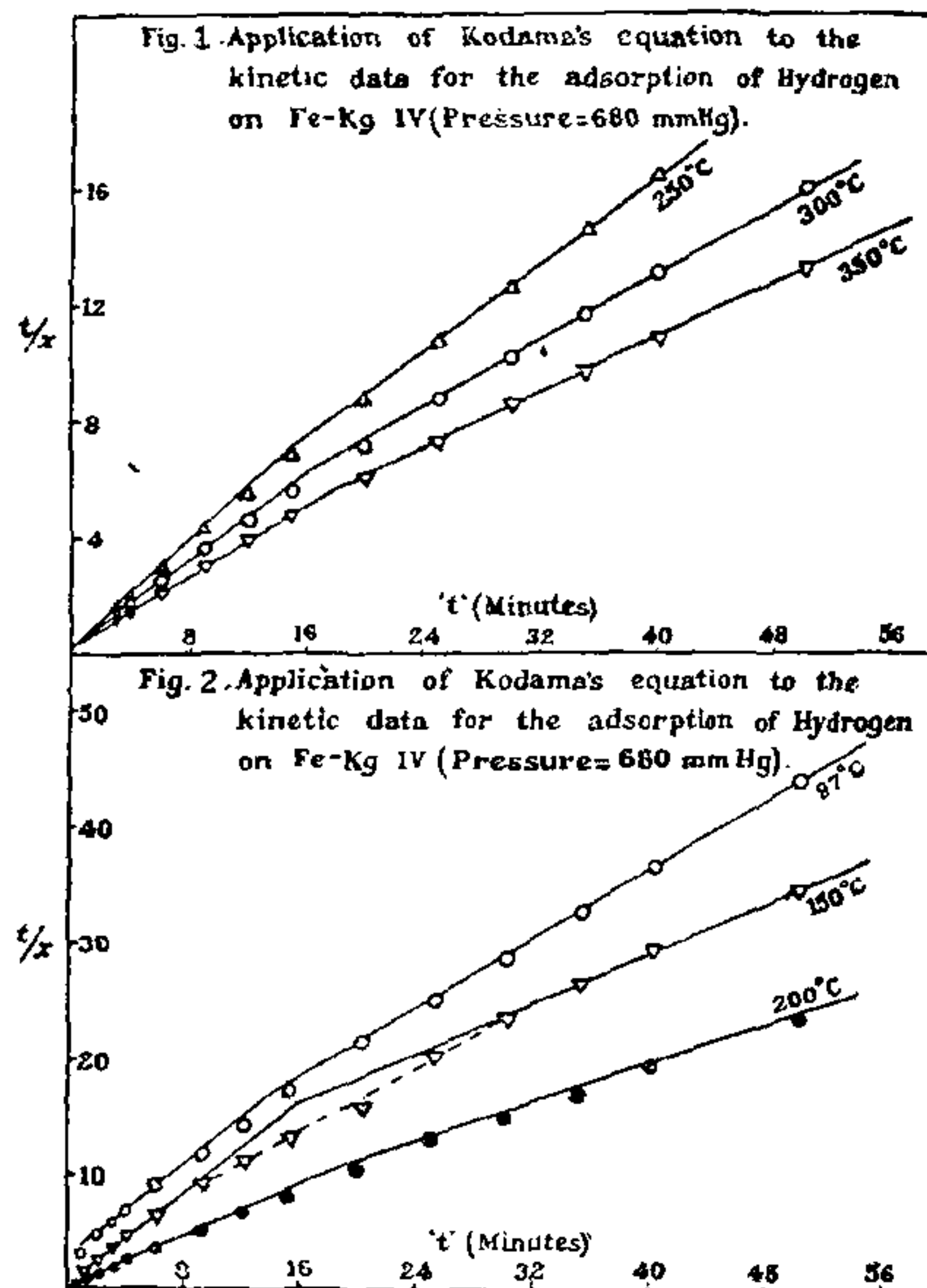
$$\frac{t}{X} = \frac{t}{A} + \frac{1}{A^2 K} \quad (2)$$

where A and K are constants. The applicability of this equation to the kinetics of hydrogen chemisorption on a few catalysts were also reported by the same authors.² In spite of the suitability of equation (2) to the treatment of kinetic data on hydrogen chemisorption, it has somehow missed the attention of the workers in this field.³ In the present paper, the equation of Kodama *et al.* has been successfully applied to the kinetics of hydrogen chemisorption on an iron catalyst.

The adsorbent was a reduced sample of Iron-Kieselguhr (5.47 gm.) prepared by the method of impregnation having a specific surface area of 27.62 m²/gm. The kinetics of adsorption of hydrogen were studied employing a conventional volumetric adsorption apparatus⁴ at a constant pressure of 680 mm. and temperatures of 97, 150, 200, 250, 300 and 350° C. taking the usual precautions.

The kinetic data were employed for testing the applicability of equation (2). The plots of t/X versus 't' at various temperatures are shown in Figs. 1 and 2. It is seen from the figures, that the points lie on two intersecting straight lines at each temperature. The points plotted from the data at 150° C. show some scatter.

The constants A_1 , K_1 and A_2 , K_2 in equation (2) were calculated for both the linear portions



FIGS. 1-2

of the plots and are shown in Table I. The value of the constants differ somewhat from those reported by Kodama *et al.*,¹ who have obtained for a similar system the values of A_1 and A_2 at temperatures of 100, 157, 207 and 255° C. as 1.83, 1.96; 1.78, 2.05; 1.80, 2.04 and 1.72, 1.93 respectively.

TABLE I

Temperature °C	A_1	K_1	A_2	K_2
97	2.00	0.993	1.23	0.105
150	2.06	0.32	1.85	0.00
200	1.87	0.722	2.30	0.097
250	2.14	1.37	2.72	0.095
300	2.70	0.595	3.46	0.060
350	3.25	0.474	4.24	0.040

The treatment of the same kinetic data through the Elovich equation⁵ revealed all the general characteristics, as reviewed by Low.³ To explain the applicability of both the equations to the same kinetic data, it was suggested⁵

that the two equations have similar terms on expansion, as shown below:

Kodama's equation

$$\frac{t}{X} = \frac{t}{A} + \frac{1}{A^2 K}$$

$$X = A^2 K t (1 + A K t)^{-1} \\ = A^2 K t - A^3 K^2 t^2 + \dots$$

Elovich equation

$$X = \frac{1}{a} \ln(1 + aat) \\ = at - \frac{a^2 at^2}{2} + \dots$$

where a and a are constants.

Kodama's equation can be expected to have a wider applicability than the Elovich equation, because of the double exponential nature of the expression.

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1. Kodama, Matsumura and Tarama, *J. Soc. Chem. Ind. Japan*, 1941, **44**, 358 B.
2. Kodama, *et al.*, *Ibid.*, 1941, **44**, 408 B; 1942, **45**, 92 B, 943.
3. Low, M. J. D., *Chem. Rev.*, 1960, p. 267.
4. Srinivasan, V., *Proc. Ind. Acad. Sci.*, 1957, **46 A** 120.
5. Swamy, C. S., *Thesis submitted for the Ph.D. of Indian Institute of Science, Bangalore*, 1962.

PHYSICOCHEMICAL STUDIES ON A THIOPROPIONIC ACID-COBALT COMPLEX

RENEWED interest on cobalt complexes with various sulphur donors as well as interesting correlations observed between their colour and stereochemistry¹⁻⁸ have prompted us to study complex formation between cobalt and thiopropionic acid HS.CH₂.CH₂.COOH (abbreviated hereafter as TPA), a hitherto little studied chelating agent.^{1-3,9,10} On adding an aqueous solution of TPA to an aqueous cobalt (II) solution, and making the resulting solution alkaline (pH 9.0) (ammonia buffer: 0.4 M NH₄OH + 0.4 M NH₄Cl), a green colouration appears, which on standing for some time in air turns dark-brown.¹⁻³ Previous workers² reported the probable oxidation of cobalt (II) to cobalt (III) during the course of potentiometric study. The present communication, however, records observations on polarographic, amperometric, magnetic, absorption spectral (ultraviolet, visible) studies on the system.

Amperometric studies reveal the 1:2 :: Cobalt : TPA stoichiometry. Polarographic studies were carried out separately in (a) absence of air and (b) presence of air.

(a) *Studies in Absence of Air.*—Increasing amounts of TPA were added to Co (II) solution (2.4×10^{-4} M) of fixed strength (0.4×10^{-4} M) at pH 9.0 (ammonia buffer). Two (polarographic) waves were observed: one anodic due to free TPA and another cathodic due to reduction of cobalt (II) to cobalt (Hg) amalgam, an irreversible wave; $E_{\frac{1}{2}} = -1.2$ V (vs. S.C.E.).

(b) *Studies in Presence of Air.*—On carrying out these studies in presence of air, apart from one anodic wave due to free TPA, two cathodic waves were observed (first starting at -0.29 V and the second one at -0.9 V). The height of the second cathodic wave is double the height of the first one.

It is known that Co (II) in the presence of complexing agents is often oxidized to Co (III). The oxidation as well as the characteristics of cobalt-ammonia complexes have been studied by Laitinen *et al.*¹¹ Evidently the first cathodic wave is due to the reduction of Co (III) to Co (II) (one-electron reduction) while the second wave is due to the reduction of Co (II) to cobalt amalgam. The height of the first wave (a one-electron reduction) is practically half of the second wave (a two-electron reduction). Thus under the above conditions practically all the Co (II) appears to be converted into a brown-coloured Co (III) complex, also confirmed by the absorption spectra of this complex.

Magnetic measurements reveal the diamagnetic ($X_g = -12.16 \times 10^{-6}$) behaviour of the complex solution (Metal:Ligand mixed in 1:2 ratio and pH brought to 9.0), as expected for octahedral spin-paired cobalt (III) ($3d^6$) complex.

Absorption spectra (recorded in solution; Metal:Ligand :: 1:2, pH 9.0, using Ligand + Buffer as reference) of the complex shows absorption bands at 18200 cm.⁻¹, 23550 cm.⁻¹ involving electronic transition $^1A_{1g} \rightarrow ^1T_{1g}$, $^1A_{1g} \rightarrow ^1T_{2g}$ respectively, a characteristic of spin-paired octahedral cobalt (III) complexes. The 10 Dq comes out to be 18200 cm.⁻¹ and the corresponding ligandfield stabilization energy 20.8 Kcals/mole.

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