4. Sasisekharan, V. and Lakshminarayanan, A. V., *Ibid.*, 1969, 8, 505.

5. Pullman, A. and Pullman, B., *Advances in Quantum Chemistry*, 1968, 4, 267.

6. Arnott, S., Dover, S. D. and Wonacott, A. J., *Acta Cryst.*, 1969, B 25, 2192.

7. Seshadri, T. P. and Viswamitra, M. A., *Pramāna*, 1974, 3, 218.

8. Crick, F. H. C. and Klug, A., *Nature*, 1975, 255, 530.

9. Viswamitra, M. A., Seshadri, T. P. and Post, M. L., *Ibid.*, 1975, 258, 542.

10. Suck, D., Manor, P. C., Germain, G., Schwalbe, C. H., Weimann, G. and Saenger, W., *Nature New Biology*, 1973, 246, 161.

11. Rubin, J., Bernnan, T. and Sundaralingam, M., *Biochemistry*, 1972, 11, 3112.

KINETICS OF DECOMPOSITION OF NITROUS OXIDE OVER NICKEL TITANATE

G. NAGASUBRAMANIAN, B. VISWANATHAN AND M. V. C. SASTRI

Department of Chemistry, Indian Institute of Technology, Madras 600 036

ON account of their greater chemical stability, structural reproducibility and catalytic activity than their parent binary oxides, ternary oxides of transition metals have generated wide-spread interest in recent years as catalysts of choice for a diverse variety of catalytic reactions. As part of a general study of the catalytic properties of these oxides, the kinetics of decomposition of nitrous oxide were studied on a series of titanates, with a view to evaluating the usefulness of this reaction for comparative assessment of their catalytic activities for oxidation reactions. No report is available of any previous study of this reaction over ternary oxides. The results obtained with nickel titanate are reported in the present communication. Similar results were obtained with the titanates of cobalt, manganese, magnesium, barium, strontium and calcium.

Nickel titanate was prepared by the method of Saikali *et al.*[1]. Its composition ($NiTiO_3$) and ilmenite structure were established by chemical analysis and X-ray diffraction. BET surface area determined with nitrogen at $-198°$ C $= 3·14$ m^2/gm. Nearly pure N_2O, was further purified by selective freezing at $-78°$ C.

The kinetics of N_2O decomposition over nickel titanate were studied in the temperature range 440–510° C in a quartz reactor, with closed circuit recirculation using an all-glass electromagnetic pump. The decomposition rate was followed by noting the increase in pressure as a function of time. After each kinetic run, the catalyst was "prepared" for the next run, by evacuation at 520° C for 6 hours followed by 8 hours exposure to oxygen (100 torr) at the temperature of the next run and a short evacuation at the same temperature for 3 minutes. This procedure for surface restoration was found to yield reproducible results in repeat runs.

Winter[2], who studied the decomposition of nitrous oxide over rare earth oxides, noted that different rate equations were to be used to express the kinetics of the decomposition at high and low pressures, namely,

$$-\frac{dP_{N_2O}}{dt} = \frac{kP_{N_2O}}{(P_{O_2})^{1/2}},$$

at N_2O pressures > 200 torr   (I)

and

$$-\frac{dPN_2O}{dt} = k'.P_{N_2O},$$

at N_2O pressures < 50 torr   (II)

The same duality of kinetic behaviour at high and low N_2O pressures was observed in the present work also, as may be seen from the consistency of the k values (low standard deviations) calculated with the appropriate rate expressions (*vide* Table I).

TABLE I

Values of rate constants deduced from differential equations I and II

Temp. °C	k (cm$^{1/2}$ min^{-1} m^{-2}) 10^4 (above 200 Torr)		k (min^{-1} m^{-2}) $\cdot$ 10^4 (below 50 Torr)	
	Equation I	Equation II	Equation I	Equation II
440	2·24±0·182	5·44±1·71	3·66±0·76	9·7±0·036
460	3·85±0·1	6·59±1·41	4·37±0·92	13·7±0·7
490	5·29±0·1	4·49±0·8	7·76±1·85	15·7±0·04
510	8·3±10·27	11·9±2·92	12·99±4·14	27·1±0·11

TABLE II

Comparison of rate constants deduced from differential and integral rate equations

	Values of rate constant (k)			
Temp. °C	Above 200 Torr		Below 50 Torr	
	From Eqn. I × 10^{+4}	From Fig. 1 × 10^{+4}	From Eqn. II × 10^{+4}	From Fig. 2 × 10^{+4}
440	2·24	2·2	9·7	10·1
460	3·85	3·82	13·7	14·0
490	5·29	5·57	15·7	15·7
150	8·31	8·27	27·1	27·5

FIG. 2. Plots of Equation II' for decomposition at pressures < 50 Torr.
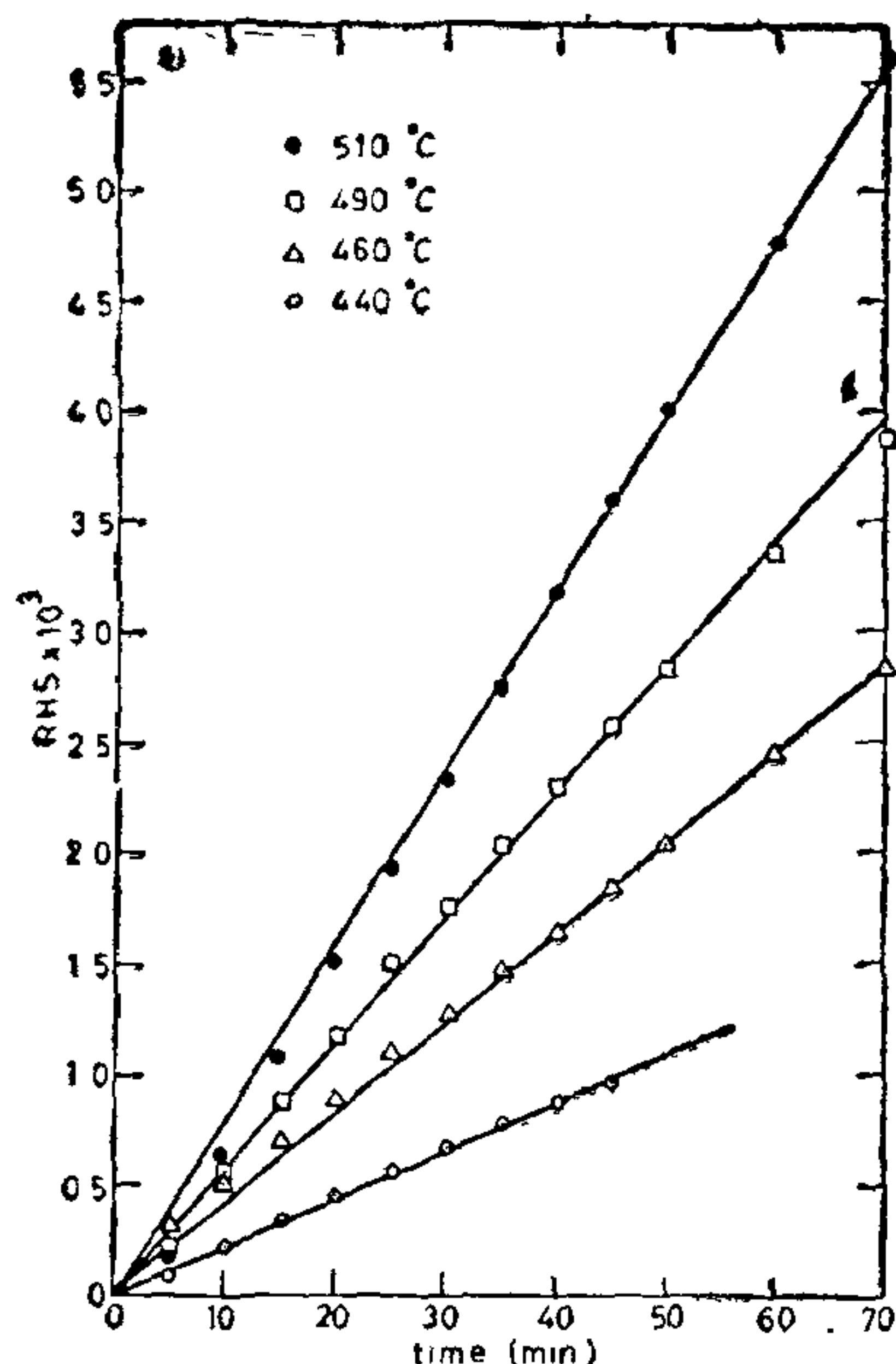

FIG. 1. Plots of Equation I' for decomposition at pressures > 200 Torr.

This could also be demonstrated by using the integrated forms of the two rate-expressions[3], namely,

$$kt = (P_1 + P_2)^{1/2} \left\{ \ln \left[\frac{(P_1 + P_2)^{1/2} + (P_1 + P)^{1/2}}{(P_1 + P_2)^{1/2} - (P_1 + P)^{1/2}} \right] \right.$$
$$\left. - 2 \frac{(P_1 + P)^{1/2}}{(P_1 + P_2)^{1/2}} \right\} \qquad (I')$$

where $2\,P_2$ = initial pressure of N_2O (> 200 torr), $2\,P$ = pressure of N_2O decomposed at time t, P_1 = initial pressure of O_2, and

$$\log P_{N_2O} (< 50 \text{ torr}) = - \frac{k' t}{2 \cdot 303} + C \qquad (II')$$
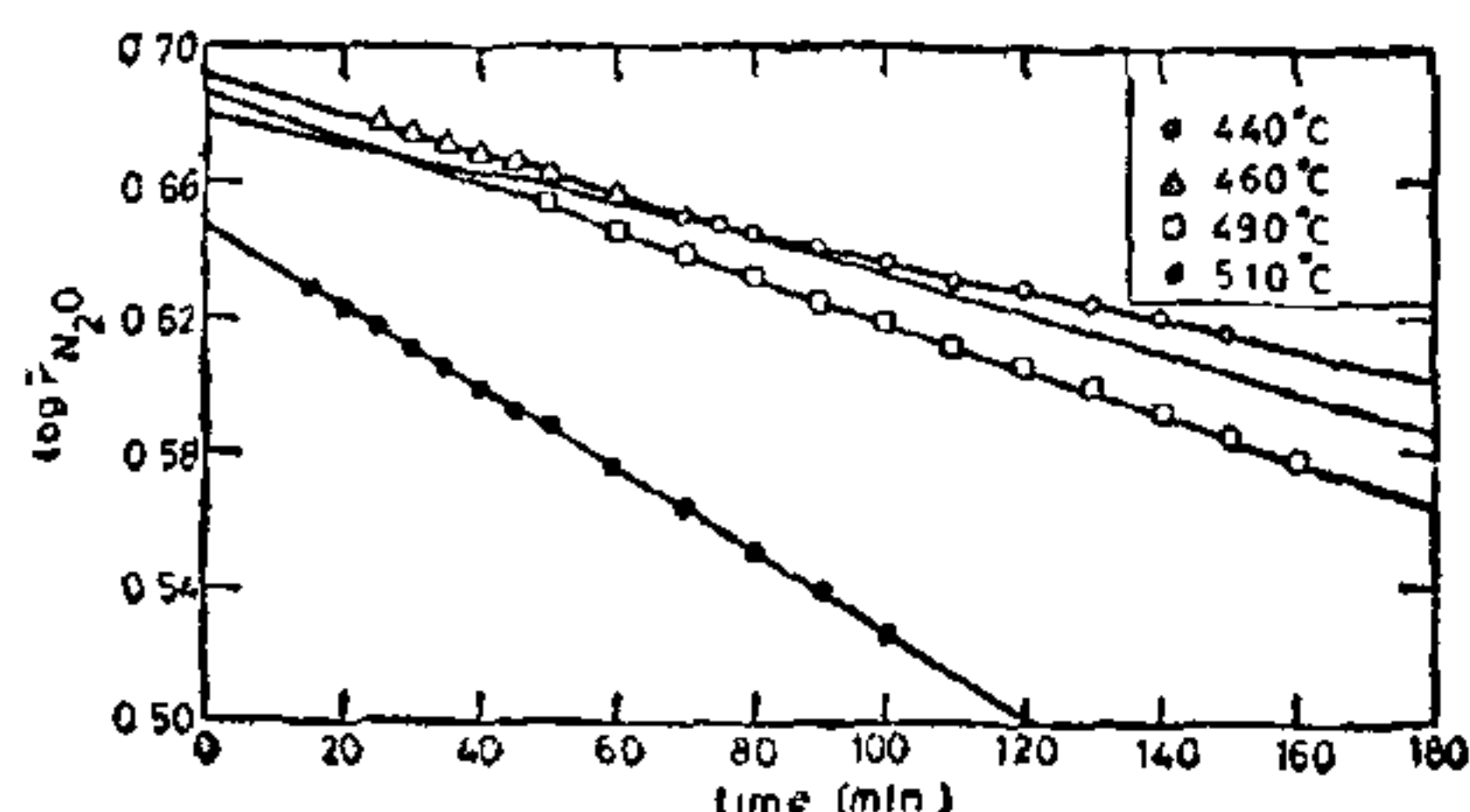
Plots of the experimental data substituted in these

equations are shown in Figs. 1 and 2, respectively. The linearity of these plots and the closer agreement between the value of the rate constants (k) deduced from the two sets of equations, shown in Table II, confirm the validity of these equations in the respective pressure regimes.

TABLE III

Kinetic parameters

Catalyst	E_a (kcals/mole)	k_0 (cm$^{1/2}$ min^{-1} m^{-2})	k at 500 °C (cm$^{1/2}$ min^{-1} m^{-2}
NiTiO$_3$	18·14	24·4	8·65 × 10^{-4}
NiO	39·5	198·3	7·46 × 10^{-7}
TiO$_2$	39·0	0·928	1·16 × 10^{-11}

The values of the apparent activation energy (E_a) and the frequency factor (k_0) for N_2O decomposition on NiTiO$_3$, NiO and TiO$_2$, above 200 torr in the temperature range 300–360° C for NiO and 440–510° C for NiTiO$_3$ and TiO$_2$ and the k values at 500° C (computed temperature) are given in Table III. The higher catalytic activity of NiTiO$_3$ relative to its constituent binary oxides, *i.e.*, the operation of a catalytic synergetic effect, is evident from these data.

1. Saikali, Y. and Paris, J. M., *C.R. Acad. Sci., Paris, Serc.*, 1967, 265 (19), 1041.
2. Winter, E. R. S., *J. Catalysis*, 1969, 15, 144.
3. —, *Discussions Faraday Soc.*, 1959, 28, 183.