The entropy at 298.16°K. is 18.13 ± 0.03 e.u. of which 0.03 e.u. was contributed by the extrapolation below 15°K.

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Catalytic Activity of Lanthanum and Strontium Manganite

BY G. PARRAVANO

Recent work of Jonker and van Santen[1] and Volger[2] has shown that compounds of the general formula $(La_{1-\delta} Sr_\delta)(Mn_{1-\delta}^{+3} Mn_\delta^{+4})O_3$ can be prepared from a mixture of the corresponding oxides or carbonates. Strontium up to $\delta = 0.7$ can be introduced in the $LaMnO_3$ phase without changing its perowskite structure. These compounds have a magnetic Curie temperature which is dependent on the amount of strontium added, and the tempera-
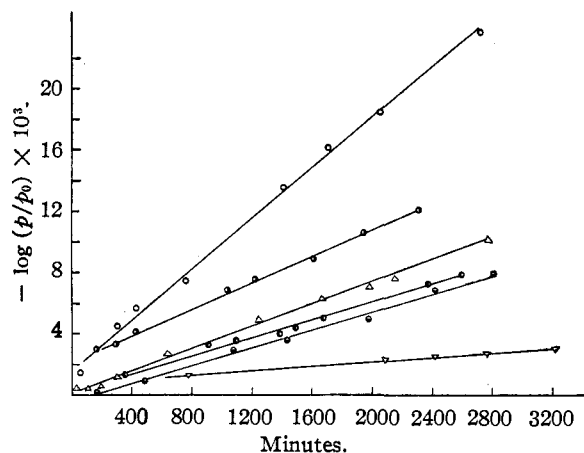

Fig. 1.—Oxidation of carbon monoxide on $La_{0.65}Sr_{0.35}MnO_3$ (2.139 g.): $CO/O_2 = 2/1$; $P_0 = 280$ mm.: ▽, 50°; ◐, 81.5°; ◓, 88°; △, 96°; ◑, 100°; O, 105°.
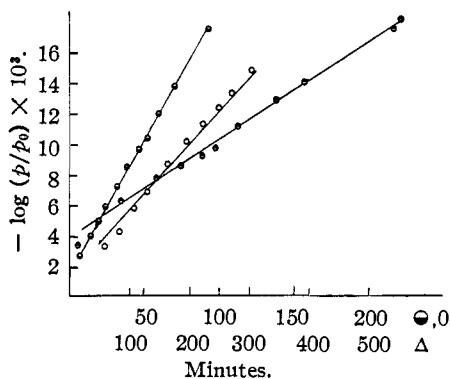

Fig. 2.—Oxidation of carbon monoxide on $La_{0.65}Sr_{0.35}MnO_3$ (2.139 g.): $CO/O_2 = 2/1$; $P_0 = 280$ mm.: △, 140°; O, 183°; ◑, 212°.

(1) G. H. Jonker and J. H. van Santen, Physica, 16, 337 (1950).

(2) "Semiconducting Materials," Butterworth Scientific Publications, London, 1951, Chapter by J. Volger.

ture coefficient of the electrical resistivity shows anomalous behavior; it is positive for the ferromagnetic state and negative above the Curie point. It was therefore considered interesting to investigate the possibility of a relationship between the anomalous behavior of the temperature coefficient of the resistivity of these compounds and the activity of the solid surface to catalyze a chemical reaction. The compound $La_{0.65}Sr_{0.35}MnO_3$ was chosen for this investigation because it possesses the highest Curie point ($\sim373°K.$) of the series, and because it was found that at that temperature the oxidation of carbon monoxide on the above compound proceeded at rates which could be experimentally detected.

$La_{0.65}Sr_{0.35}MnO_3$ was prepared by ball milling a mixture of stoichiometric amounts of C.P. manganese carbonate, strontium oxide and lanthanum oxalate for 1 hour. The mixture was then fired in a platinum crucible in air at 850° for 5 hours, milled again for 1 hour and finally heated at 900° for an additional 3 hours.

Purification of gases and apparatus used for the catalytic experiments have already been described.[3] It was found that the experimental data on the oxidation reaction could be fitted quite well to a first-order equation (Figs. 1, 2). Values for the velocity constant, $k(min.^{-1}, g^{-1})$, at different temperatures are presented in the following table and in Fig. 3, where they are plotted according to the Arrhenius equation, from which an over-all activation energy of 10.6 kcal./mole could be derived.

TABLE I

OXIDATION OF CARBON MONOXIDE ON $La_{0.65}Sr_{0.35}MnO_3$

$CO/O_2 = 2/1$, $p_0 = 280$ mm.

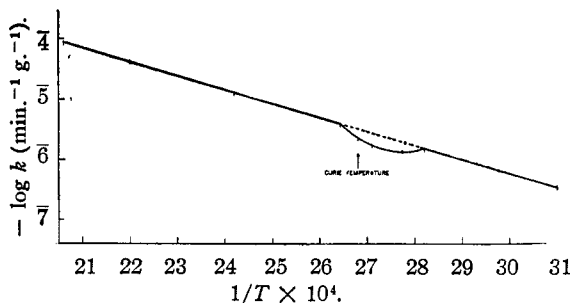| t, °C.	$k \times 10^5$, min.$^{-1}$, g^{-1}	t, °C.	$k \times 10^4$, min.$^{-1}$, g^{-1}
50	0.34	105	3.83
81.5	1.45	140	11.8
88	1.37	183	49.0
95	1.69	212	82.0
100	2.17		

Fig. 3.—Oxidation of carbon monoxide on $La_{0.65}Sr_{0.35}MnO_3$. Arrhenius plot.

From the experimental data it is clear that the oxidation reaction shows the same activation energy below and above the Curie point of the catalyst. This is in disagreement with the magneto-catalytic effect studied by Hedvall.[4] According to this effect the temperature coefficient of the activity of a catalyst is markedly different below and above its

(3) G. Parravano, THIS JOURNAL, 74, 1448 (1952).

(4) For a review on this effect see: Schwab, "Handbuch der Katalyse," Vol. 6, Springer, Verlag Wien, 1943, chapter by J. A. Hedvall.

Curie point. In the present case, however, different magnetic states of the catalyst have no effect on the reaction. The same deduction can be drawn as to the reversal of the temperature coefficient of the resistivity of the catalyst. On the other hand, the data of Fig. 3 show that in the neighborhood of the ferromagnetic transition an anomaly is present in the rate of the catalytic reaction. This is in agreement with previous findings of Forestier and Lille,[5] who reported anomalies in the rate of the reaction $CO_2 + H_2 \rightleftarrows CO + H_2$ on Fe_3O_4, $SrFe_2O_4$, $NiFe_2O_4$ around the Curie temperature of the catalyst. The anomalous behavior of the activity of a catalytic reaction reported in the present communication is quite similar to that previously found for ferroelectric transitions occurring in sodium and potassium niobate and lanthanum ferrite.[6] It is interesting to note that the anomaly sets in somewhat below the Curie temperature. This could be explained by assuming that the ferromagnetic transition occurs on the surface at a lower temperature than in the bulk.

(5) H. Forestier and R. Lille, Compt. rend., 204, 265 (1937).

(6) G. Parravano, J. Chem. Phys., 20, 342 (1952).

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Energy Relationships of Fused Ring Systems

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Using the Pitzer parameters[1] of 3.6 kcal. for the eclipsed, and 0.8 kcal. for the skew conformation (the staggered arrangement being set at zero) of the

Decalins

Fig. 1.

n-butane portion of a hydrocarbon chain, Turner[2] has calculated the difference in energy between the

(1) (a) K. S. Pitzer, Chem. Revs., 27, 39 (1940); (b) C. W. Beckett, K. S. Pitzer and R. Spitzer, THIS JOURNAL, 69, 2488 (1947).

(2) R. B. Turner, ibid., 74, 2118 (1952).

cis and trans forms of decalin to be 2.4 kcal., which, after correction for heats of vaporization, is in excellent agreement with the experimental observation. A simple method of carrying out the calculation of energy difference is as follows:

trans-Decalin is arbitrarily assigned the value zero; now cis-decalin differs from the trans isomer only in the three skew interactions involving the two polar (p) bonds as shown in Fig. 1. The energy difference, hence, is $3 \times 0.8 = 2.4$ kcal.

Applied to the perhydro-phenanthrenes and -anthracenes, this method of estimating energy differences leads to a more definitive picture of the relationships that were established qualitatively earlier,[3] and provides a criterion for establishing a more precise order of stability. In addition, this treatment affords an interrelation of the members of the phenanthrene and of the anthracene series on the same energy basis. It should be emphasized, however, that all of these energy differences are for the vapor phase at 25°, and small corrections would be expected[2] for the differences in heats of vaporization of the isomers.

The perhydroanthracenes (see Fig. 2) are conveniently considered first. Since the trans–syn–trans is the isomer of lowest energy, it is arbitrarily assigned the value zero. The cis–syn–trans form then differs from the trans–syn–trans by 3 skew interactions or 2.4 kcal. just as in the decalin series considered above. In the cis–anti–cis isomer an additional cis-decalin fusion is imposed which simply doubles the energy difference, i.e., 6 skew interactions = 4.8 kcal.

The trans–anti–trans isomer differs from the trans–syn–trans in that the central ring assumes the boat conformation,[3] which accounts for a difference in energy of 5.6 kcal., namely, the difference between the chair and boat form of cyclohexane. In addition the trans–anti–trans form has two interactions (magnitude uncertain) of the type discussed by Turner,[4] which is defined by a rotation of 60° from the staggered conformation. The total energy difference for this isomer, hence, is a value somewhat greater than 5.6 kcal. In the cis–syn–cis isomer the situation is complicated by the fact that two of the (p) bonds appear in the unfavorable 1,3-relationship on the central cyclohexane ring. This interaction is comparable to that of the (p) (p) form of cis-1,3-dimethylcyclohexane for which Pitzer[1] has arbitrarily assigned the energy difference of 5.4 kcal. In the present case the interaction of two methylene groups is estimated to be about 8/9 (skew methylene/methyl) of this value or 4.8 kcal. With this
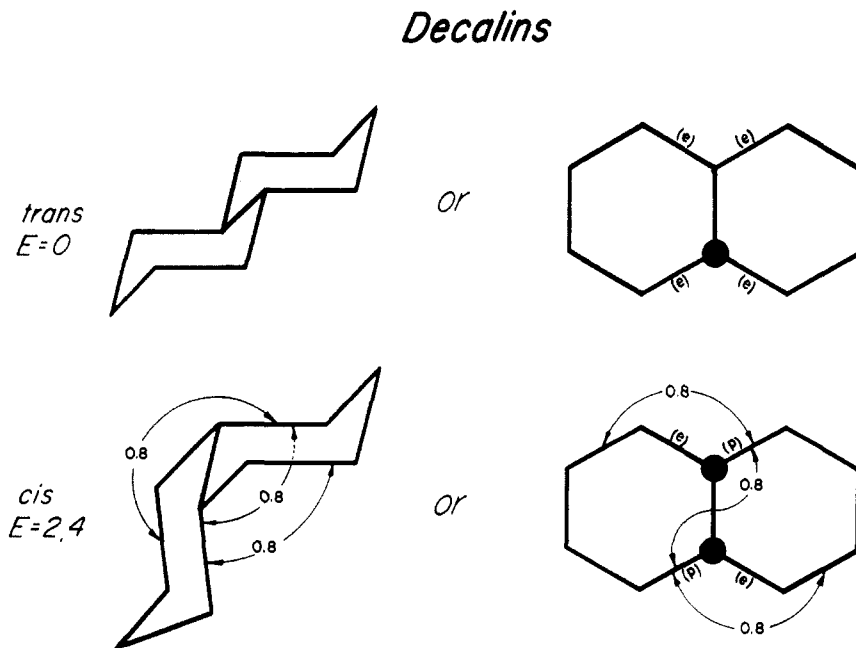
(3) W. S. Johnson, Experientia, 8, 315 (1951).

(4) See formula IX, ref. 2.