TABLE I

VAPOR PRESSURES OF DIMETHYL TARTRATES

t, °C.	$10^3\ p$, mm.	t, °C.	$10^3\ p$, mm.
d-Dimethyl tartrate (s)		*dl*-Dimethyl tartrate (s)	
35.4	3.02	42.5	1.98
40.4	6.16	49.5	5.33
44.2	10.23	55.8	11.65
		65.6	39.6
d-Dimethyl tartrate (l)		72.9	90.0
49.5	22.6	85.2	275
55.8	39.1		
63.3	73.5	*dl*-Dimethyl tartrate (l)	
85.2	381	91.8	621
91.8	625		

observed value (experimental section) was 48°. The vapor pressures of the *d*- and *dl*-ester are equal, within experimental error, at 91.8°, where both are liquid. The intersection of the curves given by (2) and (3) is at 87.8°; the observed value of the melting point of the *dl*-ester is 89°. Since both esters boil at about 280° at atmospheric pressure, the curves may be assumed to coincide at temperatures above 89°.

These relationships between the three vapor pressure curves are just the ones expected of a system of two enantiomers in which the solid racemic crystal is more stable than the crystal of one isomer, but in which the physical properties of the liquid do not depend markedly upon the configuration of the constituents.

The molar heats of sublimation of *d*- and *dl*-dimethyl tartrate, calculated from the slopes of curves (1) and (3), are 27.01 and 27.19 kcal., respectively. The heat of racemization in the solid state is therefore very small. The heats of combustion of the two esters are reported to differ by 1.0 kcal./mole.[7] Rosenberg,[8] however, has found by measurement of the heat of solution of tartaric acid that the molar heat of racemization is only about 0.15 kcal.

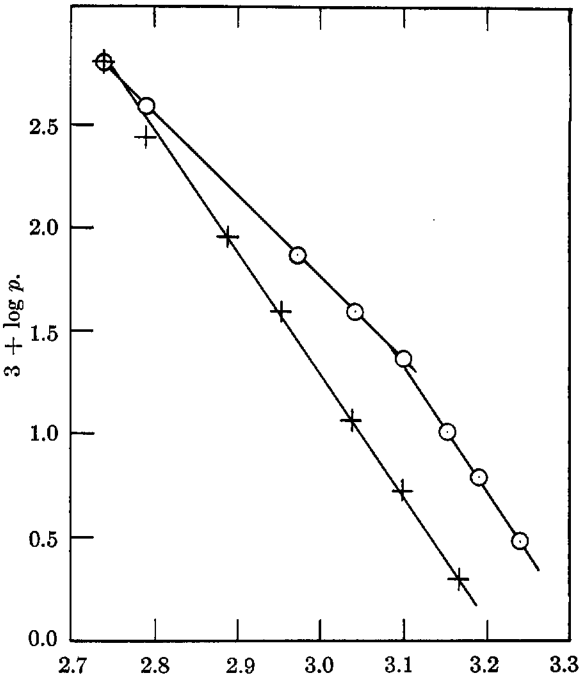

Fig. 1.—Vapor pressure of *d*-dimethyl tartrate, ○; and *dl*-dimethyl tartrate, +.

The calculated molar heat of vaporization of liquid *d*-dimethyl tartrate is 18.26 kcal. Assuming the same value for the racemic ester, the molar heats of fusion are 8.75 and 8.93 kcal. Wasserman[7] found 3.63 kcal. for the molar heat of fusion of *d*-diethyl tartrate and 5.21 kcal. for *meso*-diethyl tartrate.

[7] A. Wasserman, *Z. physik. Chem.*, **A146**, 446 (1930).

[8] T. Rosenberg, *Acta Chem. Scand.*, **2**, 740 (1948).

THE THERMAL DECOMPOSITION OF NICKEL OXALATE

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The kinetics of the thermal decomposition of anhydrous nickel oxalate have been studied in the range 280–320° by measuring the rate of evolution of carbon dioxide into an atmosphere of pure nitrogen. The reaction falls into two parts, (i) an initial reaction following an equation, $V = k_1(t - t_0)^{1/2}$, where V is the volume of carbon dioxide, t the time and t_0 a correction factor, which is succeeded by (ii) a reaction with a constant initial rate, $V = k_2t$, but which soon falls off. The activation energies for the two parts are, respectively, 47.6 and 36.4 kcal. A mechanism for the reaction is proposed in which the rate-determining step in (i) is the diffusion of anions to the free surface and in (ii) the transfer of electrons from the oxalate ion. X-Ray measurements show the absence of metallic nickel throughout (i) and its presence in (ii).

Many irreversible thermal decomposition reactions of the general type

$$\text{A(solid)} \longrightarrow \text{B(solid)} + \text{C(gas)}$$

have been studied, but only in cases in which B is a metal and C a single gas are the results likely to be interpretable in terms of our present knowledge of electronic and ionic processes in the solid state. Silver oxalate is the only metal oxalate conforming to these restrictions which has been investigated, but the photosensitivity of this substance[1] and its molecular layer lattice[2] suggest that it should not be considered as a general case.

Anhydrous nickel oxalate appeared to fulfill most of the requirements for such an investigation. It is one of the few metallic oxalates which decompose to give the metal and carbon dioxide, although traces of oxide and carbonate have been reported.[3] The salt is prepared as the dihydrate, $NiC_2O_4 \cdot 2H_2O$, by precipitation from solutions of nickel sulfate

[1] F. C. Tompkins, *Trans. Faraday Soc.*, **44**, 208 (1948).

[2] R. L. Griffith, *J. Chem. Phys.*, **14**, 408 (1946).

[3] M. Herschkowitsch, *Z. anorg. allgem. Chem.*, **115**, 159 (1921).

and oxalic acid and investigations on its preparation and dehydration have already been published.[4,5]

The dihydrate may be dehydrated under controlled conditions at a temperature of about 90° below that of decomposition which takes place at measurable rates in the range 280–320°. Nickel oxalate dihydrate is stable in air and is unaffected by prolonged exposure to ultraviolet light. There is no evidence of photosensitivity of the anhydrous salt and it is unlikely to possess a layer lattice.

The aim of the present work was to study the kinetics of the thermal decomposition of anhydrous nickel oxalate and, if possible, to formulate a mechanism for the reaction.

Experimental

(a) **Nickel Oxalate.**—Nickel oxalate dihydrate from three different sources with the characteristics listed in Table I was used as starting material.

TABLE I

Source	Description	Surface area of dihydrate, cm.² per g.	Particle character
A	Standard May and Baker	6700	Very uneven
B	Rapid precipitation from soln. 0.4 N $H_2C_2O_4$ and 0.2 N $NiSO_4$	4700	Even
C	Slow precipitation from soln. 0.02 N $H_2C_2O_4$ and 0.4 N $NiSO_4$	10000	Flaky

A was adopted as the standard material since its properties were intermediate between B and C prepared under the widely differing conditions. Unless otherwise specified all results refer to A. Dehydration to the anhydrous salt was carried out *in vacuo* at 190° for a minimum of 4 hours. For 0.2 g. of dihydrate normally used this was complete in 2 hours, the evolution of further water vapor thereafter being undetectable over 10-minute intervals. The completeness of dehydration was checked gravimetrically in test experiments.

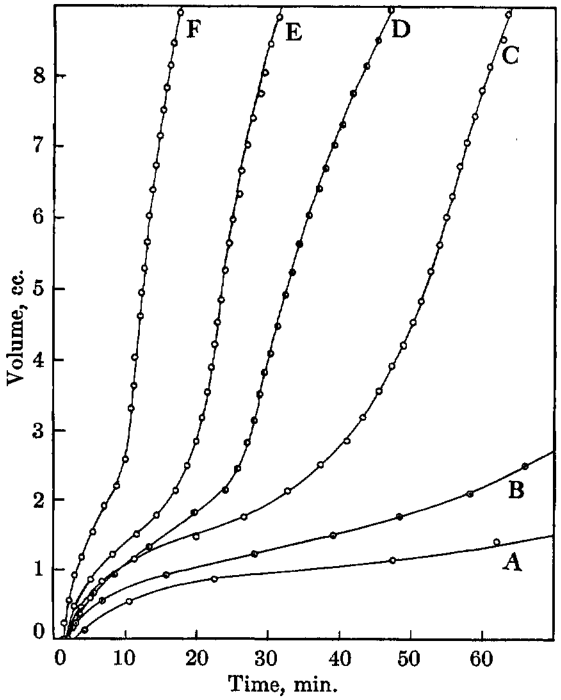

Fig. 1.—A, 279.2°; B, 291°; C, 298.5°; D, 303°; E, 309°; F, 320°.

The oxalate was enclosed in a thin-walled Pyrex ampoule about 6 mm. internal diameter; one end of this was drawn down to a strong capillary which was then bent into a hook. A loose plug of glass wool was packed into this constricted end and the sample of dihydrate weighed into the tube which was subsequently sealed off at the opposite end.

(b) **Apparatus.**—The decomposition was carried out into an atmosphere of pure nitrogen acting as a buffer gas so that the volume of carbon dioxide could be measured at constant pressure over a convenient range. The purification system for the nitrogen was similar to that used by Herington and Martin.[6]

The experimental apparatus consisted of a wide bore glass tube heated at the top by a mercury vapor jacket and cooled at the bottom by a lead coil carrying cold water. The ampoule was suspended by a thin platinum wire and could be moved in the reaction tube by means of a winch around which the wire was wound. The pressure of the pure nitrogen was measured by a wide bore mercury manometer and the volume of the carbon dioxide evolved in the reaction was measured in a water jacketed gas buret. The pressure was kept constant by using a leveling reservoir in conjunction with a differential oil manometer. The whole apparatus could be evacuated to a pressure of less than 10^{-5} mm. by a pumping system of conventional design.

The temperature gradient in the heated tube was measured and a region of sufficient length over which the variation was less than 1° was determined. This was located from a predetermined number of turns of the winch.

(c) **Procedure.**—The ampoule containing the dihydrate was attached to the platinum wire and wound into the cold section. The apparatus was continuously evacuated, the temperature of the hot section adjusted to 190° and the ampoule then wound up into this section. When dehydration was complete the ampoule was wound down to the cold section and the temperature of the hot section adjusted to that for the decomposition, 280–320°. The system was isolated from the pumps, the nitrogen admitted to the desired pressure and the differential manometer set. The ampoule was then raised into the heated section and the evolution of gas measured with time. There was an initial drop in pressure due to cooling of the gas in the heated section by the cold ampoule and it took 1.5–2.5 minutes for the sample to reach the decomposition temperature when the reaction started immediately.

Results

(a) **General Form of the Rate Curve.**—The volume of gas evolved per 0.1 g. of anhydrous nickel oxalate reduced to N.T.P. is plotted against time in Fig. 1 for a series of temperatures between 280 and 320°. The initial reaction follows the equation

$$V = k_1(t - t_0)^{1/2} \qquad \text{(i)}$$

as shown in Fig. 2, where V is the volume of carbon dioxide per 0.1 g. of anhydrous oxalate, t is the time and t_0 is a time correction for the period of heating. The initial reaction represents an average of 5.8% of the total reaction.

The second part of the rate curve does not fit any of the equations reported in the literature for reactions of a similar kind. Detailed examination of this part of the reaction, particularly at the higher temperatures, showed that it may be treated as an initially linear relation

$$V = k_2t \qquad \text{(ii)}$$

the maximum slope k_2 being characteristic of this part of the reaction. The early falling off from linearity, referred to as the decay, is not unimolecular.

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(4) J. A. Allen, THIS JOURNAL, **57**, 715 (1953).

(5) J. A. Allen and D. E. Scaife, *ibid.*, **57**, 863 (1953).

(6) E. F. G. Herington and J. F. Martin, *Trans. Faraday Soc.*, **49**, 154 (1953).

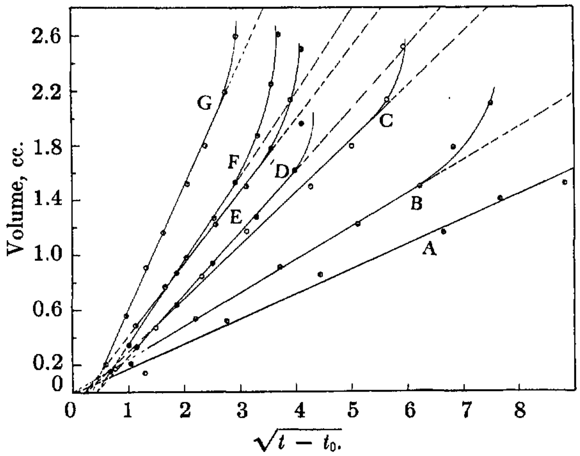

Fig. 2.—A, 279.2°; B, 291°; C, 298.5°; D, 303°; E, 309°; F, 313°; G, 320°.

(b) **Reproducibility.**—For similar samples under identical conditions the initial reaction rate is very reproducible. The duration of the initial reaction varies irreproducibly within the limits of ±20% about a mean. The initial rate of the second part of the reaction, defined by k_2 is reproducible to within ±5%. The onset of the decay tends to be variable. Typical results of identical experiments are shown in Table II.

TABLE II

Run	k_1	k_2	Duration of initial reaction, min.
17	0.45	0.45	20
18	.45	.41	25
19	.45	.44	27

(c) **Mass of Sample and Pressure of Buffer Nitrogen.**—A standard amount of 0.2 g. of dihydrate was used in most experiments. Test experiments using 0.1 g. did not yield significantly different results. For quantities ≤0.05 g. the initial reaction was too small to be followed accurately at the standard buffer pressure.

A pressure of 30 cm. of nitrogen was used in most experiments. Increasing this to 50 cm. did not yield significantly different results.

(d) **Samples of Different Origin.**—Typical results of identical experiments using samples from the three sources listed previously are shown in Table III.

TABLE III

Source	k_1	k_2	Duration of initial reaction, min.
A	0.45	0.44	27
B	.75	.43	23
C	.41	.41	31

The initial rate of the second part of the reaction is the same within the limits of reproducibility for all samples. The rate of the initial reaction is different for samples of different origin.

(e) **Purity of Nitrogen.**—The presence of oxygen in the buffer gas has a marked effect on the rate of decomposition. Figure 3 shows curves obtained from experiments in which pure nitrogen, impure nitrogen containing less than 1% oxygen and air, respectively, were used, all other conditions being identical. The features are the small effect of oxygen on the initial reaction and the systematic decrease in the initial rate of the second part of the reaction for experiments carried out in impure nitrogen and in air. The decay also appears to set in earlier with these experiments.

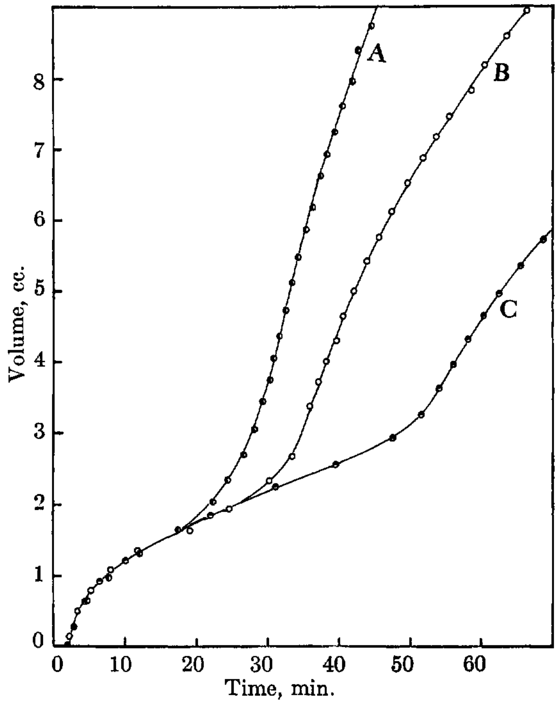

Fig. 3.—A, pure N_2; B, impure N_2; C, air.

(f) **Temperature of Dehydration.**—Dehydration at 220° instead of 190° generally employed halved the time of dehydration, but did not significantly influence the subsequent thermal decomposition. A more detailed study of this variable, particularly in relation to the surface area of the dehydrated oxalate, is to be undertaken.

(g) **Completeness of Decomposition.**—In a number of experiments the gases were evacuated from the apparatus when about 30% of the total decomposition had taken place and the remainder of the reaction carried out *in vacuo*. The yield of metallic nickel determined gravimetrically immediately after the experiment corresponded to the theoretical value to within 1.8%. The ampoule was sealed immediately on removal from the apparatus in order to minimize oxidation of the nickel. In addition, experiments using 0.05 g. of dihydrate were carried on for a long period in the presence of the nitrogen and carbon dioxide. It was found that when the reaction had proceeded to the extent of 75% the rate of evolution of gas had become very slow.

If the decomposition was interrupted by lowering the ampoule out of the heated section, the smooth curve was resumed without a break on resumption of heating. Metallic nickel residue from a previous experiment mixed in a fresh charge of oxalate to the extent of about 30% by weight prolonged the initial reaction for as much as 150 minutes. It should be noted, however, that the metallic residue used would have been contaminated with oxide as a result of exposure to the air during mixing.

(h) **Effect of Temperature.**—The over-all effect of temperature on the rate curve is seen from Fig. 1. The plot of log k_1 against $1/T$, Fig. 4, yields, by the method of least squares, the equation

$$\log_{10} k_1 = \frac{-5202}{T} + 8.669 \qquad \text{(iii)}$$

The specific reaction rate corresponding to the differential form of equation (i) is k_1^2 whence the activation energy for the initial reaction is 47.6 kcal. per mole.

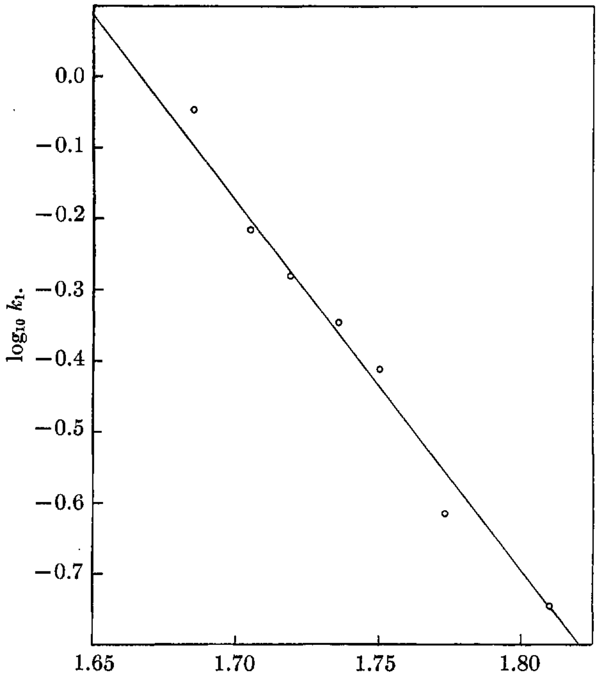

Fig. 4.

For the second part of the reaction log k_2 plotted against $1/T$, Fig. 5, gives

$$\log_{10} k_2 = \frac{-7946}{T} + 13.46 \qquad \text{(iv)}$$

whence the activation energy is 36.4 kcal. per mole.

(i) **X-Ray Analyses.**—Four samples of partly decomposed oxalate, two taken during the initial reaction and two during the second part, were examined with unfiltered copper radiation in sealed quartz tubes by Dr. G. F. Walker of the Commonwealth Scientific and Industrial Research Organization. He reported that the two samples taken during the initial reaction gave patterns identical with the undecomposed anhydrous nickel oxalate, whereas the two samples taken during the second part gave, in addition, patterns corresponding to metallic nickel. It was estimated from synthetic mixtures that 1% of metallic nickel would be observable. There was no evidence of the presence of nickel oxide or nickel carbonate in any of the samples although in the case of the latter as much as 10% might escape detection.

Discussion

The present results are substantially different from those reported for barium azide and silver oxalate for which some theoretical work has been carried out.[7] For the initial reaction the following mechanism is proposed.

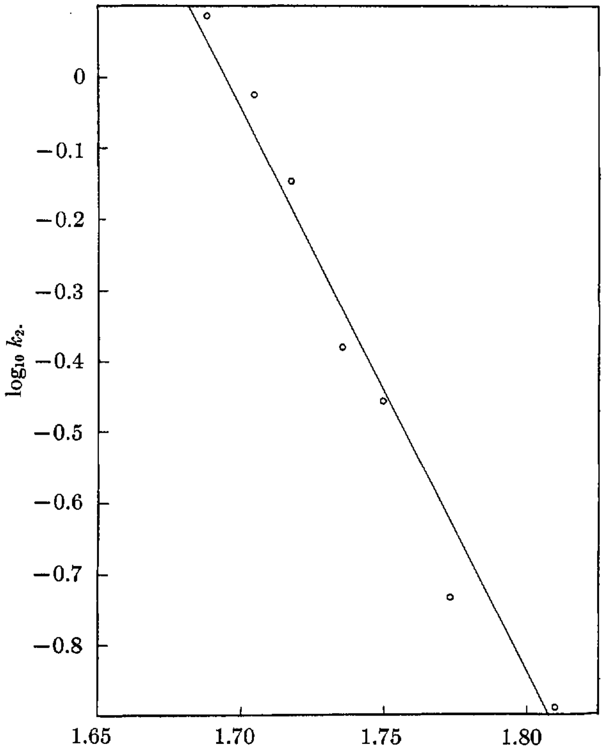

Fig. 5.

An anion situated at a favorable site at the surface loses its electrons which are trapped at impurity centers or existing vacant anion sites. The oxalate radical breaks down to give carbon dioxide which escapes leaving a vacant anion site which may function as a further electron trap.

The vacant anion sites diffuse into the body of the crystal, but, because of the large size of the anions and their expected low mobility, a quasi-equilibrium of vacant anion sites is set up in the surface layers of the crystal. The concentration gradient controlling diffusion of anions to the free surface will, under these conditions, be inversely proportional to the extent of the reaction; that is, provided the rate-determining step is the diffusion of anions to the free surface

$$\frac{dV}{dt} \propto \frac{1}{V} \qquad \text{(v)}$$

from which the experimentally found equation (i) follows.

At the end of the initial reaction the lattice in the upper surface layers has become so defective that it collapses to form metallic nuclei. An anion at the free surface so produced may now lose its electrons, the oxalate radical breaking down to yield carbon dioxide. The trapped electrons migrate to a cation adjacent to a metallic nucleus to which the resulting metal atom joins. There will now be a continuous exposure of fresh oxalate ions at the free surface in positions favorable for decomposition. This

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[7] *E.g.*, J. G. N. Thomas and F. C. Tompkins, *Proc. Roy. Soc.* (*London*), **A210**, 111 (1951).

mechanism would lead to a reaction of initially constant rate, *cf.* equation (ii).

The X-ray data give clear evidence of the absence of metallic nickel in the initial reaction and the presence of it in the second part of the reaction. The activation energy of 47.6 kcal. per mole for the initial reaction is interpreted as the activation energy for diffusion while the 36.4 kcal. per mole for the initial rate of the second part of the reaction is to be associated with the transfer of electrons from an oxalate ion at a position suitable for reaction.

The early decay of the initial rate of the second part of the reaction is attributable primarily to interference with the electron transfer processes by the gaseous product of the reaction. The decrease in the area of the free surface of the oxalate as the amount of metallic nickel increases may also be important when the reaction is well advanced.

The experimental observations are consistent with the view that both oxygen and carbon dioxide are effective poisoning agents of the surfaces of the metallic nuclei. The actual formation of a small amount of surface oxide on the metallic nuclei by reduction of the carbon dioxide is feasible thermodynamically and cannot be ignored. The effect of oxygen in extending the duration of the initial reaction is explicable since the diffusion of oxygen into the highly defective surface layers would retard the collapse to form the metal lattice.

The proposed mechanism is based on the hypothesis, that the oxalate ions can diffuse in the surface layers. To test this, ionic diffusion measurements are required and these will be undertaken in a future investigation.

Acknowledgments.—We wish to thank Dr. G. F. Walker for the X-ray analysis and Professor I. Lauder of the University of Queensland for a useful discussion of some aspects of the reaction. The work was supported by the University of Tasmania Research Fund and we are indebted to Commonwealth Industrial Gases Ltd., Tasmania, for a gift of liquid air.

NOTE

A SIMPLE CORRELATION OF GAS SOLUBILITIES

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The fact that the solubilities of the more "permanent" gases decrease with increasing "internal pressures" of the solvent was pointed out[1] in 1916. In 1924 the relation was put upon an approximately quantitative basis by aid of the theory of regular solutions.[2] In 1940, Gonikberg[3] applied this relation rather successfully to solubilities of hydrogen. (The one discordant case, in carbon disulfide, can now be definitely ascribed to an inaccurate measurement.) In 1949 Gjaldbaek[4] and I published a detailed treatment of solubility data for nitrogen by means of the equations for regular solutions, both with and without the Flory–Huggins correction for unequal molar volumes.

The Flory–Huggins expression for the entropy of athermal mixing of two liquids of unequal molar volumes contains the implicit assumption that the free volumes of the pure liquids and the solution are simply related if the appropriate one of the several kinds of free volume is selected.[5] But a good part of the considerable success of that formulation, as indeed of regular solution theory, comes from the fact that, as Scott[6] has recently stated, "the solution properties which interest us . . . are usually differences or ratios referred to the pure

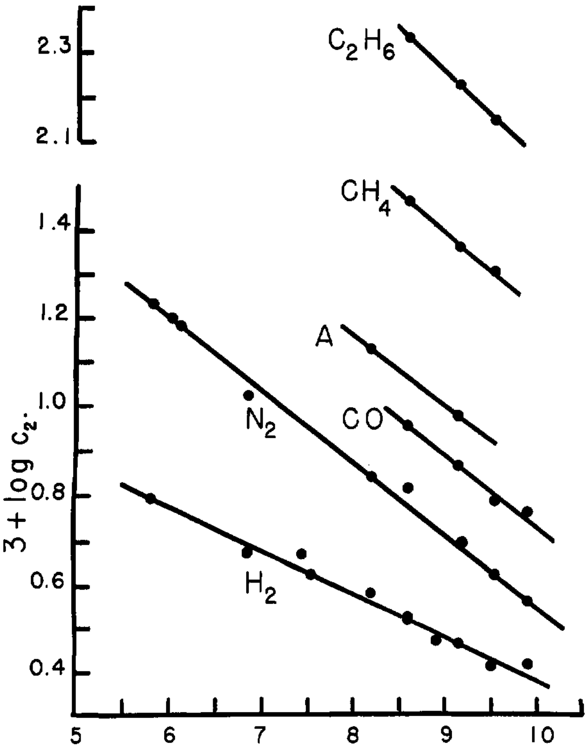

Fig. 1.—Relation between molar concentrations of gases and solubility parameters of solvents.

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[1] J. H. Hildebrand, *J. Am. Chem. Soc.*, **38**, 1452 (1916). See also *Phys. Rev.*, **21**, 46 (1923); N. W. Taylor and J. H. Hildebrand, *J. Am. Chem. Soc.*, **45**, 682 (1923).

[2] J. H. Hildebrand, "Solubility of Nonelectrolytes," 2nd Edition, 1924, p. 135; 3rd Edition, with R. L. Scott, 1950, p. 244, Reinhold Publ. Corp., New York, N. Y.

[3] M. G. Gonikberg, *J. Phys. Chem., U.S.S.R.*, **14**, 582 (1940).

[4] J. C. Gjaldbaek and J. H. Hildebrand, *J. Am. Chem. Soc.*, **71**, 3147 (1949).

[5] A. Bondi, in preparation.

[6] R. L. Scott, *J. Chem. Educ.*, **30**, 542 (1953).