UNFAMILIAR OXIDATION STATES IN LIQUID AMMONIA

BY ARTHUR W. DAVIDSON AND JACOB KLEINBERG

Department of Chemistry, University of Kansas, Lawrence, Kansas

Received November 28, 1952

This paper reports the attainment of unfamiliar oxidation states of certain elements in liquid ammonia by means of two widely diverse methods: (1) electrolytic oxidation of metallic anodes; (2) reduction by alkali metals (a) of gaseous oxygen, (b) of cyanide complexes of transition metals.

(1) In the anodic oxidation of aluminum, coulometric measurements indicate a mean initial oxidation state lower than 3 whenever the electrolyte contains nitrate ion. Evidence is presented to support the hypothesis of primary oxidation of the metal to a cation of low charge (presumably +1), which reduces nitrate ion to free nitrogen in a secondary reaction concurrent with the electrolysis. In the cases of gallium and thallium, stable mixtures of unipositive and tripositive ions are obtained by anodic oxidation. In the case of indium, the ion of charge lower than 3 formed by primary oxidation immediately disproportionates into metallic indium and In(III) ion. (2) (a) It has long been known that liquid ammonia solutions of potassium, rubidium and cesium, upon rapid oxidation with free oxygen, give good yields of the superoxides. It may now be added that sodium, under suitable conditions, yields a product of empirical formula $Na_{1.67}$, and that in the case of lithium there is evidence for the existence of a superoxide stable at −78°, which, however, has not been isolated. (b) The existence of Ni(I) as $Ni(CN)_3^{--}$ and of Ni(0) as $Ni(CN)_4^{-4}$, both obtained by the reduction of tetracyanonickelate(II) ion, has been previously reported, as has the formation of Pd(0) as $Pd(CN)_4^{-4}$ from tetracyanopalladate(II) ion. In our laboratory, the reduction of hexacyanochromate(III) ion has been found to yield a product containing Cr(I), while under similar conditions hexacyanomanganate(III) ion yields a product of empirical formula $K_{11}Mn_2(CN)_{12}\cdot 2NH_3$, containing both Mn(I) and Mn(0).

The fact that liquid ammonia is an especially useful and convenient medium for the carrying out of reactions with very strong reducing agents was pointed out many years ago by Kraus,[1] and has been re-emphasized in more recent reviews by Fernelius and Watt.[2,3] As a corollary, it follows that elements may be expected to exist in liquid ammonia in low valence states which, in aqueous solution, would be subject to rapid oxidation by the solvent. Further, the relatively low degree of self-ionization of ammonia permits the preparation in this medium of certain substances, such as superoxides, which are subject to immediate and extensive hydrolysis in water.

The purpose of this paper is to bring together the results of a number of relatively recent studies of the existence of elements in unfamiliar oxidation states, either as ions in liquid ammonia solution or in compounds formed by reactions which take place in liquid ammonia as a medium. The many instances of compounds between alkali metals and other metals, especially those of Groups IV and V of the periodic system, in which the latter metals exist either as simple anions or as homopolyatomic anions have been extensively reviewed by others[1-4] and will not be discussed here.

In our laboratory, two general types of reaction have been studied: (1) the electrolytic oxidation of metallic anodes; (2) reduction by means of solutions of alkali metals.

Electrolytic Oxidation of Metals of the Aluminum Family

Aluminum.—The anodic oxidation of aluminum[5] was carried out by passing a direct current between an aluminum anode and a platinum cathode, through a solution either of a single salt or of a mixture of two salts in liquid ammonia. An inert atmosphere of nitrogen was maintained throughout the electrolysis, which was usually carried out at −33°. The quantity of electricity which passed through the circuit was determined by means of a silver coulometer in series with the electrolytic cell, while the amount of aluminum anodically oxidized was determined from the weight of the anode at the beginning and at the end of each electrolysis.

A quantity designated as the apparent initial valence number, V_i, of the aluminum ion produced by electrolysis was calculated by means of the equation

$$V_i = \frac{\text{wt. of Ag deposited in coulometer} \times 26.98}{107.9 \times \text{wt. of Al lost from anode}}$$

In the case of anodic oxidation to the familiar tripositive aluminum ion, this quantity would, of course, have the value 3.

In a number of electrolyses carried out as just described in ammonia solutions of single salts other than nitrates, the values found for V_i were close to 3 (within 0.1 unit). In a few other instances, values *higher* than 3 were observed; this result may be regarded as indicative of partial passivity, in that the anodic reaction must have included oxidation of some substance other than metallic aluminum. In every instance, however, in which a nitrate was used as electrolyte, whatever the cation, the value of V_i was found to be less than 3—usually in the neighborhood of 2.7. This value, furthermore, showed little dependence upon concentration of electrolyte, current density or duration of the electrolysis. Since there was no evidence of direct (non-electrolytic) reaction between aluminum and any of the solutions, these results were interpreted as indicating that the anode was electrolytically oxidized, in part, to an aluminum ion of charge lower than +3.

Since the results just described pointed toward the presence of nitrate ion as the determining factor in bringing about the anodic dissolution of aluminum in this lower oxidation state, experiments were made to determine whether or not this effect of nitrate would persist in electrolytes containing both nitrate and other anions. It was found that in nitrate–chloride and nitrate–bromide mixtures it was possible to attain apparent initial valence

---

(1) C. A. Kraus, *Chem. Revs.*, **8**, 251 (1931).

(2) W. C. Fernelius and G. W. Watt, *ibid.*, **20**, 195 (1937).

(3) G. W. Watt, *ibid.*, **46**, 289 (1950).

(4) F. W. Bergstrom, *J. Am. Chem. Soc.*, **47**, 1503 (1925).

(5) W. E. Bennett, A. W. Davidson and J. Kleinberg, *ibid.*, **74**, 732 (1952).

numbers much lower than those found for solutions of nitrates alone. The value of V_i, in fact, was found to vary regularly with the *ratio* of the concentrations of nitrate and halide, reaching a minimum close to 1.5 for mixtures containing about 2 moles of nitrate to 1 of bromide, regardless of the total concentration of electrolyte. Again, the original mixtures were found to have no action upon test rods of aluminum; further, an aluminum rod used as *cathode* in some of the electrolyses underwent no detectable loss of weight, nor was any significant change in initial valence number observed when an intermittent instead of a continuous direct current was used for electrolysis. These facts appear to preclude the possibility of nonelectrolytic corrosion as a disturbing factor.

Most of the electrolyses of bromide–nitrate mixtures were carried out in a cell in which the anode and cathode were separated by a sintered Pyrex disk, in order that the separate examination of anodic and cathodic processes might be facilitated. No compound of lower valent aluminum could be detected in the grayish anodic deposit, nor in solution in the anolyte, after electrolysis; both of these phases were quite devoid of reducing power. It was noted, however, that an appreciable diminution in the concentration of nitrate took place during the electrolysis, and that measurable quantities of nitrogen were evolved at both anode and cathode. Furthermore, the quantity of hydrogen evolved at the cathode was always somewhat less than that calculated from coulometric data, on the assumption of hydrogen liberation as the sole cathode reaction.

In order to account for the phenomena which have been described, the following electrode reactions were postulated.

$$\text{Cathode: } 2NH_4^+ + 2e^- = 2NH_3 + H_2$$

$$2NO_3^- + 12NH_4^+ + 10e^- = N_2 + 12NH_3 + 6H_2O$$

$$\text{Anode: } \left.\begin{aligned} Al &= Al^{+++} + 3e^- \\ Al &= Al^+ + e^- \end{aligned}\right\}\text{primary}$$

$$5Al^+ + 2NO_3^- + 12NH_4^+ = 5Al^{+++} + N_2 + 12NH_3 + 6H_2O \quad \text{secondary}$$

If these hypotheses are correct, the total number of gram-equivalents of nitrate ion reduced during the electrolysis, or of free nitrogen evolved, should be given by the equation

$$\text{No. of gram-equivalents} = 3 \times \text{no. of g.-atoms of Al dissolved} - \text{no. of g.-equiv. of } H_2 \text{ evolved}$$

while the number of *moles* of nitrate lost, or of nitrogen evolved, should be 1/5 and 1/10, respectively, of this figure. Several experiments were carried out in which the amount of nitrate lost during electrolysis was determined by analysis, while the total volume of gas evolved was measured, and its hydrogen content determined by combustion. Results of these experiments are shown in Table I; the fairly good agreement between columns (E) and (F) is in accord with the postulated electrode reactions.

TABLE I

REDUCTION OF NITRATE DURING ELECTROLYSIS

(A) Quantity of elect., faraday	(B) Al dissolved, g.-atom	(C) V_i, from (A) and (B)	(D) H_2 evolved, g.-equiv.	NO_3^- reduced or N_2 evolved, mole (E) calcd. from (B) and (D)		(F) observed
0.003783	0.001928	1.96	0.002513	0.000654	NO_3^-	0.000641
.004460	.002080	2.14	.002560	.000736		.000751
.003593	.002002	1.79	.001955	.000810		.000773
.004917	.003235	1.52	.004240	.000547	N_2	.000478
.002573	.001354	1.90	.002450	.000161		.000165

In the anodic oxidation of gallium, indium and thallium in liquid ammonia solutions[6] under conditions similar to those used with aluminum, the initial mean valence number of the cations produced was almost always appreciably lower than 3, but otherwise the results obtained varied markedly from one element to another, as well as from those observed for aluminum.

Gallium.—Electrolyses were carried out in a divided cell with a gallium anode and a platinum cathode in solutions of ammonium bromide, which had been found to show no appreciable nonelectrolytic reaction with gallium. No measurable quantity of gas was evolved from the anode during electrolysis. The values of V_i, calculated by means of an equation exactly analogous to that used for aluminum, *i.e.*

$$V_i = \frac{\text{wt. of Ag deposited in coulometer} \times 69.72}{107.9 \times \text{wt. of Ga lost from anode}}$$

were found to be in the neighborhood of 2.25. With ammonium nitrate–ammonium bromide mixtures as electrolyte the value of V_i, as in the case of aluminum, was found to be a function of the fraction of nitrate in the mixed solute, with a minimum of 2.0 at about 17 mole % nitrate. This *minimum* value need not be regarded as evidence for the formation under these conditions of dipositive gallium, since it may more plausibly be interpreted as corresponding to an equimolar mixture of unipositive and tripositive gallium ions.[7]

In contrast to the observations reported for aluminum, the anodic deposit and the anolyte resulting from anodic oxidation of gallium were found to exhibit measurable reducing properties; in this case, therefore, the ion of lower charge is relatively stable in the presence of liquid ammonia. The primary anode reactions were postulated to be

$$Ga = Ga^{+++} + 3e^-$$

$$Ga = Ga^+ \quad + e^-$$

The grayish-white residue remaining on evaporation of ammonia from the anolyte after electrolysis, and the insoluble solid which had been formed in the anode compartment, were tested separately for reducing power in the following way. Each was dissolved in standard aqueous iodine solution which had been acidified with acetic acid. After 15 minutes, the excess iodine was titrated with standard sodium thiosulfate solution. The gallium, now completely oxidized to the tripositive state, was determined by precipitation with 8-hydroxyquinoline. The reducing power, *R.P.*, in each case, expressed in gram-equivalents, was equal to the number of gram-equivalents of iodine reduced; and the mean valence number of the gallium at the

---

[6] A. D. McElroy, J. Kleinberg and A. W. Davidson, *J. Am. Chem. Soc.*, **74**, 736 (1952).

[7] A. W. Davidson and F. Jirik, *ibid.*, **72**, 1700 (1950).

end of the reaction, V_f, as determined from the reducing power, was calculated by means of the equation

$$V_f = 3 - \frac{R.P. \times 69.72}{\text{wt. of Ga found in solution}}$$

A few typical results of these experiments are shown in Table II.

TABLE II

ANODIC OXIDATION OF GALLIUM IN LIQUID AMMONIA SOLUTIONS OF AMMONIUM BROMIDE

V_i coulometric	V_f Anolyte	V_f Anode deposit	V_f Over-all	% of theoretical reducing power recovered
2.26	2.24	2.44	2.32	90
2.23	2.12	2.56	2.29	91
2.27	2.27	2.60	2.33	91

Indium.—Metallic indium is not attacked by liquid ammonia solutions of ammonium bromide. In electrolyses carried out on this electrolyte in a divided cell with an indium anode and an aluminum cathode, the results were found to vary in a highly erratic manner. Values of V_i ranged all the way from 2.01 to 4.72; the values higher than 3 can be accounted for only on the basis of the occurrence of some anode reaction other than the oxidation of indium. Noteworthy observations on these electrolyses included the evolution of hydrogen in the anode compartment as well as at the cathode, the occasional liberation of nitrogen at the anode, and the precipitation of finely divided indium in the anolyte.

These observations may be accounted for in terms of the following hypotheses. (1) Indium is anodically oxidized to a mixture of indium(I) and indium(III) ions. (2) The anodic hydrogen results from the reduction of the electrolyte by indium(I) ion. (3) The anodic nitrogen results from a competing primary reaction involving the oxidation of ammonia. (4) Indium(I) ion, unlike the corresponding ions of aluminum and gallium, is subject to disproportionation into indium(III) ion and free metal.

Thus the anode reactions may be listed as

$$\left.\begin{aligned} In &= In^+ + e^- \\ In &= In^{+++} + 3e^- \\ 8NH_3 &= N_2 + 6NH_4^+ + 6e^- \end{aligned}\right\}\text{primary}$$

$$\left.\begin{aligned} In^+ + 2NH_4^+ &= 2NH_3 + H_2 + In^{+++} \\ 3In^+ &= 2In + In^{+++} \end{aligned}\right\}\text{secondary}$$

After several of the electrolyses, the ammonia was allowed to evaporate, the residue was extracted with water, and the finely divided indium was weighed. The water solution was then titrated with standard potassium dichromate solution, and the reducing power, in gram-equivalents, was calculated from the equation

$$R.P. = \frac{\text{wt. of } Cr_2O_7^{--} \text{ reduced}}{36.01} + \frac{3 \times \text{wt. of pptd. In}}{114.8}$$

The mean valence number of the indium at the end of the electrolysis, V_f, as determined from the reducing power of the residue, was calculated from

$$V_f = 3 - \frac{R.P. \times 114.8}{\text{wt. of indium lost from anode}}$$

Before the mean valence number so calculated might properly be compared, however, with the coulometric value, it was necessary that the former be modified to V_f' to take into account the oxidation of In(I) ion in solution by ammonium ion

$$\left(V_f' = V_f - \frac{2 \times \text{no. of moles of anodic } H_2}{\text{no. of g.-atoms of In lost from anode}}\right)$$

and that the latter be corrected to V_i' to allow for the competing anode reaction

$$\left(V_i' = V_i - \frac{6 \times \text{no. of moles of } N_2 \text{ liberated}}{\text{no. of g.-atoms of In lost from anode}}\right)$$

As shown in Table III, the agreement between the corrected values is, in most cases, fairly good, lending support to the validity of the postulated electrode reactions.

TABLE III

ANODIC OXIDATION OF INDIUM IN LIQUID AMMONIA SOLUTIONS OF AMMONIUM BROMIDE

V_i	V_f	V_i'	V_f'
2.60	2.75	2.60	2.62
3.20	2.86	2.28	2.61
2.53	2.70	2.53	2.60
2.75	2.80	2.27	2.32
2.72	2.89	1.98	2.10
2.92	2.94	1.89	2.15
2.82	2.92	2.30	2.58
2.01	2.22	2.01	2.16
4.48	2.98	2.91	2.85

Thallium.—Unlike the other metals of this family, thallium reacts fairly rapidly with liquid ammonia, especially in the presence of certain dissolved salts. Although this non-electrolytic dissolution was taken into consideration in the calculation of the mean valence number on electrolytic oxidation by the method previously described, yet the results obtained must be regarded as no more than approximate.

Although anodic oxidation of thallium in nitrate solutions was found to yield thallium(I) ion exclusively, yet in chloride, bromide or amide solutions a mixture of thallium(I) and thallium(III) ions was formed. Both of these ions remained unchanged throughout the electrolysis, and could be identified by qualitative tests in the final product.

Reduction of Gaseous Oxygen by Alkali Metals

It has long been known[3] that when potassium, rubidium or cesium in solution in liquid ammonia is treated with a rapid stream of oxygen, at temperatures ranging from −70 to −33°, the superoxide of the metal is formed. In a recent investigation of the oxidation of sodium under similar conditions,[8] it was found that if a solution of sodium in liquid ammonia was slowly added to another portion of ammonia through which oxygen was being passed rapidly, a product of constant composition was obtained, regardless of the temperature of the solution. In the absence of moisture, this yellow product was fairly stable at room temperature. Analysis of eleven samples by measurement of the oxygen liberated on treatment with an

---

(8) W. H. Schechter, J. K. Thompson and J. Kleinberg, *J. Am. Chem. Soc.*, **71**, 1816 (1949).

aqueous suspension of manganese dioxide, and determination of the sodium by titration with standard acid, yielded from 1.65 to 1.70 atoms of oxygen per atom of sodium, the average being close to 1.67. This composition corresponds to a mixture of four moles of sodium superoxide, NaO_2, to one of sodium peroxide, Na_2O_2.

The product prepared as just described was highly paramagnetic, having a specific susceptibility at 20° of 21.6×10^{-6} c.g.s. unit, as compared with an estimated value of 33.0×10^{-6} unit for pure sodium superoxide.[9] Although the accuracy of the measurement of susceptibility was not very high, yet when the observed value was compared with a linear plot of specific susceptibility against weight percentage in synthetic Na_2O_2–NaO_2 mixtures,[9,10] the percentage of sodium superoxide found in this way, 67.5%, was in fair agreement with the figure of 73.8% calculated from the analytical data.

In a study of the oxidation of lithium in liquid ammonia,[11] it was found that when the metal was dropped into liquid ammonia at −78° through which a stream of oxygen was being passed, a bright yellow solution was formed. When this solution was allowed to warm up to −33°, the yellow color disappeared and a white suspension of lithium monoxide and lithium peroxide appeared. However, a study of the absorption spectrum of the yellow solution showed a marked maximum in absorption at a wave length of 380 mμ. Since solutions of sodium and potassium superoxides exhibit absorption maxima at the same wave length, it may be concluded that lithium forms a superoxide which is stable in liquid ammonia solution at −78°.

Reduction of Transition Metals by Alkali Metals

It has been previously reported[12] that when excess potassium tetracyanonickelate(II), $K_2Ni(CN)_4$, is treated with sodium or potassium in liquid ammonia, a bright red precipitate of potassium tricyanonickelate(I), $K_2Ni(CN)_3$, is formed. This compound is soluble in water, giving a red solution which slowly loses its color, with the evolution of hydrogen. When potassium tetracyanonickelate(II) is treated with an excess of potassium in liquid ammonia, the product is a yellow precipitate of potassium tetracyanonickelate(0), $K_4Ni(CN)_4$. When freed from ammonia, this is a copper-colored solid, which reacts with water to give hydrogen and a red solution of potassium tricyanonickelate(I).

Similarly, the reduction of potassium tetracyanopalladate(II), $K_2Pd(CN)_4$, by potassium in liquid ammonia[13] yields a light yellow crystalline precipitate of potassium tetracyanopalladate(0), $K_4Pd(CN)_4$. In water, this substance momentarily gives a clear solution; then hydrogen and hydrogen cyanide are evolved and metallic palladium is precipitated.

In our laboratory, in a recent study[14] of the reduction of potassium hexacyanochromate(III) by potassium in liquid ammonia, a dark brown product was obtained which was extremely susceptible to oxidation by air or moisture. In order to determine its reducing power, an excess of solid silver nitrate was added to a suspension of the chromium compound in liquid ammonia; a black precipitate of silver was immediately formed. After the excess silver nitrate had been washed out with liquid ammonia, the precipitated silver was washed with water and with dilute hydrochloric acid, and then dissolved in hot dilute nitric acid. Silver was determined in the resulting solution by precipitation as the chloride. The mean of five values of the reducing power so determined (in gram-atoms of silver per gram-atom of chromium) was found to be 2.09. This result appears to indicate the presence in the compound of Cr(I).

A more intensive investigation was made of the reduction by potassium in liquid ammonia of potassium hexacyanomanganate(III).[15] A yellow product, difficulty soluble in liquid ammonia and possessing strong reducing properties, was obtained. The characterization of this product was carried out by four different methods, all of which gave concordant results.

(a) A study was made of the ratio by weight in which potassium and the starting compound reacted with each other. It was found that the blue color due to excess potassium persisted in the solution for more than a few minutes only when more than 2.5 atoms of potassium were added per mole of compound. This fact suggested that the stoichiometry of the reaction might be represented by the equation

$$2K_3Mn(CN)_6 + 5K = K_5Mn(CN)_6 + K_6Mn(CN)_6$$

and that the product might contain unipositive and zerovalent manganese, atom for atom.

(b) After a scheme of analysis applicable to manganese complexes had been devised and shown to be valid on known synthetic mixtures containing potassium, manganese and cyanide, the reduction product, which contained some ammonia which was slowly lost on standing, was subjected to complete analysis. The ratio $K:Mn:CN:NH_3$ as calculated from the analytical data (mean of several determinations of each constituent on freshly prepared samples) was 5.42:1:5.93:1.11. These results indicate a compound of the empirical formula $K_{11}Mn_2(CN)_{12} \cdot 2NH_3$, as may be seen also from the following figures.

Anal. Calcd. for $K_{11}Mn_2(CN)_{12} \cdot 2NH_3$: K, 48.53; Mn, 12.40; CN, 35.23; NH_3, 3.84. Found: K, 48.29; Mn, 12.51; CN, 35.11; NH_3, 4.29.

(c) The reducing power of the product was determined by treating a liquid ammonia suspension with an excess of an ammonia solution of silver nitrate, and proceeding just as in the case of the chromium compound. The mean of four values of the reducing power (in gram-atoms of silver per

---

[9] S. E. Stephanou, W. H. Schechter, W. J. Argersinger, Jr., and J. Kleinberg, *J. Am. Chem. Soc.*, **71**, 1819 (1949).

[10] The sodium superoxide used in the preparation of these mixtures had been prepared by reaction between sodium peroxide and oxygen at elevated temperatures and pressures.

[11] J. K. Thompson and J. Kleinberg, *J. Am. Chem. Soc.*, **73**, 1243 (1951).

[12] J. W. Eastes and W. M. Burgess, *ibid.*, **64**, 1187 (1942).

[13] J. J. Burbage and W. C. Fernelius, *ibid.*, **65**, 1484 (1943).

[14] E. Colton, unpublished work.

[15] V. J. Christensen, Ph.D. Thesis, University of Kansas, 1952

gram-atom of manganese) was found to be 1.53. Since the manganese was oxidized by silver ion to the dipositive state, the results of these experiments pointed toward an initial mean valence state of one-half, a figure which is in complete accord with the observed reaction ratio and with the analytical data.

(d) The magnetic susceptibility of the reduction product was measured. As might have been expected of a substance containing manganese in the zerovalent state, it was found to be distinctly paramagnetic. When the molar weight was calculated on the basis of the formula $K_{11}Mn_2(CN)_{12}\cdot 2NH_3$, the mean of five values found for the effective magnetic moment was 1.25 Bohr magnetons, as compared to a calculated value for one unpaired electron of 1.73 Bohr magnetons. The discrepancy, however, is less serious than it might at first appear, since a very slight degree of oxidation of the product would appreciably lower the value of the effective magnetic moment. Thus a mixture of 40 mole % of the zerovalent and 60 mole % of the unipositive manganese compound would have a theoretical moment of the same magnitude as that found experimentally.

In view of the substantial concordance of all four lines of evidence, there can be little doubt that the reduction product contains manganese in both the unipositive and the zerovalent state, in at least approximately the atomic ratio of 1:1. Its composition may perhaps best be represented by the formula $K_5Mn(CN)_6\cdot K_6Mn(CN)_6\cdot 2NH_3$.

Acknowledgment.—The authors are indebted to the Research Corporation for a Frederick Gardner Cottrell grant which made possible some of the work described in this paper.

THE SOLUBILITY OF NAPHTHALENE IN SUPERCRITICAL ETHYLENE. II

By G. A. M. Diepen and F. E. C. Scheffer

Contribution from the Laboratory for Inorganic and Physical Chemistry at The Technical University, Delft, Holland

Received September 23, 1952

A previously described apparatus for the precise measurement of the saturation concentration of slightly volatile solids in fluids above their critical temperature has been used to determine the saturation concentration of naphthalene in ethylene at 12, 25, 35, 45, 50 and 60° at various pressures. It was found that these measured concentrations are, to high degree, dependent on the pressure and the temperature and that they vary from a tenth of a per cent. to 80% by weight.

In an earlier paper[1] we reported the solubilities of naphthalene in supercritical ethylene at temperatures of 12, 25 and 35° and for pressures to about 110 atmospheres. Since the above publication, we have measured the second critical endpoint in the ethylene–napthalene system and it appears to be at 52° and 174 atmospheres.[2] Thus between the temperatures of the first (11°) and the second critical end-point (52°) concentration measurements can be made without the formation of a second fluid phase. In other words, between 11 and 52° it is impossible at all pressures, for another

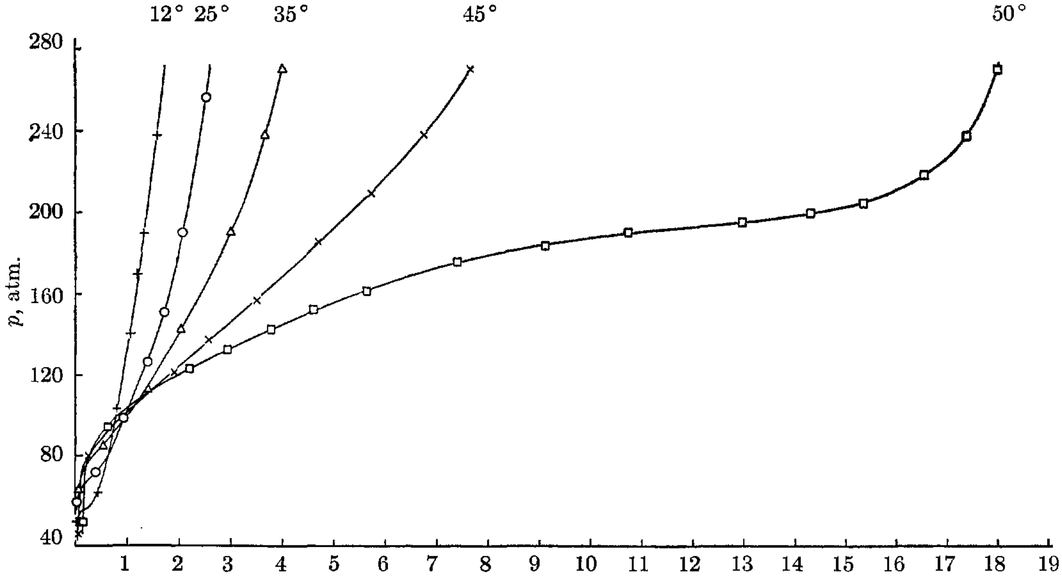

Fig. 1.—Pressure composition sections of the system ethylene–naphthalene at 12, 25, 35, 45 and 50°.

---

[1] G. A. M. Diepen and F. E. C. Scheffer, *J. Am. Chem. Soc.*, **70**, 4085 (1948).

[2] C. A. van Gunst, F. E. C. Scheffer and G. A. M. Diepen, This Journal, **57**, 578 (1953).