[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

Magnetic Susceptibility of Iron Tetracarbonyl

BY H. G. CUTFORTH AND P. W. SELWOOD

Iron tetracarbonyl, which has a molecular weight roughly corresponding to the formula $Fe_3(CO)_{12}$, is, like other carbonyls, diamagnetic. The susceptibility has been reported by Freundlich and Cuy[1] to be -1.3×10^{-6}, and by Berkman and Zocher[2] to be -0.01×10^{-6}. The first value is very large and suggests some kind of resonating layer lattice as in graphite. The crystalline carbonyl would thus be expected to have a large magnetic anisotropy. On the other hand, a susceptibility of -0.01×10^{-6} is very small and suggests contamination with paramagnetic or even with ferromagnetic impurities.

Experimental

Preparation of the Carbonyl.—Iron tetracarbonyl was prepared from iron pentacarbonyl.[3] The enneacarbonyl was first prepared as follows.[4] Iron pentacarbonyl was dissolved in an equal volume of glacial acetic acid. The mixture was cooled with running water while it was irradiated with light from a "Photoflood" lamp. Periods of irradiation were about six hours. The average temperature of the mixture during its irradiation was 15°. As the golden crystals of the enneacarbonyl, $Fe_2(CO)_9$, were formed they precipitated and were filtered. The filtrate was returned to the irradiation chamber until no appreciable further yield of enneacarbonyl was obtained.

In order to prepare the tetracarbonyl,[5] the enneacarbonyl was dried and then dissolved in toluene. The solution was heated to 70° on a steam-bath until it had a very dark green color. The solution was then filtered with suction while hot.

The filtrate was cooled to about 0° in an ice-bath. The black crystals of iron tetracarbonyl were filtered and dried.

The over-all yield by these procedures was not over 10%, but the product was nicely crystalline and seemed well adapted for the magnetic measurements.

Magnetic Measurements.—These measurements were made on the Gouy balance previously described.[6]

The sample of $Fe_3(CO)_{12}$ weighed 0.7500 g.

Results

Preliminary measurements showed the iron tetracarbonyl to be paramagnetic, with a susceptibility of about 0.3×10^{-6}. This strongly suggested the presence of paramagnetic or ferromagnetic impurities. With the purpose of detecting the latter, measurements were made over a range of field strength. The results showed a marked field strength dependence of susceptibility which established the presence of a ferromagnetic impurity. The results are shown in Table I.

The susceptibility of a diamagnetic or a paramagnetic substance is, of course, independent of field strength. The susceptibility of a ferromagnetic substance, when plotted against reciprocal field strength at sufficiently high fields, gives a straight line. The slope of this line is the specific magnetization, σ. The intercept of the line on the susceptibility axis, that is, the susceptibility of the substance at infinite field strength is, in the present case, roughly a measure of the susceptibility of the impurity-free carbonyl. We find from the data in Table I that the specific magnetization is $\sigma = (\chi - a)H$, where a is the intercept on the susceptibility axis and H is the field strength, and that $\sigma = 6 \times 10^{-3}$. The intercept, a is -0.07×10^{-6}.

TABLE I

FIELD STRENGTH DEPENDENCE OF SUSCEPTIBILITY FOR $Fe_3(CO)_{12}$

Current in amperes	Δw^a for H_2O	Field strength, oersteds $\times 10^4$	Δw for $Fe_3(CO)_{12}$, mg.	$\chi \times 10^6$ for $Fe_3(CO)_{12}$
12.50	−4.596	1.411	2.003	0.353
10.00	−3.863	1.302	1.898	.398
5.00	−1.541	0.819	1.286	.676

[a] Δw is the apparent change in weight on application of the field.

It was found, furthermore, that the susceptibility of the carbonyl changed with time. For instance, Δw, the apparent change in weight, on application of the field, increased over a period of four days by a total of 104 micrograms, corresponding to an increase in paramagnetism of about 5%. This change occurred when the sample was suspended in the magnetic balance in the dark. When the sample was exposed to sunlight for thirty minutes the paramagnetism promptly dropped about 2%.

It appears from these results that the carbonyl undergoes a slow, reversible, photochemical change and that this change is responsible for the ferromagnetic impurity. The simple decomposition

$$Fe_3(CO)_{12} \rightleftarrows 3Fe + 12CO$$

is excluded because a sample of the tetracarbonyl sealed in an evacuated tube and connected to a mercury manometer showed no evolution of carbon monoxide over a period of a week. An alternative explanation is a disproportionation reaction, such as

$$5Fe_3(CO)_{12} \underset{\text{light}}{\overset{\text{dark}}{\rightleftarrows}} 3Fe + 12Fe(CO)_5$$

although the enneacarbonyl might be involved instead of, or in addition to, the pentacarbonyl.

This reaction is consistent with the magnetic results. The only other ferromagnetic substances which could be formed are Fe_3O_4, γ-Fe_2O_3, and

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(1) Freundlich and Cuy, *Ber.*, **B56**, 2264 (1923).

(2) Berkman and Zocher, *Z. physik. Chem.*, **124**, 318 (1926).

(3) Obtained through the courtesy of General Aniline Works of New York.

(4) Speyer and Wulf, *Ber.*, **B60**, 1424 (1927).

(5) Dewar and Jones, *Proc. Roy. Soc.* (London), **A76**, 558 (1905); **A79**, 66 (1907).

(6) Preckel and Selwood, THIS JOURNAL, **63**, 3397 (1941).

Fe_3C. The low thermal stability of the carbonyl prevents a Curie point determination which would clearly establish the nature of the ferromagnetic impurity. If, however, we assume that the impurity is metallic iron, we may estimate the amount of iron necessary to give the observed ferromagnetism. The specific magnetization of pure iron is about 216.[7] The observed specific magnetization of the carbonyl is 6×10^{-8}. The fraction of metallic iron present as impurity is $6 \times 10^{-8}/216$ or about 0.003% by weight. Under the conditions of the magnetic measurements in the dark, at room temperature, the iron concentration is increasing at such a rate that it would become twice as great in about eighty days.

The susceptibility of the pure carbonyl was estimated as -0.07×10^{-6} but from this must be subtracted algebraically the *paramagnetism* of the iron impurity. There is no easy way of obtaining the paramagnetism of metallic iron at room temperature but from Stern-Gerlach experiments and from the known susceptibility of metallic manganese we may estimate the paramagnetic susceptibility of iron as certainly not much over 10^{-4}. A fraction of iron amounting to 0.003% would then contribute only 3×10^{-9} unit of susceptibility, which is negligible compared with an observed susceptibility for the carbonyl of about 70×10^{-9}.

It may, therefore, be concluded that the diamagnetic susceptibility of iron tetracarbonyl is, while rather small, nevertheless normal. The small magnitude of the susceptibility may be due to paramagnetic impurities, such as γ-Fe_2O_3 for which no good test is available. A second possible explanation is the presence of a rather large temperature independent paramagnetism.

Summary

The magnetic susceptibility of iron tetracarbonyl at room temperature, corrected for ferromagnetic impurity, is -0.07×10^{-6}. The carbonyl appears to undergo a slow change, with an increase in susceptibility, when it stands in the dark.

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[7] International Critical Tables, Vol. VI, p. 376.

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF LAWRENCE COLLEGE AND OF INDIANA UNIVERSITY]

The Surface Tensions and Parachors of the Methyl and Ethyl Amines

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A comparison of the boiling points of the methylamines and freezing points of the ethylamines is somewhat surprising. The boiling points of the methylamines are reported as -6.79,[2] $+6.9$,[3] and $+3.2°$,[4] and the freezing points of the three ethylamines as -83.8,[5] -50,[6] and $-114.8°$.[7,8]

Having on hand carefully purified samples of these compounds, measurements of the surface tensions were undertaken with the hope that if the lower values for the tertiary amines were caused by structural abnormalities of the liquids, this might show up in the parachor values.

Purification of Materials.—The three ethylamines and the di- and trimethylamine were samples whose purification has been described previously.[9] In addition each sample used was dried over potassium hydroxide or with sodium fluorenone[10] in the absence of air and distilled in vacuum, a second slow evaporation without spattering then being made directly into the evacuated apparatus.

A second sample of diethylamine was prepared by another method. Eastman Kodak Co. diethylamine hydrochloride was treated with potassium nitrite and hydrochloric acid and the resulting nitroso compound washed with distilled water and steam distilled. It was then treated with tin and hydrochloric acid and reduced to the amine hydrochloride, which was made alkaline with potassium hydroxide to drive out the amine. The purified compound was twice fractionated in a 30-cm. packed column. The boiling point (uncor.) was 55° and no change in this temperature was observed during the distillation of the accepted fraction. The product was dried over potassium hydroxide and twice distilled *in vacuo*, leaving no visible residue.

For the preparation of the methylamine,[11] Eastman Kodak Co. methylamine hydrochloride was extracted with pure dry chloroform for thirty hours to remove higher amines, then recrystallized from absolute alcohol and extracted for an additional twenty hours with chloroform. The resulting product was treated with excess potassium hydroxide and the gaseous methylamine passed over potassium hydroxide and yellow mercuric oxide to remove any traces of ammonia. The amine was liquefied with dry-ice and ether, desiccated by dissolving sodium fluorenone in it and then distilled into the evacuated apparatus.

Method of Measurement.—The surface tensions of the compounds were measured by the capillary rise method in the capillarimeter sketched in Fig. 1. About 20 ml. of the pure amine was distilled in through A, which was then sealed off. Sufficient amine was poured into B, by tilting the apparatus, so that the level of the liquid in the capillary just reached point C, indicated by a small scratch on the tube. The liquid meniscus was always brought

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[1] Present address, Institute of Paper Chemistry, Appleton, Wis.

[2] W. A. Felsing and A. R. Thomas, *Ind. Eng. Chem.*, **21**, 1269 (1929).

[3] A. Simon and J. Huter, *Z. Elektrochem.*, **41**, 28 (1935).

[4] H. W. Thompson and J. W. Linnett, *Trans. Faraday Soc.*, **32**, 681 (1936).

[5] "International Critical Tables," McGraw-Hill Publishing Co., New York, N. Y., 1928.

[6] A. W. Hofmann, *Ber.*, **22**, 705 (1889).

[7] J. Timmermans, *Chem. Zentr.*, **85**, I, 618 (1914).

[8] There is considerable disagreement on the exact values of these freezing points. However, diethylamine is the only one of the three which can be frozen with ether–dry-ice mixtures.

[9] E. Swift, Jr., THIS JOURNAL, **64**, 115 (1942).

[10] H. E. Bent and H. M. Irwin, *ibid.*, **58**, 2072 (1936).

[11] B. A. Kelso and W. A. Felsing, *ibid.*, **60**, 1949 (1938).