ity of the scattered particle will be Oα or u and be given by

$$u^2 = \rho^2 v^2 + (1 - \rho)^2 v^2 + 2\rho\,(1 - \rho) v^2 \cos\theta \quad (1)$$

or

$$\frac{u^2}{v^2} = \rho^2 + (1 - \rho)^2 + 2\rho\,(1 - \rho)\cos\theta \quad (1')$$

or

$$\frac{E}{E_0} = \rho^2 + (1 - \rho)^2 + 2\rho\,(1 - \rho)\cos\theta \quad (1'')$$

where E is the final energy and E_0 the initial in the laboratory system.

Considering the probabilities of various values of θ we see that due to the integration around OA as polar axis the solid angle lying between θ and $\theta + d\theta$ will be $2\pi \sin d\theta$ so the fraction dP of all scattered particles lying in this band will be

$$dP = \frac{1}{4\pi}\ 2\pi \sin d\theta = \frac{\sin\theta d\theta}{2} \quad (2)$$

Differentiating equation (1″)

$$dE = -E_0\, 2\,(1 - \rho)\sin\theta d\theta \quad (3)$$

or

$$dE = -E_0\,\gamma dP \quad (3')$$

where

$$\gamma = \frac{4MM'}{(M + M')^2} \quad (4)$$

Integrating (3)′

$$E = E_0(1 - \gamma P) \quad (5)$$

where P is now the fraction of the particles scattered between 0 and θ.

Now the average value of $\ln \frac{E_0}{E}$ can be obtained. From (5)

$$\ln \frac{E_0}{E} = -\ln\,(1 - \gamma P) \quad (6)$$

So

$$\ln \frac{E_0}{E} = K = \int_1^0 -\ln\,(1 - \gamma P)_{dP} \quad (7)$$

$$= \frac{1 - (1 - \gamma)\,1 - \ln(1 - \gamma)}{\gamma}$$

For a complete discussion of the problem of neutron slowing, refer to "Theory of the Slowing Down of Neutrons in Heavy Substances," G. Placzek, *Phys. Rev.*, **69**, 423 (1946).

Summary

1. The variety and nature of the recoil excitations suffered by atoms whose nuclei partake in the various possible nuclear reactions is reviewed. The chemical kinetics of the recoiling (frequently radioactive) atoms is treated by considering first the nature of the cooling deceleration process—predominantly non-ionizing collisions—and subdividing the problem into one class involving no change in atomic number, *e. g.*, the Szilard–Chalmers reactions, and another class in which changes in atomic number occur.

2. In the first class previously published data on organic halides are considered in some detail and a mechanism developed. The essential features of this mechanism are that the classical collision theory and the Franck–Rabinowitch "cage" are sufficient to explain the main facts.

3. In the second class where changes in atomic number occur the principal cases discussed are ionic solids. Few data are available. A suggestion is made for a concentration procedure consisting of baking fine irradiated crystals to drive the activity to the surface.

CHICAGO, ILLINOIS RECEIVED OCTOBER 10, 1946

[CONTRIBUTION FROM THE MALLINCKRODT CHEMICAL LABORATORIES, HARVARD UNIVERSITY]

The Determination of the Gases in Meteoritic and Terrestrial Irons and Steels

BY LEONARD K. NASH AND GREGORY P. BAXTER[1]

In connection with an investigation of the gases present in siderites, a general survey has been made of the methods by which gases may be liberated from meteoritic and terrestrial irons and steels. A really satisfactory method of extraction must release all the gases present as such without change of composition or addition of contaminating reaction gases. Since none of the currently available procedures fully satisfies these criteria, attention has been focussed on the choice of the method which most nearly meets the criteria, together with an estimate of the unavoidable errors. In the following text each of the possible methods is considered, the finally adopted method is described in detail, and the results are compared with similar data secured by other methods.

I. Discussion of Methods

A. Heating *in Vacuo*.—This classical method, developed by Graham[1a] for the investigation of the gas content of meteoritic irons, has since been applied to a wide variety of meteoritic and terrestrial materials. It has been established that the composition of the extracted gas is strongly dependent on the fineness of subdivison of the sample,[2] duration of heating,[3] extraction temperature,[4] and duration of the contact between the gas and the sample.[5] The variable re-

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(1) This work was initiated and supervised by the Committee on Meteorites of Harvard University: G. P. Baxter (Chairman), K. T. Bainbridge, H. A. Berman (deceased 1942), Francis Birch, A. B. Greninger, F. G. Watson.

(1a) T. Graham, *Proc. Roy. Soc.* (*London*), **15**, 502 (1866).

(2) A. W. Wright, *Am. J. Sci.*, **9**, 249 (1875).

(3) J. W. Mallet, *Proc. Roy. Soc.*, **20**, 365 (1872).

(4) A. W. Wright, *Am. J. Sci.*, **10**, 44 (1875).

(5) A. W. Wright, *ibid.*, **12**, 165 (1876).

sults are hardly surprising in view of the fact that the reductants Fe, FeO, Fe_3O_4, H_2, CO and C have been heated at high temperatures with the oxidants Fe_2O_3, H_2O, CO_2, etc., and extensive equilibration must have occurred. "Any gas which is evolved which does not possess the composition necessary for equilibrium . . . for the temperature of the experiment will tend to react with the steel until it does possess this composition. Thus the composition found must have been modified in a quite indeterminate manner by reactions taking place at lower temperatures."[6]

B. Fusion *in Vacuo*.—Extraction of the gas sample must be much more nearly complete, but the high temperature required (*circa* 1800°) facilitates even more extensive equilibration.

C. Vacuum Fusion with Metallic Flux.—By the introduction of an antimony–tin alloy, Goerens and Paquet[7] were able to secure fusion of steel samples at temperatures as low as 1200°. This temperature is still far too high, and search for substantially lower melting alloys has been unsuccessful.

D. Solution in "Fused" Salts.—Several low-melting salts have been tested for their solvent action on steel. Those tested fall in two classes: (a) Anhydrous ferric chloride, an historically important solvent for steel in slag analysis,[8] was found to act very slowly on massive fragments of steel at 300°. Cuprous chloride had a similar slow effect at 480°. However, in both instances there is every probability that part or all of the hydrogen present will be lost through reaction with the fused salt.[9] (b) Anhydrous stannic chloride, antimony pentachloride, mercuric chloride mixed with mercuric iodide, and mercuric iodide alone, showed negligible attack on steel samples at low temperatures. In short, the fused salt method appears to fail because most salts do not show adequate reactivity; and where such reactivity is present, it is not sufficiently selective to avoid attack by the reagent on any hydrogen present. Falsification of the hydrogen results through the presence of an accidental trace of water also constitutes a serious hazard.

E. Solution in Aqueous Salt Solutions. 1. Copper Salts.—A variety of copper salts, in aqueous solution, has been used for the estimation of the gases in terrestrial steel by Goutal,[10] Vita,[11] Maurer,[12] Klinger,[13] and Cain and Pettijohn.[14] Most of the difficulties inherent in this method are revealed in these investigations. Klinger has emphasized the tenacious retention of carbon monoxide by the cuprous salts inevitably present in the solution at the end of the reaction. Cain and Pettijohn state that commercial potassium cupric chloride reagent gives unsatisfactory blanks, releasing appreciable quantities of carbon monoxide and carbon dioxide, and recommend the use of a specially prepared salt, free of all carbonaceous impurities. The evolution of hydrocarbon gases also has been noted by Cain and Pettijohn and by Klinger. Last, and most serious, is the evolution of substantial quantities of carbon monoxide and carbon dioxide as side reaction gases, even when the specially purified reagent is used. This contamination is found to increase with increasing carbon content of the sample, with increasing concentration of the reagent solution, with increasing time of contact of the sample and the solution, and, to some extent, with increasing temperature.

Despite the considerable weight of adverse evidence, there seems to be nothing in the published reports to exclude the possibility of a successful process based on the use of a cold unacidified solution of purified potassium cupric chloride. This method was therefore studied further.

2. Mercuric Salts.—The use of aqueous solutions of mercuric salts in the determination of the gases present as such in steel has been studied by Maurer,[12] Klinger[13] and Oberhoffer and Piwowarsky.[15] Maurer and Klinger both note the evolution of carbon monoxide and carbon dioxide during the breakdown of a steel sample in hot solutions, increasing near the boiling point. Oberhoffer and Piwowarsky state that the cold solution does not produce any reaction gas (*i. e.*, gas not present as such but produced in the process of extraction), basing this conclusion on the good agreement in the quantities of carbon monoxide and carbon dioxide found when samples of the same steel were subjected to cold solution by the mercuric chloride method and by a bromine method. Since it will be shown that it is highly unlikely that a bromine method does not produce reaction gases, it would seem that the agreement was fortuitous, and that reaction gases in some quantity were evolved during cold solution with the mercuric reagent. Another danger, emphasized by Klinger, is due to the extreme rapidity of the reaction of steel shavings with mercuric chloride solutions. The reaction is so strongly exothermic that, unless precautions are taken, the solution is warmed to a point where hydrolysis of the reagent may occur. The free acid so produced might then, in reaction with the metallic sample, produce hydrogen gas as a side reaction.

Because of the numerous uncertainties both the hot and cold solution methods have been reexamined.

3. Other Salts.—Many other salts might be used to accomplish the solution of iron samples, and several of these were selected for further experimental study.

F. Solution in Non-aqueous Salt Solutions.—While solutions of such salts as ferric chloride in

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(6) McCance, *Trans. Faraday Soc.*, **14**, 221 (1919).

(7) Goerens and Paquet, *Stahl u. Eisen*, **35**, 1136 (1915).

(8) Troilius, *Jernkontorets Ann.*, **39**, 432 (1884).

(9) Bagdasarian, *Trans. Am. Electrochem. Soc.*, **51**, 484 (1927).

(10) Goutal, *Rev. met.*, **7**, 6 (1910).

(11) Vita, *Stahl u. Eisen*, **42**, 445 (1922).

(12) Maurer, *ibid.*, **42**, 447 (1922).

(13) Klinger, *ibid.*, **46**, 1245, 1284 (1926).

(14) Cain and Pettijohn, *U. S. Bur. Standards Tech. Paper*, 126 (1919).

(15) Oberhoffer and Piwowarsky, *Stahl. u. Eisen*, **42**, 801 (1922).

organic solvents dissolve steel samples,[16] the use of these reagents in the determination of the gas content presents difficulties. In order to provide a satisfactorily clean separation of the evolved gases from the solvent vapor, the solvent would have to be a relatively involatile one, *i. e.*, one of high molecular weight, and in such a medium the reaction rate is low and the salts involved are but sparingly soluble. The high purity required in the solvent, the danger of decomposition of the latter with the formation of volatile products, combined with other difficulties, suggest that this is not a very promising approach.

G. Reaction with a Halogen. 1. Chlorine and Bromine.—Chlorine vapor rapidly attacks steel at elevated temperatures,[17,18] but practically all the hydrogen is lost by reaction with the chlorine. The same difficulty attends the use of bromine vapor.

Bromine in non-aqueous solution was used for the determination of gaseous inclusions in steel by Oberhoffer and Piwowarsky,[15] but the somewhat cumbersome method did not, according to Klinger,[13] yield satisfactory results. Since iodine, a much milder reagent, brings about solution of steel under much the same conditions as does bromine, it is apparently more worthy of attention. The results with this weaker reagent were unsatisfactory in any case (*vide infra*).

2. Iodine.—Iodine vapor has been used in the study of the occluded gases in silver[19] and copper.[20] While iodine vapor attacks steel rapidly at 500°, this temperature is too high for the present research. Sealed tube experiments showed that up to 250° (the maximum temperature considered permissible) the reaction is extremely slow.

Iodine in non-aqueous solution suffers from the same disadvantages enumerated above for non-aqueous salt solutions.

Iodine in aqueous solution has been used by Goutal[10] and Klinger[13] in the study of the occluded gases in steel. Klinger's painstaking work closely followed the pattern of Oberhoffer and Piwowarsky's "kaltumsetzung" technique with aqueous bromine solutions, and led him to the conclusion that " . . . the gases obtained by solution of steel in this solvent also contain components arising from side reactions, which were not originally present in the steel." However, various uncertainties about Klinger's experimental methods have made it appear desirable to reëxamine this possibility.

H. Electrolysis.—Several systems for slag analysis based upon electrolytic breakdown of steel in aqueous media have been proposed.[21] In view of the numerous experimental difficulties, particularly those connected with complete suppression of gassing at the electrodes and close control of *p*H throughout the cell, this did not appear to be a very promising possibility.

Some of the difficulties involved in the use of aqueous electrolytes might be avoided by electrolysis through a fused salt, but no salt with the desired properties of low melting point and high electrical conductivity of the melt has been found.

I. Solution in Acids.—Involatile acids like sulfuric acid might be used to dissolve steel samples, to provide a more accurate estimate of the carbon gases.[14] Of course, no hydrogen value could be secured. The difficulties involved in the separation of a small amount of genuine occluded gas from about 5000 times its volume of hydrogen and complex hydrocarbon material[22] are so serious as to discourage investigations of this method.

J. Liberation of Gases by Positive Ray Bombardment.—Moreau and his co-workers have developed a cold, dry method for the extraction of the gases present in metals, based upon high-voltage positive ion bombardment of thin chips of sample.[23] Recent work[24] seems to show conclusively that it is very difficult, if not impossible, to prevent a major dilution of the true gas sample by similar gases released from the target supports and the tube walls by the vacuum discharge. At the present stage of development, therefore, this method does not appear to be capable of providing reliable data.

K. Liberation of Gases by Mechanical Broaching.—Partial release of the gases present in steel has been attained by boring out (broaching) the sample under a sealing liquid, followed by analysis of the gas accumulated in the cavity,[25] However, the release of occluded gases by broaching is inevitably incomplete (and the results are deceptive because of the great predominance of gas liberated from blow-holes.)

Various possible approaches to the problem of extraction have now been considered. None is completely satisfactory, and Klinger's collected work shows enormous variations when a single steel was investigated by different methods. On the basis of the considerations enumerated above this research was directed toward further development of extraction methods using as reagents aqueous solutions of iodine or of inorganic salts (in particular of cupric and mercuric salts). An estimation of the magnitude of the residual errors in the improved methods was also sought.

II. Preparation of Reagents

Copper Reagent.—The salt used in these trials was potassium copper chloride which, of all cupric salts, appeared to be the most rapid in its action. Some trials were made with the Baker C. P. reagent, which will be de-

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(16) A. Naumann, *Ber.*, **32**, 1002 (1899).

(17) Klinger and Fucke, *Arch. Eisenhüttenw.*, **7**, 615 (1934).

(18) Chem. Fabrik. Breckau, German Patent 309,277.

(19) Baxter and Parsons, This Journal, **44**, 577 (1922).

(20) Guichard, *Compt. rend.*, **153**, 272 (1911).

(21) Treje & Benedicks, *Jernkontorets Ann.*, **116**, 166 (1932); Fitterer, *et al.*, U. S. Bur. of Mines Repts. of Invest., 3205 (1933). Scott, *Ind. Eng. Chem., Anal. Ed.*, **4**, 121 (1932); Styri, *Trans. Am; Min. Met. Eng.*, **105**, 183 (1933).

(22) Schenk, *et al.*, *Z. anorg. Chem.*, **127**, 101 (1923).

(23) Moreau, *et al.*, *Compt. rend.*, **201**, 212 (1935).

(24) Bobalik and Schrader, *Ind. Eng. Chem., Anal. Ed.*, **17**, 545 (1945).

(25) Müller, *Ber.*, **12**, 93 (1879).

noted as Cu-a. A second sample, as free as possible of all carbonaceous contamination, was prepared by a method similar to that described by Cain and Pettijohn. The copper material was derived from metal electrolytically deposited on a large platinum dish from an acidified solution of recrystallized copper sulfate. The copper was dissolved in dilute nitric acid, and the solution was repeatedly evaporated to dryness with hydrochloric acid. The cupric chloride so obtained was combined in molecular proportions with potassium chloride produced by cautious pyrolysis in a platinum dish of C. P. potassium chlorate. The potassium cupric chloride was thrice recrystallized with centrifugal drainage. The reagent so prepared will be referred to as Cu-b.

Mercury Reagent.—Mallinckrodt reagent grade mercuric chloride, denoted as Hg-a, was used in most of the trials. A second sample, referred to as Hg-b, was prepared by thrice recrystallizing the C. P. salt with centrifugal drainage in platinum Gooch crucibles.

Iodine Reagent.—The addition of citrate to an iodine reagent to prevent hydrolysis has been recommended,[26] but since no hydrolysis occurs in the absence of oxygen,[27] this component seems superfluous. The addition of potassium iodide or ferrous iodide to aid the initial solution of the iodine[26,27] unfortunately profoundly reduces the reaction rate, presumably because of the reduction of the free iodine concentration through formation of the I_3^- complex. Ferrous iodide will be formed during the reaction, but the addition of other iodides appears injudicious. The problem therefore is to treat the steel sample with gas-free water and gas-free iodine.

Iodine was freed of cyanogen and organic material by two sublimations in a stream of oxygen, over rolls of platinum foil heated to bright redness in a quartz tube. The product was twice sublimed *in vacuo*, little or no permanent gas coming off during the second sublimation; and was then distributed among a number of glass capsules, which were thereupon separately sealed off at the heavy-walled constrictions joining them to the line. Only glass and quartz came in contact with the iodine throughout these operations. The capsules were provided with breakable joints through which the gas-free iodine could be withdrawn when desired.

III. Apparatus and Methods

The all-glass apparatus built for the study of the dissolving reactions is shown in Fig. 1.

The steel sample was placed in the side-arm C, and the reagent solution was poured into the 500-cc. flask A through the tube B, which was then sealed. The branch F was then attached through a short length of thick rubber tubing to a water aspirator. The flask was immersed in a boiling water-bath and a pinch clamp on the rubber line to the aspirator was gradually opened to its fullest extent. The vigorous boiling of the solution in the flask swept the permanent gas from the system. The breakable joint manifold was continuously flamed to prevent any pocketing of air behind water condensed in the capillaries. After boiling for one-half hour the capillary in F was sealed with the aspirator running, and the solution in the flask still boiling vigorously. The permanent gas then remaining in the flask amounted to less than 0.002 cc. Although it was not always considered necessary, this trace of gas could be removed by connecting one of the flask's breakable joints, through a large Dry Ice trap, with a high vacuum line, pumping for a short time, and then sealing off the flask at the constriction under the fractured breakable joint.

The reagent solution was brought to the desired temperature, and the flask was tipped so that the sample fell from the side-arm into the solution. At the end of the allotted reaction period the flask was attached to a collecting line consisting of a large Dry Ice trap, an Anhydrone tube, and a Töpler pump. After evacuating the collecting line, the break-off was fractured and the sample collected with the Töpler pump. For further study of the reaction mixture the flask could be sealed off under the fractured break-off, and, after the appropriate processing, a second gas sample was collected as before, through another one of the breakable joints. The influence of the reagent and/or the reaction mixture on the more sensitive of the gases involved was ascertained with a determinate gas mixture of methane, carbon monoxide and hydrogen previously sealed into the sample capsule D. At the appropriate moment the breakable joint on D was broken, and the gas sample introduced over the solution in the flask. After some time, the gas sample was collected again through another of the breakable joints, and analyzed to detect any change in its quantity or composition.

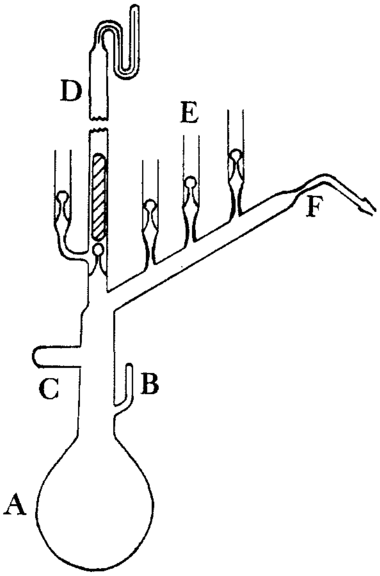

Fig. 1.

For the analysis of the gas samples secured in these studies a special apparatus was devised, which has been described elsewhere.[28] This apparatus provided results accurate to 1% (of the total volume) with samples as small as 0.1 cc.

A slightly different procedure was required for the experiments with iodine, since the reagent solution could not then be introduced directly into the body of the flask as described above. Instead the iodine capsule was attached, through a heavy-walled constriction, to substantially the same form of dissolving flask as has been described—the flask containing the water, and, in a side-arm, the steel sample. After purging the air from the system by boiling the water, the breakable joint of the capsule was fractured, the capsule immersed in an oil-bath, and the iodine distilled into the reaction vessel. The capsule was then sealed off from the flask. To test for the presence of any permanent gas, one of the flask's breakable joints could be attached to the high vacuum-line. No more than a very few thousandths of a cc. were ever found. A second sublimation of the iodine within the flask resulted in the release of but 0.001 cc. of gas. Thus, after sealing the flask from the vacuum line the desired condition was attained, *i. e.*, gasless iodine and water had been brought together with the sample in an evacuated vessel.

In the final determinations a slightly modified form of reaction flask, shown in Fig. 2, was used. Here a stopcock, protected by a small condenser, replaced the manifold of breakable joints. Operations with this form of vessel were substantially the same as those already described. This apparatus was not used in the blank trials,

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[26] Cunningham and Price, *Ind. and Eng. Chem., Anal. Ed.*, **5**, 27 (1933).

[27] Willem, *Arch. Eisenhüttenw.*, **1**, 625 (1927–1928).

[28] Nash, *Ind. Eng. Chem., Anal. Ed.*, **18**, 505 (1946).

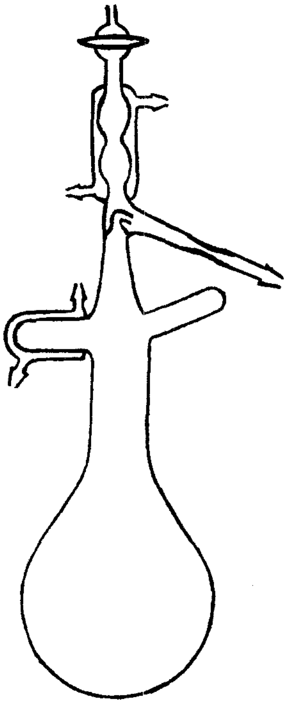

Fig. 2.

which were to be conducted in a device entirely free of organic material (*i. e.*, stopcock grease), but in further work with the copper and mercury reagents it was found to give the same results as the breakable joint form, together with greatly increased convenience.

Other things being equal, cold solution methods are said to produce minimal quantities of reaction gases; but, particularly with copper reagents, reaction in the cold is inordinately slow. However, by agitating the reaction mixture on a continuous shaker, the reaction was profoundly accelerated.

With the mercuric chloride reagent and, to a lesser extent, with the iodine reagent, the initial reaction with the sample is extremely violent and strongly exothermic. Gas-producing side reactions may then occur in the heated solution. To control the violence of the initial reaction massive samples were used. Shaking was then required to drive the reaction to completion. As a further precaution, the outgassed reagent solution was always partially frozen before dropping in the sample; and the reaction mixture was allowed to stand for one hour in an ice-bath before the flask was attached to the shaker.

IV. The Trials

The effect of the selected reagents on three different samples was studied: sample R, nickel steel rod of high nickel content (*circa* 20%); sample G, vacuum-fused ("gasless") steel containing 20% nickel and 1% graphitic carbon; Sample D, vacuum-fused ("gasless") steel containing 10% carbide. Samples D and G were obtained through the kindness of Prof. Greninger.

Experiments were made with 1–5 g. portions of the various samples, cut very slowly from the bulk of the specimen with a sharp hack-saw blade. The trial samples were in the form of one or two massive fragments. The quantity of reagent used was ordinarily about 20% in excess of the minimum required to secure stoichiometric reaction. The volume of the reaction solution was in the range of 250–350 cc.

Both hot and cold solution methods were studied. While there was some evidence of hydrolysis when the solution was heated, cold solution methods appeared to proceed free of hydrolytic changes. The copper reagent resulted in the production of a very dark green solution which remained perfectly clear. The same was true of the iodine reagent, which yielded a clear, very deep red solution. With the mercuric chloride reagent a clear, light green solution was obtained, a considerable deposit of mercurous chloride and a little metallic mercury settling out at the bottom of the reaction vessel.

The results secured in these trials are summarized in Table I.

V. Conclusions

A. Hot Solution Methods.—1. The trials made with hot solution methods (lines 1 and 2) entirely confirmed the reported unsuitability of this approach. Large quantities of reaction gases were evolved for many hours after complete solution of the sample–indicating gas-forming side reactions between the non-gaseous constituents present in the reaction mixture. No simple separation of the contaminating gases from those originally present as such appearing possible, the method was abandoned forthwith.

B. Cupric Chloride Method.—(1) Probably because of its lower content of carbonaceous impurities, the specially prepared cupric reagent yielded much less reaction gas with a given steel sample than did the commercial reagent (lines 5 and 6), and was therefore used throughout the remaining trials.

(2) Small amounts of carbon monoxide and substantial quantities of carbon dioxide were evolved during the solution of a sample of vacuum-fused graphitic steel; and the solution of a sample of vacuum-fused carbide steel resulted in the liberation of much larger quantities of these gases, together with a possible trace of hydrogen. These observations indicate the obvious limitations to this method.

(3) In the trial in which a known gas sample was present during the solution process, the hydrogen and methane were recovered practically intact. The carbon monoxide, however, was so powerfully absorbed that, even when continuously collected over a two-hour period, its complete recovery was entirely impractical.

(4) On the basis of these trials it was concluded that while a cold cupric reagent may provide significant values for the hydrogen and nitrogen present as such in the steel, the values for carbon monoxide and carbon dioxide are of limited significance.

C. Iodine Reagent Method.—(1) Relatively large quantities of carbon dioxide and carbon monoxide were freed (lines 9 and 10), very much more than when mercuric chloride or cupric chloride were used to dissolve the same sample of graphitic steel. Thus the rate of reaction gas production is prohibitively high with an iodine reagent.

(2) The reaction mixture was without apparent effect on a test mixture containing the more sensitive of the gases involved.

(3) The iodine method presents no advantages and very considerable disadvantages, and was abandoned. It hardly seems possible that any more satisfactory results could have been secured with a bromine reagent.

D. Mercuric Chloride Method.—(1) The solution of the graphitic steel in this reagent resulted in the liberation of a quantity of carbon

TABLE I

THE TRIALS OF DISSOLVING REAGENTS

No.	Sample	Reagent	Temp.	Duration of trial	Gas volumes, cu. mm. N. T. P./g. Total	CO_2	CO	H_2	CH_4	N_2	Remarks
1	R	Cu-a	Hot	Stand 5 hours	187	28	5	148	2	3	Average two runs
2	R	Hg-a	Hot	Stand 4 hours	86	25	12	41	1	5	Average four runs
3	. .	Cu-a	Cold	Stand 25 hours	Trace	Trace					40 g. reagent; 250 cc. H_2O
4	. .	Cu-b	Cold	Stand 10 hours	—						25 g. reagent; 250 cc. H_2O
5	G	Cu-a	Cold	Shake 60 hours Stand 8 hours	30	28	2				
6	G	Cu-b	Cold	Shake 45 hours	6	4	2				
				Shake 27 hours more	—						
7	D	Cu-b	Cold	Shake 60 hours Stand 10 hours	170	89	74	<7			
				Shake 24 hours Stand 36 hours more	14	14					
8	G	Cu-b	Cold	Shake 60 hours Stand 12 hours	*1221*[a]	*5*	*426*	*746*	*44*		Known gas sample added at start of expt.: CO, 517; H_2, 738; CH_4, 47 cu. mm. N. T. P.
9	G	I_2	Cold	Shake 84 hours	102	86	16	Trace			
				Stand 18 hours Shake 48 hours more	32	31					
10	G	I_2	Cold	Shake 22 hours Stand 18 hours	67	53	14				
				Shake 4½ hours Stand 42 hours more	22	21					
				Shake 22 hours Stand 8 hours more	*1227*	*19*	*403*	*772*	*36*		Known gas sample added at start of expt.: CO, 412; H_2, 787; CH_4, 33 cu. mm. N. T. P.
11	. .	Hg-a	Cold	Stand 6 hours	1	1					33 g. reagent; 350 cc. H_2O
12	G	Hg-a	Cold	Shake 10 hours Stand 8¼ hours	7	6					Used second form of dissolving flask with greased stopcock
13	G	Hg-a	Cold	Shake 9 hours Stand 2 hours	11	9					
				Shake 9 hours Stand 2 hours more	12						Used second form of dissolving flask with greased stopcock
14	G	Hg-b	Cold	Shake 15 hours Stand 1 hour	8.5	7	1.5				
				Stand 54 hours more	10						
15	D	Hg-a	Cold	Shake 5 hours Stand 1 hour	83						
				Shake 4 hours Stand 15 hours more	53						
16	D	Hg-a	Cold	Shake 6¼ hours Stand 2½ hours	77	55	22				
				Shake 12 hours Stand 2½ hours more	67	61	6				
17	G	Hg-a	Cold	Shake 18 hours Stand 4 hours	9	8					
				Shake 18 hours Stand 4 hours more	17	15					
				Shake 23 hours more	*1948*	*17*	*499*	*1394*	*55*		Known gas sample added at start of expt.: CO, 507; H_2, 1407; CH_4, 55 cu. mm. N. T. P.

[a] Italics denote total volumes of the various gases found, rather than volumes per gram of sample as in all other cases.

dioxide and a trace of carbon monoxide; the carbide steel yielded greater quantities of carbon dioxide and significant amounts of carbon monoxide. Since all the samples of steel had been vacuum fused, these gases must be the products of side reactions.

(2) That this side reaction gas was not connected with impurities in the commercial mercuric chloride reagent was shown by the nearly identical results secured in the trial in which a thrice recrystallized reagent was used. This possibility of using the commercial reagent gives the mercuric chloride method a considerable advantage over the cupric salt method.

(3) The successful outcome of the control trial in which known quantities of carbon monoxide, hydrogen and methane were introduced over the reacting mixture seems to exclude the possibility of loss of these gases by side reactions—a notable advantage over the cupric salt method.

(4) When a mercuric reagent was used, evolution of reaction gases continued long after complete solution of the sample. When a cupric reagent was used the carbonaceous residue, because of its enclosure in a rather coherent copper shell, was largely protected from the further action of the solution. Application of the mercuric chloride method to a number of vacuum-fused carbon-bearing steels has furnished an approximate relationship between the amounts of reaction gas liberated during the primary period, during solution of the sample; and a defined secondary period after completion of the solution process. This relationship is of use in practical analysis in that it allows an estimated correction for the amount of reaction gas in the primary gas sample on the basis of the quantity of reaction gas freed during the secondary period.

(5) Final Estimate: This method appears quite serviceable for steels of low graphitic carbon content. For higher contents of graphitic carbon, the carbon dioxide value will be in some doubt. For carbide steels there will be some doubt about both the carbon dioxide and the carbon monoxide values, the inaccuracy depending on the precision with which a corrective factor can be deduced. In any case, for the reasons enumerated above, the mercuric chloride method seems far superior to the cupric salt method.

E. Other Salts.—Hot aqueous solutions of ionic ferric salts dissolve steel with some rapidity, but hydrolysis is extensive. Cold solutions of ferric citrate were then tested, but not only were such solutions inordinately slow in their action on a massive sample; but there also appeared to be considerable spontaneous evolution of gas (largely carbon dioxide) from the reagent itself. No remedy for these difficulties could be found.

Many other salts dissolve steel more or less rapidly. However, since even such mild oxidants as copper chloride and mercuric chloride will be shown to cause oxidation of the carbon present, it seems highly improbable that any salt strong enough as an oxidant to convert metallic iron to a soluble iron salt with sufficient rapidity will not also react with the carbonaceous inclusions.

F. Origin of the Reaction Gases.—The considerable quantities of carbon dioxide (and carbon monoxide) evolved from the carbide steel cannot be due to direct interaction of the carbide and water.[29] Consequently a search has been made for a reaction between carbon and the reagents used.

Reactions in which carbon is active toward solutions of easily reducible salts have been studied by Weppen[30] and others, but the uncertain purity of the reagents used renders the results of doubtful value. However, Avery[31] has made a painstaking study of the reduction of auric chloride with pure cocoanut charcoal and was able to demonstrate that the following reaction takes place

$$4AuCl_3 + 6H_2O + 3C \longrightarrow 4Au + 12HCl + 3CO_2$$

We have conducted similar experiments, using approximately 0.5 *M* solutions of mercuric chloride and (purified) potassium copper chloride. The carbon samples were (1) purest graphite—from a spectroscopic carbon; and (2) sugar charcoal freed as far as possible of hydrocarbon impurities by treatment at 800° with live steam. With the graphite sample no reaction could be detected; but when the charcoal was treated with the mercuric chloride or copper chloride solutions at their respective boiling points, a quantity of carbon dioxide was evolved and a significant decline of the *p*H of the solution was noted. The reaction was much slower, though still perceptible, at lower temperatures.

These data strongly suggest that the mercuric and cupric salts enter into reactions similar to that written above for auric chloride. Since graphite does not appear to be active in these reactions, the small quantities of reaction gases evolved by graphitic steels are readily understood. However, large quantities of reaction gas are only to be expected when a carbide steel is dissolved since relatively large quantities of amorphous carbon are ordinarily associated with such materials. Moreover, a direct reaction of the reagents with iron carbide has not been excluded. Finally, this mechanism of reaction of carbon with the reagent renders intelligible the previous observations of increasing reaction gas with increasing carbon content of the steel, with increased concentration of the reagent, and with rise of temperature.

A similar oxidizing action of iodine on carbonaceous inclusions in the steel seems probable, but no attempt has been made to check this mechanism experimentally.

Although the postulated reaction produces free acid, no appreciable effect on the hydrogen values need be anticipated since only a very small quantity of acid is thereby added to a considerable volume of solution which shows an original *p*H of approximately 3. However, it must be conceded that there is little hope that reaction gas evolution can be avoided completely in any process in

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[29] Mylius, *et al.*, *Z. anorg. Chem.*, **13**, 38 (1897).

[30] Weppen, *Ann.*, **55**, 241 (1845).

[31] D. Avery, *J. Soc. Chem. Ind.*, **27**, 255 (1908).

TABLE II

ANALYSES OF GASES LIBERATED FROM A SERIES OF METEORITIC AND TERRESTRIAL IRONS

Sample	State of sub-division	Rea-gent	Duration of experiment	Primary evolution Gas volumes, cu. mm. N. T. P./g. Total	H_2	CO	CO_2	N_2	CH_4	Secondary evolution Prolongation of experiment	Cu. mm. N. T. P./g. Total	CO_2	CO
				Meteorites									
Canyon Diablo	Turnings	$HgCl_2$	Shake 10 hours Stand 2 hours	31.5	2.8	2.2	26.3	1.3	0.0	Shake 24 hours Stand 10 hours	6.9	6.8	
Canyon Diablo	Turnings	$CuCl_2$	Shake 33 hours	33.6	3.0	6.6	23.8	0.8		Shake 24 hours	1.5	0.9	0.6
Canyon Diablo	Turnings	$HgCl_2$	Shake 8$^1/_2$ hours	30.7	2.25	1.9	24.8	1.65					
Cumpas	Fragments	$HgCl_2$	Shake 21 hours	5.65			1.5						
Cumpas	Fragments	$HgCl_2$	Shake 33 hours Stand 1$^1/_2$ hours	5.5	1.2	1.1	3.0	0.1		Shake 12 hours Stand 10 hours	0.9	0.9	
Cumpas	Fragments	$CuCl_2$	Shake 37 hours	5.5	1.4	1.6	2.3	0.3		Shake 23 hours	—		
Cumpas	Filings	$HgCl_2$	Stand 9 hours Shake 2 hours	9.7	2.0	1.8	5.6	0.5					
Cosby Creek	Fragments	$HgCl_2$	Shake 10 hours Stand 1 hour	59.9	2.1	5.1	52.2	0.4		Shake 24 hours	38.6	37.2	1.4
Cosby Creek	Fragments	$CuCl_2$	Shake 24 hours	119.0	2.8	47.9	67.7	0.5	0.1	Stand 70 hours	36.6	26.5	10.0
Bethany	Fragments	$HgCl_2$	Shake 10 hours Stand 1 hour	2.8	1.1	0.4	1.0	0.2		Shake 12 hours Stand 12 hours	0.6	0.6	
Bethany	Fragments	$HgCl_2$	Shake 5 hours Stand 1 hour	3.05	1.0	0.4	1.0	0.6					
Babbs Mills	Fragments	$HgCl_2$	Shake 10 hours Stand 1 hour	2.5	0.5	0.5	1.3	0.4		Shake 6 hours Stand 17 hours	0.7	0.7	
Williamstown	Fragments	$HgCl_2$	Shake 25 hours Stand 4 hours	9.0	4.5	0.8	3.5	0.3		Stand 28 hours	0.14	0.14	
				Terrestrial steels									
Nickel-steel rod	Fragments	$HgCl_2$	Shake 12 hours Stand 3 hours	18.1	2.4	4.0	11.7	0.25		Stand 20 hours	4.6	4.6	
Crucible steel	Fragments	$HgCl_2$	Shake 18 hours Stand 1 hour	29.1	1.5	8.5	19.9	0.2		Stand 32 hours	2.7	2.2	0.5
Open-hearth steel	Fragments	$HgCl_2$	Shake 14 hours Stand 1 hour	24.4	3.4	5.75	15.4	0.5		Shake 25 hours Stand 3 hours	3.3	3.3	

which solution of a carbon-bearing steel is attained by treatment with an aqueous solution of a reducible salt, or under any oxidizing conditions whatsoever.

VI. Determinations of Unknowns

Having reached the conclusion that the mercuric chloride method is certainly the most nearly satisfactory and that at any rate confirmatory data might be obtained from the cupric chloride method, a series of determinations with meteoritic and terrestrial irons and steels has been made with these reagents, using the modified form of dissolving flask.

For these runs massive fragments, weighing about three grams, were used. The customary use of shavings or filings was avoided whenever possible because of (1) the greater opportunity for contamination of the larger surface by adsorbed gases or by traces of grease; (2) the possibility that a portion of the gas sample may be lost during subdivision; and (3) the great violence of the initial reaction of the finely divided sample with the dissolving reagent. The fragments used were cut very slowly with a sharp hacksaw. Any traces of rust were removed with a file, and the fragments were washed successively with hot toluene, hot absolute alcohol, and ice-cold water, and stored in a desiccator.

The results of these trials are shown in Table II. Although they may be subject to small inaccuracies due to analytical errors or segregation of the gaseous content of the samples, certain major conclusions may be drawn from them.

1. The effect of the dissolving agent on the results is seen to be insignificant as far as the hydrogen and nitrogen values are concerned, but the values for the carbon gases are higher when the copper reagent is used. This divergence is obviously dependent on the carbon content of the sample, and becomes negligibly small with samples of low carbon content. These observations confirm the conclusion previously drawn, that the copper reagent causes greater gasification of carboniferous inclusions than does the mercuric reagent. In computing the final results, therefore, the values were based on the mercuric chloride figures only.

(II) The magnitude of the effect of the state of subdivision on the results can be deduced from the difference between the results secured with massive fragments of the Cumpas siderite and with saw filings from the same material. Despite all possible precautions, the initial reaction of the filings with the reagent was one of great violence, with strong local heating in the reaction mixture. Such a temperature rise accelerates the side reaction producing the carbon gases, causing a parallel local development of free acid (aside from any free acid produced by hydrolysis in the warmed solution) which may then react with the metal to give free hydrogen. Consequently this method cannot be expected to yield good results with a finely divided sample.

(III) The duration of the experiment has a variable effect on the results. For low carbon materials, like the Bethany Meteorite, runs made in six and eleven hours are almost indistinguishable, so that there is no time effect. For high carbon materials, like Cosby Creek, however, the evolution of the side reaction gases was copious and long-continued so that to keep this contamination to a minimum the solution period should be made only as long as is necessary to secure complete solution of the sample.

(IV) The prolonged liberation of the reaction gases carbon monoxide and carbon dioxide is of particular significance. The control trials made with vacuum fused steels provide a rough relationship between the quantity of reaction gas liberated during the primary period, when the sample is dissolving, and a secondary period of equal length, after full solution has been attained. With this relationship and the observed magnitude of the secondary evolution for these samples, a correction of the primary values may be made to bring them closer to the true values. The results of such correction are shown in Table III.

TABLE III

PART A: CORRECTION OF OBSERVED VALUES

	Cu. mm. per g. at N. T. P.					
	CO_2			CO		
Sample	Observed	Correction	Corrected	Observed	Correction	Corrected
	Meteorites					
Canyon Diablo	26.3	1.8	24.5	2.2	0.1	2.1
Canyon Diablo	24.8	1.4	23.4	1.9	.0	1.9
Cumpas	3.0	1.2	1.8	1.1		1.1
Cosby Creek	52.2	10.8	41.4	5.1	1.2	3.9
Bethany	1.0	0.2	0.8	0.4		0.4
Bethany	1.0	.1	0.9	.4		.4
Babbs Mills	1.3	.3	1.0	.5		.5
Williamstown	3.5	.1	3.4	.8		.8
	Terrestrial steels					
Nickel-steel rod	11.7	4.2	7.5	4.0		4.0
Crucible steel	19.9	1.7	18.2	8.5	1.2	7.3
Open-hearth steel	15.4	1.3	14.1	5.75		5.75

PART B: FINAL RESULTS

	Gas volumes, cu. mm. N. T. P./g.				
Sample	Total	H_2	CO_2	CO	N_2
	Meteorites				
Canyon Diablo	30.7	2.8	24.5	2.1	1.3
Canyon Diablo	29.2	2.25	23.4	1.9	1.65
Cumpas	4.2	1.2	1.8	1.1	0.1
Cosby Creek	47.8	2.1	41.4	3.9	0.4
Bethany	2.5	1.1	0.8	0.4	0.2
Bethany	2.9	1.0	0.9	0.4	0.6
Babbs Mills	2.4	0.5	1.0	0.5	0.4
Williamstown	9.0	4.5	3.4	0.8	0.3
	Terrestrial steels				
Nickel-steel rod	14.15	2.4	7.5	4.0	0.25
Crucible steel	27.2	1.5	18.2	7.3	0.2
Open-hearth steel	23.75	3.4	14.1	5.75	0.5

Minimum values of the corrective factors have been used, so that the final figures still represent the maximum possible gas contents for these samples. While the absolute magnitude of this correction rests on the assumption of an approximate relationship determined with material differing in composition from the unknown samples, it is undoubtedly in the right direction. Furthermore, it will be observed that with the exception of the highly carboniferous Cosby Creek Meteorite, all the corrections are gratifyingly small, suggesting that the contamination by reaction gases has not been a major effect. No attempt has been made to correct the copper chloride results since not only are they initially further in error (*vide supra*), but also the correlation between the primary and the secondary gas evolution is very uncertain.

(V) In Table IV are gathered together the average results secured in this research and some of the values secured in other similarly directed investigations. Inter-comparison of these data is of some interest.

The meteorite results in this investigation are strikingly different from the older meteorite data secured by thermal extraction methods.[32] It has already been shown, however, that the thermal values are seriously subject to side reactions involving non-gaseous components of the sample. On the other hand, the results of Travers,[33] secured by solution in a copper salt reagent much as in this research, are similar to our own, with the exception of his inordinately high carbon dioxide value. This may have been due to carbonaceous contamination of his reagent or of his sample.

The results of Oberhoffer and Piwowarsky are of peculiar interest since they were obtained by "kaltumsetzung" with a mercuric chloride reagent, following a procedure similar to our own, though differing in important details—for example, they sought to hasten completion of the reaction by heating. It will be seen that Oberhoffer and Piwowarsky's results are completely different from those obtained with the mercuric chloride method finally adopted in this research, but show a striking similarity to the values secured when a nickel–steel rod was treated by the hot solution method. The same rod, when treated by the cold solution method, yielded very much less gas. This further confirmation of the extensive production of reaction gases in the hot solution method suggests that the gases analyzed by Oberhoffer and Piwowarsky contained a considerable proportion of gaseous reaction products, so that agreement with the results of this research cannot be expected.

Recent determinations of hydrogen thermally extracted from terrestrial steels[34] are in excellent agreement with the values yielded by the final mercuric chloride method. The former discrepancy between chemical and thermal methods is thus removed, and the possibility of getting accurate hydrogen values by a chemical method is opened.

Nitrogen values obtained by thermal extrac-

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(32) Merrill, *Proc. Am. Phil. Soc.*, **65**, 119 (1926).

(33) Travers, *Proc. Roy. Soc.* (London), **64**, 130 (1898).

(34) Holm and Thompson, *Bur. of Standards J. Research*, **26**, 245 (1941).

TABLE IV

COMPARISON OF RESULTS FROM DIFFERENT SOURCES

Investigation	Method	Iron sample	Total gas sample	Gas, volumes, cu. mm. N. T. P./g.				
				H_2	CO	CO_2	N_2	CH_4
This research	Cold solution in aq. $HgCl_2$	Average six meteoritic irons	16.0	2.0 (2.5%)	1.4 (8.8%)	12.1 (75.6%)	0.5 (3.1%)	...
This research	Cold solution in aq. $HgCl_2$	Average three terrestrial irons	21.7	2.4 (11.0%)	5.7 (26.3%)	13.3 (61.3%)	0.3 (1.4%)	...
Several previous investigations	Heating *in vacuo*	Average several meteoric irons	358	211 (58.9%)	85 (23.7%)	27 (7.5%)	30 (8.4%)	3 (0.8%)
Travers	Solution in aq. $HgCl_2$	Unspecified iron meteorite	753	14 (1.9%)		739 (98.1%)	....	...
Oberhoffer and Pinowarsky	"kaltumsetzung" in aq. $HgCl_2$	Three terrestrial irons	92.3	41.5 (45.0%)	15.0 (16.25%)	17.3 (18.75%)	18.5 (20.0%)	...
			96.4	40.3 (41.9%)	12.7 (13.2%)	9.4 (9.8%)	34.0 (35.2%)	
			358.0	188 (52.5%)	85.0 (23.7%)	53.0 (14.8%)	34.0 (9.0%)	...
This research	Hot solution in aq. $HgCl_2$	Nickel–steel rod	86	41 (47.7%)	12 (14.0%)	25 (29.1%)	8 (9.3%)	1 (1.2%)
Holm and Thompson (H_2)	Heating or fusion *in vacuo*	Several terrestrial steels		2.2				
Chipman and Fontana (N_2)							25	

tion, for example those of Chipman and Fontana[35] are noticeably higher than the chemically obtained values. However, while thermal extraction should liberate all the nitrogen, including that which is present as a nitride,[36] the chemical method appears to liberate only the nitrogen which is present as such, since any nitride which is attacked by the reagent is converted to involatile ammonium salts.[37] Therefore thermal methods show the total nitrogen content, the chemical methods, always lower, reflect only the nitrogen which is present as such.

The carbon oxides found in thermally extracted gases are generally acknowledged to be reaction gases and so cannot be related to the data of chemical extraction. No methane was found in the chemically extracted gases, and the methane occasionally found in thermally extracted gases is now believed to have been formed by side reactions.[38]

VII. Presence of Cyanogen

The possible presence of cyanogen has not been discussed since it would not have been noted in the foregoing experiments (any cyanogen escaping from the reaction mixture would have been absorbed by the ascarite and recorded as carbon dioxide), but it has been investigated by dissolving several grams of (meteoritic or terrestrial) iron in warm dilute sulfuric acid in a slow stream of nitrogen. The effluent nitrogen was bubbled through a small volume of dilute potassium hydroxide, and this solution was examined for cyanide by several methods: (1) conversion of the cyanide to ferrocyanide and test through the development of Prussian Blue; (2) conversion of the cyanide to thiocyanate and test for thiocyanate with ferric ion[39]; and (3) a procedure recently described by Kolthoff and Lingane[40] for trace analysis for copper with a phenolphthalin reagent has been adapted for trace analysis of cyanide. All of these methods gave negative results with terrestrial steels and with the Canon Diablo, Williamstown and Bethany meteorites.

The final conclusion is that if cyanogen is present in terrestrial or meteoritic irons, it occurs in amounts considerably less than 1 cu. mm. per gram; or less than 2×10^{-5} weight per cent.

Summary

Consideration has been extended to the methods whereby a determination of the gases present as such in terrestrial and meteoritic irons and steels might be accomplished; and it has been concluded that no method is completely satisfactory, but that solution with an aqueous mercuric chloride reagent, under prescribed conditions, is the most nearly satisfactory. This method may be made to yield good results for steels which do not contain too large a quantity of combined carbon.

It has been indicated that the previous, thermally determined, values for the gases in meteorites are seriously in error, and it has been demonstrated that actually iron meteorites contain be-

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(35) Chipman and Fontana, *Ind. Eng. Chem., Anal. Ed.*, **7**, 391 (1935).

(36) Maxted, *J. Soc. Chem. Ind.*, **37**, 107T (1918).

(37) Fowler, *J. Chem. Soc.*, **79**, 285 (1901).

(38) Sloman, *Iron Steel Inst. (London), Special Rept.*, **25**, 47 (1939).

(39) Kolthoff, *Z. anal. Chem.*, **57**, 11 (1918).

(40) Kolthoff and Lingane, *Mikrochemie*, Molisch Festschr., 274 (1936).

tween 2 and 50 cu. mm. per gram of hydrogen, nitrogen, carbon monoxide and carbon dioxide, and no readily detectable quantities of methane or cyanogen.

A previous discrepancy between chemically and thermally determined hydrogen contents of terrestrial steels has been explained.

The essential similarity of the gases in terrestrial and meteoritic steels has been demonstrated.

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[CONTRIBUTION FROM THE KEDZIE CHEMICAL LABORATORY, MICHIGAN STATE COLLEGE, AND THE CHEMISTRY DEPARTMENT OF THE UNIVERSITY OF CALIFORNIA AT LOS ANGELES]

The Electric Moments and Ultraviolet Absorption Spectra of Some Derivatives of Cyclopropane and of Ethylene Oxide

BY MAX T. ROGERS

A number of studies have shown that derivatives of cyclopropane behave in many ways like the corresponding ethylene derivatives. Thus, the ultraviolet absorption spectra of a series of derivatives of benzoyl and anisoyl cyclopropane,[1] and of some steroids containing cyclopropane rings,[2] have been investigated and shown to resemble those of the corresponding compounds with conjugated double bonds.[3] Also the electric moments of the cyclopropyl halides lie between the values of the corresponding vinyl and isopropyl (or cyclopentyl) halides,[4] and the molecular refractions of cyclopropyl compounds[5] show an exaltation (≅ 0.8 cc.) about half that of the carbon–carbon double bond (1.73 cc.). The chemical properties of cyclopropyl compounds have long been considered as evidence that the cyclopropane ring possesses a considerable degree of unsaturation.[6]

The electric moments and ultraviolet absorption spectra of some simple derivatives of cyclopropane are reported here and compared with the moments and spectra of the corresponding compounds in which the cyclopropane ring is replaced by a carbon–carbon double bond or by an aliphatic group. It should be possible to interpret the effect of the small ring on the spectrum with more confidence than in the previous studies on more complex derivatives. Two derivatives of ethylene oxide have been included since no data were available on compounds containing an ethylene oxide ring adjacent to a double bond.

Experimental Part

Materials

Benzene.—J. T. Baker C. P. benzene was dried over sodium and filtered before use, d^{25}_{4} 0.87340, n^{25}_{D} 1.49785.

Cyclopropyl Methyl Ketone.—Eastman Kodak Company White Label cyclopropyl methyl ketone was dried and fractionated through an efficient packed column; b. p. 110.5° (750 mm.), n^{25}_{D} 1.4222, d^{25}_{4} 0.8967.

3,4-Epoxybutene-1.—Eastman Kodak Company White Label material was dried and fractionated; b. p. 66.8° (750 mm.), n^{25}_{D} 1.4143, d^{25}_{4} 0.8697.

Propylene Oxide and Acrylonitrile.—Commercial samples were fractionated through an efficient packed column: propylene oxide b. p. 34° (750 mm.), n^{20}_{D} 1.3664, d^{20}_{4} 0.8311; acrylonitrile, b. p. 76.8° (748 mm.), n^{25}_{D} 1.3888, d^{25}_{4} 0.8003.

Vinyl Methyl Ketone.—A sample of the azeotrope was supplied by the Organic Chemicals Department of du Pont and Co. According to their directions, the pure ketone was prepared by cooling the azeotrope, treating with solid potassium carbonate, drying the non-aqueous layer over calcium chloride and fractionating; b. p. 80.8° (752 mm.), n^{25}_{D} 1.4086, d^{25}_{4} 0.8407.

2-Methylcyclopropanecarbonitrile.—A pure sample of this chemical was kindly supplied by Professor J. B. Cloke[7]; b. p. 144.5–145.5°, n^{25}_{D} 1.4258, d^{25}_{4} 0.8732.

Phenylcyclopropane.—This was prepared, according to the directions of Roberts and Byerly,[8] by a modification of the method of Kishner.[9] Cinnamaldehyde was converted to the pyrazoline using hydrazine hydrate and this was purified and decomposed with potassium hydroxide in the presence of platinized asbestos. The crude product was fractionated using a packed column, b. p. 77.5° (30 mm.), n^{25}_{D} 1.5302, d^{25}_{4} 0.9374.

Apparatus and Method

The absorption spectra were measured (in 95% ethanol unless otherwise stated) with a Beckman Quartz Ultraviolet Spectrophotometer using calibrated fused silica cells with widths (d) close to 1 cm. Molar extinction coefficients (ϵ) were calculated from the observed optical densities ($\log_{10} I_0/I$) and molar concentrations (c) using the equation $\epsilon = 1/cd \log_{10} I_0/I$. Measurements down to about λ = 2080 Å. were made (Table III).

Dielectric constants ϵ and densities d of dilute benzene solutions of solute mole fraction f_2 were measured at 25° using the apparatus and technique described previously.[3] The experimental data and the calculated molar polarizations P_2, at each concentration, are shown in Table I. The values of the molar polarization at infinite dilution, P_∞, obtained by graphical extrapolation are shown in Table II along with the measured values of the molecular refractions MR_{D} and the calculated dipole moments, μ.

Discussion of Results

The ultraviolet absorption bands of the compounds studied containing a three-membered ring adjacent to a double bond tend to occur at wave lengths about midway between those of analogous compounds with alkyl groups adjacent to the

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(1) E. P. Carr and C. P. Burt, THIS JOURNAL, **40**, 1590 (1918).

(2) I. Klotz, *ibid.*, **66**, 88 (1944).

(3) See also J. D. Roberts and C. Green, *ibid.*, **68**, 214 (1946).

(4) M. T. Rogers and J. D. Roberts, *ibid.*, **68**, 843 (1946).

(5) See, for example, N. Zelinsky and J. Zelikow, *Ber.*, **34**, 2856 (1901).

(6) E. P. Kohler and J. B. Conant, THIS JOURNAL, **39**, 1404 (1917).

(7) J. B. Cloke, E. Stehr, T. R. Steadman and L. C. Westcott, *ibid.*, **67**, 1587 (1945).

(8) J. D. Roberts and J. E. Byerly, private communication.

(9) N. Kishner, *J. Russ. Phys.-Chem. Soc.*, **45**, 950 (1913).