above the precipitate was quite clear. Sometimes the precipitate was filtered off at once, and sometimes after twenty-four hours. The clear liquid was poured through a Neubauer crucible (to avoid the use of a filter paper) and the precipitate transferred to the crucible with a minimum amount of a dilute solution of silver nitrate (5 g. of the salt in 1000 cc. of H_2O). It was washed seven to eight times by letting from 4–5 cc. of the wash-solution flow from a pipet around the upper rim of the crucible and then drawing it off with the pump. The small amount of silver nitrate remaining in the precipitate was washed out with 15 cc. of 96% alcohol, 5 cc. being used each time. Finally, after removing the alcohol as thoroughly as possible with the pump, the precipitate was dried to constant weight at 110°. At this temperature it still contained traces of water (0.0003 g., average of many determinations), and a further heating to 250° was necessary. This was carried out as follows. A large porcelain crucible of about 75-cc. capacity was adjusted 11 cm. above the top of a Bunsen burner and a 550° thermometer clamped upright with its bulb in contact with the bottom of the crucible. By regulating the length of the burner flame the desired temperature could be obtained roughly. When the temperature was reached and remained constant the thermometer was removed and the Neubauer crucible introduced. During the heating the precipitate became pink and then purple in color, which slowly disappeared above 250° and was completely discharged at 350°.[2] The disappearance of the purple color was not accompanied by any perceptible change in weight of the precipitate. During all the operations care was taken to protect the precipitate from direct sunlight.

1. Seven samples of Merck blue label ammonium molybdate ranging between 0.2642 and 0.5104 g. were analyzed and, when corrected for traces of water in the Ag_2MoO_4 dried at 110°, gave an average value of 54.40% Mo, with an average deviation of 0.02% and a maximum deviation of 0.08%. Calcd.: Mo, 54.36%. Found by the ignition method: Mo, 54.43%.

2. Three determinations next were made in another sample of Merck blue label salt, which by the ignition method gave 54.48% Mo. Found: Mo (average), 54.47%. The course of procedure was exactly that given above.

3. Some sodium molybdate which had lost a part of its water of crystallization was recrystallized and carefully dried. Found in it by ignition 14.82% H_2O; calculated, 14.87% H_2O. Five determinations of the molybdenum in this recrystallized salt averaged 39.69%, the lowest result being 39.65% and the highest 39.75%. The theoretical percentage is 39.67. Nothing is gained by dissolving the precipitate in nitric acid and titrating the silver according to Volhard. The solution goes on too slowly—indeed, is only complete when the acid has been heated for some time. The results, however, are satisfactory.

For the determination of molybdenum in alkali molybdates the method is easier and more expeditious than are those of Berzelius–Rose (precipitation as Hg_2MoO_4) and Chatard (precipitation as $PbMoO_4$).

Summary

It has been shown that the molybdenum in alkali molybdates can be determined easily and accurately by converting them into silver molybdate, which while slightly soluble in water is practically insoluble in water containing silver nitrate.

PRINCETON, NEW JERSEY RECEIVED JULY 12, 1934

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[2] Smith and Bradbury (*loc. cit.*) noticed this purple color. Their statement that the salt when moderately heated melts to a clear, yellow liquid is not in accord with the experience of the writer, who finds that the liquid is purple and on cooling solidifies to a yellowish-white mass.

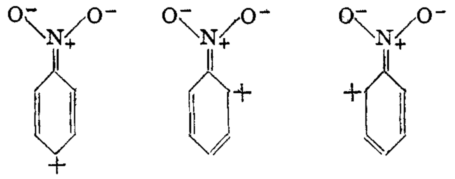
[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

Dipole Moments and Molecular Structure of Amides

BY W. D. KUMLER AND C. W. PORTER

The fact that certain groups of atoms have different moments when attached to the benzene ring than when attached to aliphatic radicals has been ascribed to the inductive and electromeric effects of the benzene ring.[1] Resonance involving essentially the same idea as electromerism gives perhaps a more precise picture of this phenomenon. In many cases the structure of a molecule is not one definite form, but a combination of several electromeric configurations. The large moments of most simple aromatic compounds as compared with the corresponding simple aliphatic compounds are due, in part, to the contributions made by excited forms in which certain atoms are positively charged and others are negatively charged.

In nitrobenzene the excited forms



contribute appreciably to the structure of the molecule and these excited forms raise the moment of the aromatic compound considerably above that of an aliphatic nitro compound in

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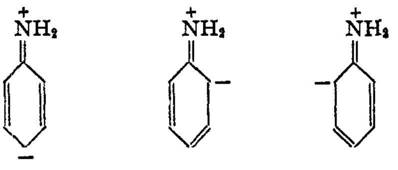
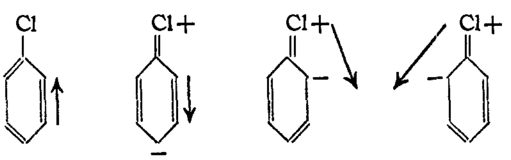
[1] Sutton, *Proc. Roy. Soc.* (London), **133A**, 668 (1931).

which corresponding excited states do not occur. Likewise in the case of aniline the forms



raise its moment above that of methylamine.

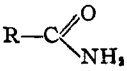
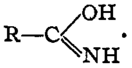
In some cases the moment of the aromatic compound is lower than the moment of the corresponding aliphatic compound. Chlorobenzene is an example, but here the moments in the excited forms are opposite in direction to the moment in the normal form, thus making the moment of chlorobenzene less than that of methyl chloride.

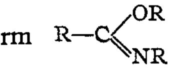


The group moment calculated from one compound cannot be applied accurately to the calculation of the moment of another compound unless the two have practically the same amount of resonance or the change in moment due to resonance can be evaluated. *p*-Nitroaniline long presented an anomaly because aniline has a moment of 1.56, nitrobenzene a moment of 4.0 and *p*-nitroaniline a moment between 6 and 7. Even if we assume the moment of the NH_2 group to be in the plane of the ring (which is not correct) the maximum calculated moment for *p*-nitroaniline is 5.56, which is considerably less than any of the measured values reported in the literature (7.1, 6.4 and 6.1).[2] We measured the moment of this compound, using dioxane as a solvent, and obtained a value of 6.68. The great tendency of the nitrogen in the amino group to acquire a positive charge and of the oxygen atoms in the nitro group to acquire negative charges causes the form

to contribute much more to the moment of *p*-nitroaniline than the excited forms given above contribute to nitrobenzene and aniline, for in *p*-nitroaniline each group enhances the tendency of the other group to pass into the excited state.

When the measured and calculated values do not agree it has been the general practice to explain the discrepancy by assuming induction. We are convinced that in many cases the discrepancy is due in part to resonance. The difference between the observed and the calculated values, in molecules that present the possibility of resonance, is usually in the direction one would expect from the contributions made by the excited forms. Moreover, many of these discrepancies are too large to be explained by induction. The difference of about 1.8 in *p*-nitroaniline is an example.[2]

Pauling and Sherman[3] have pointed out from thermochemical considerations that unsubstituted amides resonate. The excited form  $R—C\begin{smallmatrix}O^-\\ \overset{+}{N}H_2\end{smallmatrix}$ has a moment of the order of 10. Since the moment in the excited form is in approximately the same direction as the resultant moment in the normal form,  $R—C\begin{smallmatrix}O\\ NH_2\end{smallmatrix}$ the moments of amides should be greater than the values calculated from bond moments derived from ketones and amines. The problem is complicated, however, by several factors. First, there is some uncertainty in regard to bond angles. Second, the NH_2 group may be either rotating or fixed.[4] Third, the compound may be partly in the tautomeric form  $R—C\begin{smallmatrix}OH\\ NH\end{smallmatrix}$.

If resonance occurs in unsubstituted amides it is highly probable that it occurs also in substituted amides. By using substituted amides we eliminate the possibility of complications arising from the tautomeric form  $R—C\begin{smallmatrix}OR\\ NR\end{smallmatrix}$ since such a tautomeric shift of a radical is ruled out on chemical evidence. We measured diethyl acetamide and dimethyl acetamide and found that their moments are 3.72 and 3.79, respectively. Now if we calculate the moment of these compounds, using the generally accepted bond moments (C═O) = 2.3, (C—N) = 0.4, (H—C) = 0.4 (the positive end of the dipole is written first), an angle of 110° for the carbon and nitrogen valence angles, and if we assume the radicals of the amido group are fixed in such a position as to give the largest possible moment to the molecule, we get a value of 3.14 for these compounds, which is considerably below the measured moments of 3.79 and 3.72. (Changing the nitrogen valence

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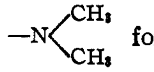
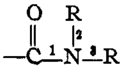
[2] Smyth, "Dielectric Constant and Molecular Structure," Chemical Catalog Co., New York, 1931.

[3] Pauling and Sherman, *J. Chem. Phys.*, **1**, 606 (1933).

[4] Zahn, *Physik Z.*, **33**, 525 (1932).

angle to 120° would reduce the calculated moment.) It is highly probable that the NR_2 group is not in a position to give the largest moment. The OH group in a carboxylic acid is fixed in a position of minimum moment.[5] This freezing has been explained as due to the interaction of the OH and $C{=}O$ dipoles. The same kind of interaction should take place in substituted acetamides between the NR_2 and $C{=}O$ dipoles, also in the case of substituted acetamides there should be a steric effect between the R groups and the CH_3 of the acetyl group that would tend to force the R groups into a position of minimum moment. The calculated moment in this minimum position is 1.82, a value 1.9 less than the smallest measured moment. Even if the groups occupied positions giving the maximum moment, the difference between the calculated and observed values would be 0.65 (3.79 − 3.14) and the probability that this difference could be accounted for as due to induction alone seems remote. The $C{=}O$ bond moment was calculated from acetone. Any inductive effect of the $C{=}O$ on the CH_3 groups is already taken into account in the value 2.3 for $C{=}O$. In going from acetone to dimethylacetamide we have to consider the change in inductive effect caused by substituting  $—N(CH_3)_2$ for a methyl group. Judging from the behavior of the cyanides the inductive effect on any group near the dipole is about half that on the same group one atom closer to the dipole producing the induction.[6] Thus the inductive effect of $C{=}O$ on two methyl groups in dimethylacetamide should just about equal the effect on one methyl group in acetone. Since nitrogen is more negative than carbon, bond 1 in the formula  $—C({=}O)\overset{1}{—}N(\overset{2}{—}R)\overset{3}{—}R$ opposes the development of an induced dipole in the NR_2 group. This would not only reduce the induced moments in bonds 2 and 3 but would cut down those in the two CH_3 groups as well so the moment induced in them is less than that induced in one CH_3 group in acetone. To explain the difference in observed and calculated moment on a basis of induction would mean that a moment greater than 0.65 would have to be induced in bonds 2 and 3 across bond 1 which opposes such an induction—a condition that seems highly improbable. Since the interaction of dipoles and the steric effect would tend to place the NR_2 group in a position to give a minimum moment (1.82) and the induced moment is probably not greater than 0.3, the observed moment of 3.79 affords definite evidence that the dimethyl acetamide is a resonating molecule. The same thing holds for diethylacetamide.

We can estimate the contribution the excited form makes to the structure of the molecule as follows. The excited form has a moment determined primarily by the charges on the nitrogen and oxygen atoms. This separation of charge would give a dipole equal to $e \times l$ where e is the electronic charge and l is the distance between the charges. If this distance is 3 Ångström units the resultant dipole is $4.77 \times 10^{-10} \times 3 \times 10^{-8} = 14 \times 10^{-18}$. (Calculations of this type tend to give high results because the attraction of the oppositely charged atoms brings these atoms closer together than they would be in an unexcited form.) Taking the two extremes for the position of the R groups referred to above, the normal form would have a moment of 1.82×10^{-18} or 3.14×10^{-18}. The observed moment is 3.72×10^{-18}. Let x be the fraction the excited form contributes to the structure of the molecule. Then

$$14x + 1.82\,(1 - x) = 3.72$$
$$x = 0.15$$

or

$$14x + 3.14\,(1 - x) = 3.72$$
$$x = 0.058$$

The contribution of the excited form, therefore, is of the order of 10%.[7]

The calculated moment of acetamide with the NH_2 in a maximum position is 3.9 and in a minimum position 1.7. In analogy with the carboxylic acids and for reasons given in case of the substituted amides, the NH_2 group in acetamide is probably frozen in a position of minimum moment. The observed moment of 3.72 is therefore evidence for resonance in this compound.

The moment of ethylacetimino ether is interesting because it enables us to make an estimate of the moment of the tautomeric form of acetamide, the only difference between the two being replacement of hydrogen by an ethyl group.

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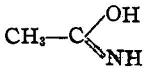
(5) Meyer, *Z. physik. Chem.*, **8B**, 27 (1930).

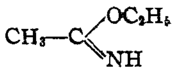
(6) Werner, *ibid.*, **4B**, 371 (1929).

(7) Vector equations should ordinarily be used in such calculations but in this case the resultant moment in the normal form is in nearly the same direction as the resultant moment in the excited form, so scalar equations can be used to calculate the approximate contribution the excited form makes to the structure of the molecule. These two forms are not to be thought of as a mixture of two dipoles, in which case a mean square calculation would apply [Lewis, *J. Chem. Phys.*, **1**, 26 (1933)].

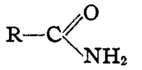

$CH_3-C(OH)=NH$

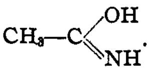
I

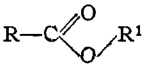
and

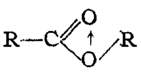

$CH_3-C(OC_2H_5)=NH$

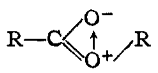
II

Certain arguments have been given for the existence of amides in form I.[8] Chemists have considered the formula  $R-C(=O)NH_2$ more probable, but, heretofore, there has been no definite evidence as to which form actually predominates.

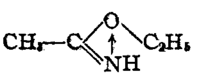
The tautomers of acetamide have never been isolated, but ethylacetimino ether is fairly stable. This compound was measured and found to have a moment of 1.33. The corresponding compound with a hydrogen on the oxygen would be expected to have a moment at most not more than 0.5 higher. This relatively small moment in comparison with the observed moment of acetamide indicates that if the compound is tautomeric only a small amount is in the form  $CH_3-C(OH)=NH$.

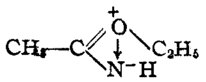
The moment of the imino ether enables us to estimate the value of the C=N moment. Taking the generally used bond values (C—O) = 0.7, (H—N) = 1.5, (H—C) = 0.4, angles of 110° for carbon, nitrogen and oxygen valence angles, assuming no resonance, and placing the C_2H_5 group as far as possible from the CH_3 group we calculate a value of 1.6 for the C=N bond. The result is the same no matter which of the two possible positions the imino hydrogen occupies. There may be a small amount of resonance in this compound. Pauling and Sherman[3] have given evidence from thermochemical data that there is considerable resonance in esters and structurally the imino ethers are very similar to esters. The low observed moment in an ester  $R-C(=O)-O-R^1$ (1.6 − 1.9) is not inconsistent with resonance if we consider the R^1 group to be in a position farthest away from the R group and nearest the =O, for then the calculated moment is 1.4 and the direction of the dipole in the excited form, II, is such that it would tend to augment the resultant moment in the normal structure, thus increasing the moment.


I


II

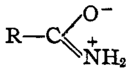
In the imino ether the resultant moment of the excited structure opposes that in the normal structure

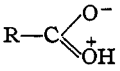


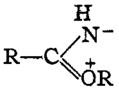


so the low moment of 1.33 is not inconsistent with resonance in this molecule. However, we would expect the amount of resonance here to be much less than in esters or amides, for the excited form that takes part in the resonance of the imino ethers would have a much higher energy (be much more unstable) due to the negatively charged nitrogen than the excited forms which take part in the resonance of amides or esters.

According to the thermochemical data the amount of resonance in acids (1.2 volt electrons for acetic acid) is greater than in amides (0.89 volt electrons for acetamide).[3] The dipole moment measurements indicate a considerably larger resonance for amides than for esters. The minimum calculated moment for acids 1.1 and the observed moment of 1.7 gives 0.6 of a dipole unit for resonance if we neglect inductive effects. The minimum calculated moment of 1.82 and the observed moment of 3.72 for amides gives a resonance of 1.9 dipole units. This seems to be somewhat anomalous. The fact that all amides boil at higher temperatures than do the corresponding acids indicates that they have a salt-like character. Also from chemical considerations one would expect the stability of the excited forms in amides, acids and imino ethers to decrease in the order


$R-C(O^-)=\overset{+}{N}H_2$


$R-C(O^-)=\overset{+}{O}H$


$R-C(N^-H)=\overset{+}{O}R$

Experimental

Apparatus.—The dielectric constants were measured with an apparatus similar to that described elsewhere,[9] consisting of two oscillating circuits, one of which was regulated by a quartz crystal with a frequency of about 750 kilocycles, the other circuit containing a fixed condenser in which the solution to be measured was placed with a calibrated variable condenser connected in parallel. The beat between these circuits was picked up on a radio receiving set and was matched with a 1000-cycle tuning fork. Densities were measured in a pycnometer of approximately 26 cc. capacity. Refractive indices were taken with a Pulfrich refractometer, using the D sodium line. Temperatures were controlled to within 0.05° by electrically regulated thermostats.

Nitrobenzene was run to check our technique, and a value of 3.9 was obtained for its moment in good agreement with the values 3.9 and 4.08 reported in the literature.

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[8] Claisen and Meyerowitz, *Ber.*, **22**, 3273 (1887); Tafel and Ensch, *ibid.*, **23**, 103 (1888); Pinner, *ibid.*, **25**, 1435 (1890).

[9] Williams and Weissberger, THIS JOURNAL, **50**, 2332 (1928).

Preparation and Purification of Materials

Dioxane.—Commercial 1.4-dioxane was refluxed for several hours over metallic sodium, distilled, refluxed over sodium again for several hours and fractionally distilled from sodium. The dioxane was found to contain peroxides which were eliminated by extended treatment with sodium but, upon standing. peroxides slowly form again even in sealed containers. This is perhaps one cause of the lack of reproducibility experienced by some who have worked with this substance. The final product had a boiling point of 101.0–101.1° (corr.) at 755 mm. pressure.

Acetamide.—Acetamide was distilled, crystallized once from ethyl acetate. sublimed in a vacuum. crystallized once more from ethyl acetate and three times from chloroform. It was dried in an oven at 70° and kept in a vacuum desiccator over phosphorus pentoxide. The final product was odorless and melted at 80.0–80.1°.

Dimethylacetamide.—Dimethylacetamide was prepared from Eastman dimethylamine hydrochloride and acetic anhydride. The hydrochloride was treated with sodium hydroxide and the free amine was passed into a solution of freshly distilled acetic anhydride in dry ether. The products were stirred with potassium carbonate and a little water until alkaline. and the ether portion was then dried with anhydrous potassium carbonate and fractionated. The fraction boiling at 165.3–165.5° at 750 mm. was used. One drop of 0.1 *N* sodium hydroxide gave a pink coloration to phenolphthalein in a 0.5-cc. sample.

Diethylacetamide.—Diethylacetamide was prepared from Eastman diethylamine and acetic anhydride. The amine was added to the freshly distilled anhydride in dry ether. The mixture was stirred with moist potassium carbonate and the ether layer was then dried with anhydrous potassium carbonate and fractionated. Fractions boiling at 185.2–185.4°, 185.4–185.6°. 185.6–185.8° under 750 mm. were collected. Three fractions had identical refractive indices. One drop of 0.1 *N* sodium hydroxide gave a pink color to phenolphthalein in a 0.5-cc. sample.

Monoethylacetamide.—Monoethylacetamide was prepared from Kahlbaum ethylamine and Eastman acetic anhydride. The anhydride was freshly distilled and both reagents were dissolved in three times their volumes of dry ether. The ether solutions of the amine were added slowly to the anhydride. The product was purified by the method described under dimethylacetamide. The fraction boiling at 209.0–209.1° was used.

Ethylacetimino Ether.—Ethylacetimino ether hydrochloride was prepared by the method of Pinner.[10] Equal molal quantities of absolute alcohol and methyl cyanide were mixed in one-third their volume of dry ether. Dry hydrogen chloride was passed through them continuously and the whole kept at 0° for about five days. The imino ether hydrochloride was filtered. washed with ether. then stirred in ether with aqueous sodium hydroxide. The ether layer was dried over anhydrous potassium carbonate and fractionally distilled. The fraction boiling at 90.6–91.2° was used. The compound when titrated with hydrochloric acid using methyl orange as an indicator gave an equivalent weight of 89.2. calculated for C_4H_9NO 87.1.

***p*-Nitroaniline.**—Eastman *p*-nitroaniline gave a sharp melting point and was used without further purification (m. p. 147°).

Results

All the measurements were made at 30°, using dioxane as the solvent. The values of P_∞ (P_2 extrapolated to zero concentration) were calculated using the equations

$$P_{12} = \frac{\epsilon - 1}{\epsilon + 2}\,\frac{c_1M_1 + c_2M_2}{d}$$

$$P_2 = \frac{P_{12} - P_1}{c_2} + P_1$$

The values of μ were calculated from the equation

$$\mu = 0.0127 \times 10^{-18}\sqrt{(P_\infty - P_{E_{2a}})T}$$

$P_{E_{2a}}$ was taken equal to P_{E_2} + 10% of P_{E_2}. For the total polarization of dioxane we get a value of 24.91.

TABLE I

c_2	d	ϵ	P_2
	Acetamide		
0.007703	1.02161	2.3762	300
.015695	1.02186	2.5362	287
.027562	1.02218	2.8074	281
	Monoethylacetamide		
.007471	1.02060	2.3950	355
.013146	1.02011	2.5520	368
.022580	1.01917	2.8400	375
	Dimethylacetamide		
.006451	1.02074	2.3523	318
.009483	1.02052	2.4184	317
.014676	1.01990	2.5235	308
	Diethylacetamide		
.0053011	1.02044	2.3325	318
.008287	1.01988	2.3970	314
.011979	1.01919	2.4783	311
	Ethylacetimino ether		
.005394	1.02102	2.2187	64.7
.009074	1.02074	2.2274	63.6
.017606	1.01885	2.2492	64.8
.038323	1.01498	2.2924	61.5
	p-Nitroaniline		
.001681	1.0216	2.3284	954
.007298	1.0236	2.6998	891
.014583	1.0265	3.1833	814

TABLE II

	P_{E_2}	μ
Acetamide	15.3	3.72
Monoethylacetamide	24.0	3.87
Dimethylacetamide	23.3	3.79
Diethylacetamide	33.7	3.72
Ethylacetimino ether	24.6	1.33
p-Nitroaniline	40.0	6.68

Just what influence the solution effect, recently discussed by Müller, has on the moments of these

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[10] Pinner, *Ber.*, **16**, 1643 (1883).

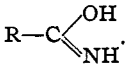
compounds we cannot say.[11] However, we have measured the moment of diethylacetamide in benzene and in dioxane, obtaining the values 3.8 and 3.72, respectively. In dioxane, therefore, this compound does not represent one of those rare cases in which the solution method of measurement gives results that are too high. It is probable that our values are a little low.

We wish to express our thanks to Professor G. E. K. Branch for helpful suggestions and constructive criticism during the entire time that this investigation was in progress.

Summary

The dipole moments of acetamide, of mono-alkyl and di-alkyl acetamides, of ethylacetimino ether and of *p*-nitroaniline have been determined.

The use of bond and group moments in the calculation of moments of resonating compounds has been discussed and an explanation, based upon resonance, has been given for the high moment of *p*-nitroaniline and for the differences in moments of simple aromatic and aliphatic compounds.

Evidence has been given to show that amides are resonating compounds, and that the unsubstituted amides do not exist to a very large extent in the form  $R{-}C\begin{smallmatrix}OH\\NH\end{smallmatrix}$.

The moment of the C=N bond has been evaluated.

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[11] Müller, *Physik. Z.*, **34**, 589 (1933).

[CONTRIBUTION FROM THE CHEMICAL ENGINEERING DEPARTMENT OF THE UNIVERSITY OF WASHINGTON]

Some Equilibrium Relations in the System Calcium Oxide–Sulfur Dioxide–Water (Acid Region) at Pressures below Atmospheric[1]

BY FRANK H. CONRAD AND W. L. BEUSCHLEIN

I. Introduction

This research describes the system $CaO-SO_2-H_2O$ when brought to equilibrium at various pressures of sulfur dioxide plus water vapor, ranging from the vapor pressure of water, at the temperature in question, to atmospheric pressure.

The system is of significance because of the extensive use of the "Sulfite Process" in the manufacture of wood pulp. The "raw acid" as it comes from the absorption towers is essentially such a system. Numerous workers have investigated the system sulfur dioxide and water but no literature is available for the system $CaO-SO_2-H_2O$ at pressures up to atmospheric and at room temperatures.

For the system, Schwarz[2] reported no definite pressures of sulfur dioxide, whereas Smith and Parkhurst[3] make no mention of a solid phase. Jarl Enckell[4] has determined, for the temperature range 40 to 90°, the solubility of sulfur dioxide in solutions unsaturated with calcium sulfite.

The system $CaO-SO_2-H_2O$ is one of three components. By working at a constant temperature, such a system may be made univariant, in which case the existence of a single solid phase is indicated by a variation in the pressure and hence in the composition of the solution. For this investigation only those conditions under which at least three phases—gas, solid and solution—exist in equilibrium were of interest and the isotherms at 15 and 25° were determined. The composition of the solid phase was found by extrapolation, using a modification of the residue method of Schreinemakers.[5]

II. The Experimental Part

1. Materials Used.—The calcium oxide was prepared by igniting "C. P. Analyzed" calcium oxalate monohydrate to constant weight. Sulfates and magnesia were negligible.

The sulfur dioxide was of "refrigeration grade" manufactured by the Virginia Smelting Company. It was examined for sulfur trioxide by passing a stream through an acidified barium chloride solution which failed to show a precipitate of barium sulfate at the end of twenty minutes. From this test, and those of Eckman[6] who

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[1] This paper is based on a Dissertation presented by Frank H. Conrad in June, 1934, to the Faculty of the Graduate School of the University of Washington in candidacy for the degree of Doctor of Philosophy.

[2] Robert Schwarz and Hellmuth Müller-Clemm, *Z. angew. Chem.*, **34**, Aufsatzteil 272 (1921); *ibid.*, **34**, Aufsatzteil 599 (1921).

[3] Wm. Thompson Smith and Reginald B. Parkhurst, THIS JOURNAL, **44**, 1918 (1922).

[4] Jarl Enckell, *Der Papier-Fabrikant*, **23**, Tech.-wiss. Teil, 633 (1925).

[5] F. A. H. Schreinemakers, *Z. physik. Chem.*, **11**, 75 (1893).

[6] J. R. Eckman, Scientific Papers of the Bureau of Standards No. 554, 1927.