isomers are intermediate to those of the ortho and para compounds. It would seem therefore not at all unlikely that other factors of equal or greater importance are effective in determining the ease of reducibility of the *o*-, *m*- and *p*- isomers at a given electrode.

Summary

Electrolytic reduction experiments have been made on the *o*-, *m*- and *p*-tolyldiazonium chlorides with varying current densities and using cathodes of different metals. The ease of reduction does not seem to be related to the polar properties of the compounds, although a possible correlation may be obscured by other experimental factors.

Columbus, Ohio Received June 9, 1934

[Contribution from the Chemical Laboratory of the University of Texas]

The Adsorption of Methylamine on Silica Gel, Alumina Gel and Charcoal;[1] The Heats of Adsorption of Ammonia and the Methylamines on Silica Gel[2]

By W. A. Felsing and Carl T. Ashby

Object of the Investigation.—The object of this investigation was the determination of the extent of adsorption of monomethylamine on coconut charcoal at 0, 30 and 40°, and the determination of the heats of adsorption of ammonia and mono-, di- and trimethylamines on silica gel at 25 and 40°. This paper is a continuation of a study by Felsing and co-workers[3] of the properties and thermodynamic constants of monomethylamine with a view to the possible use of this substance as the refrigerant in the adsorption type of refrigerating unit. Di- and trimethylamine and ammonia are included in the heat measurements because they are possible refrigerants, and also because it was thought that the heats of adsorption of the members of this series would present an interesting comparison.

Previous Investigations.—Pearce and Knudson[4] have determined the extent of adsorption of monomethylamine on coconut charcoal, and Magnus and Kieffer[5] have determined the heat of adsorption of ammonia on silica gel. The literature records no other work than these on the adsorption of the methylamines.

Experimental

The apparatus and the method used in determining the isotherms were essentially those used by Foote and Dixon[6] in their determination of the extent of adsorption of water and benzene vapors by manganese dioxide. The apparatus and the method used in the heat of adsorption determinations were very similar to those of Pearce and McKinley,[7] the construction of the adsorption vessel being exactly the same. The reservoir system, however, consisted of two large round-bottomed flasks, one being arranged so that it could be filled with mercury when high pressures were desired in the adsorption vessel.

Thermocouple.—All temperature measurements were made with a twenty-four junction copper–constantan thermocouple constructed according to the specifications of Robertson and La Mer.[8] The thermocouple was calibrated differentially as it was used. The standard arm was placed in a Dewar flask containing oil at the temperature of the surrounding box, and the other arm in a Dewar flask containing oil, a Beckmann thermometer graduated in 0.002°, a heating coil and a stirrer. After the apparatus had stood for two hours, the oil in the latter flask was stirred until the temperature remained constant, the Beckmann was read, and the voltage of the thermocouple measured. The temperature of the oil was then raised about a degree and a half and the Beckmann reading and the voltage recorded again. In this manner the values 0.00104075°/v. at 25° and 0.00102015°/v. at 40° were obtained for (dT/dE). The temperature of the oil in the standard flask was checked by letting it stand with the Beckmann thermometer in it. After an interval of an hour and a half the temperature remained constant to within 0.001° for a period of twenty minutes, though usually the change was less than that.

The thermocouple voltage was measured by means of a volt box made of No. 28 copper wire which stepped up the voltage two hundred times, the total voltage of the volt box being measured with a Leeds and Northrup Type K potentiometer.

The method of determining the water equivalent of the calorimeter and the specific heat of the light colorless mineral oil used as the calorimeter fluid was that used by Pearce and McKinley.[7]

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(1) From a thesis presented by Carl T. Ashby to the faculty of The University of Texas in 1931 in partial fulfilment of the requirements for the degree of Master of Arts.

(2) From a thesis presented by Carl T. Ashby to the faculty of The University of Texas in 1934 in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

(3) Felsing and Thomas, *Ind. Eng. Chem.*, **21**, 1269 (1929): Felsing and Wohlford, This Journal, **54**, 1442 (1932); Felsing and Jessen, *ibid.*, **55**, 4418 (1933).

(4) Pearce and Knudson, *Proc. Iowa Acad. Sci.*, **34**, 197 (1927).

(5) Magnus and Kieffer, *Z. anorg. allgem. Chem.*, **179**, 215 (1929).

(6) Foote and Dixon, This Journal, **52**, 2170 (1930).

(7) Pearce and McKinley, *J. Phys. Chem.*, **32**, 360 (1927).

(8) Robertson and La Mer, *ibid.*, **35**, 1962 (1931).

Accuracy.—The temperature could be read to 0.001° and the water equivalent of the calorimeter system, including the oil, was 130 cal./°C.; hence the system should respond to a heat transfer of 0.13 cal. Since the average amount of heat liberated was about 50 cal., most of the measurements were accurate to 2.6 parts in 1000.

Materials.—The methylamine gases used in this investigation were generated by the action of 40% potassium hydroxide solution on their highly purified hydrochlorides. The ammonia was taken from a cylinder of pure anhydrous ammonia. The gases were dried by passing them through long tubes filled with potassium hydroxide pellets, and finally through a trap filled with glass wool, the trap being kept at −15°.

The charcoal was an activated coconut charcoal obtained from Eimer and Amend. The ash content of the charcoal as received was 1.95%. This was reduced to 0.15% by treatment according to the method of Hand and Shiels.[9] The alumina was obtained from the Aluminum Company of America, and the silica gel from the Silica Gel Corporation. All three adsorbents were degassed at 300° for about three hours before they were used for adsorption. The density[10] and percentage loss in weight on degassing were determined in order to correct for the amount of adsorbate remaining in the adsorption vessel as gas.

Results

The experimental data for the adsorption isotherms are given below in tabular form; Tables I to IX give the data for monomethylamine on the adsorbent named, the first column giving the equilibrium pressure in cm. of mercury and the second the number of cc. of monomethylamine at

Table I

Monomethylamine on Silica at 0°

P, cm.	Q, cc./g.
0.119	87.85
.448	98.46
.835	105.32
2.169	114.34
3.828	123.66
5.350	129.07
6.617	130.95
9.409	137.80
15.154	141.63

Table II

Monomethylamine on Silica at 30°

P, cm.	Q, cc./g.
0.080	58.98
.378	77.82
.826	84.31
1.951	92.04
3.502	98.99
5.980	105.54
8.286	111.60
10.940	115.50
13.897	118.82
18.764	123.22

Table III

Monomethylamine on Silica at 40°

P, cm.	Q, cc./g.
0.149	61.29
.438	70.09
1.214	79.91
3.492	90.31
6.240	97.74
8.178	100.05
13.902	105.83

Table IV

Monomethylamine on Charcoal at 0°

P, cm.	Q, cc./g.
0.349	45.48
.587	59.41
1.084	85.04
2.289	118.89
4.362	149.43
7.035	168.92
9.631	177.22

Table V

Monomethylamine on Charcoal at 30°

P, cm.	Q, cc./g.
0.149	14.15
.428	29.89
.727	40.57
1.274	58.69
3.166	90.81
6.059	119.25
7.732	131.45
11.044	145.75
13.911	154.84

Table VI

Monomethylamine on Charcoal at 40°

P, cm.	Q, cc./g.
0.109	7.80
.239	13.72
.488	21.87
.826	30.97
2.090	49.66
5.004	83.16
7.672	99.04
10.423	112.83
13.377	123.37

Table VII

Monomethylamine on Alumina at 0°

P, cm.	Q, cc./g.
0.070	8.52
.298	16.03
.697	17.90
1.742	19.78
4.636	22.02

Table VIII

Monomethylamine on Alumina at 30°

P, cm.	Q, cc./g.
0.189	11.69
.398	13.50
.816	15.16
1.393	16.46
3.762	19.06

Table IX

Monomethylamine on Alumina at 40°

P, cm..........	0.607	1.373	3.154	5.781
Q, cc./g........	11.84	13.79	16.53	18.77

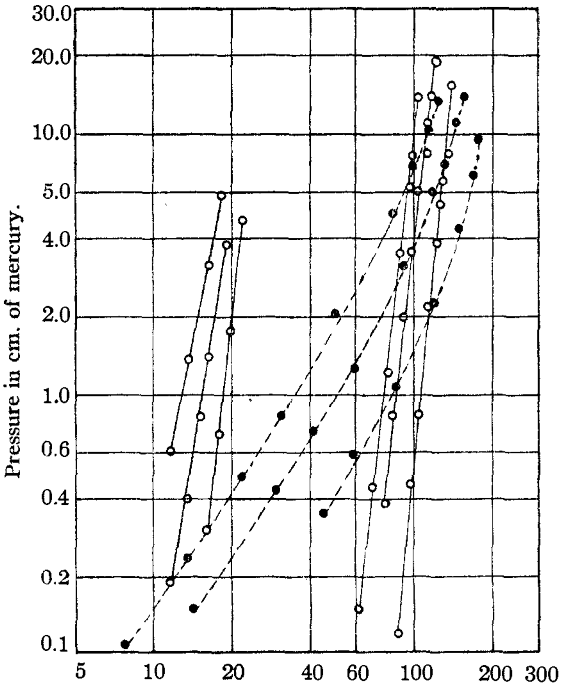

Fig. 1.—Isotherms of methylamine on coconut charcoal (broken curves); alumina (solid curves at left); silica gel (solid curves at right).

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(9) Hand and Shiels, *J. Phys. Chem.*, **32**, 452 (1928).

(10) Cude and Hulett, This Journal, **42**, 391 (1920).

N. T. P. adsorbed by one gram of 10–14 mesh adsorbent. In Fig. 1 the equilibrium pressures are plotted against the number of cc. adsorbed per gram of adsorbent on log–log paper. It is seen that alumina and silica gel give straight lines while the isotherms with charcoal are slightly concave to the pressure axis.

In place of the somewhat bulky experimental tables on the heat of adsorption the deviation chart of Fig. 2 is given. In the following discussion Q is the number of cc. of gas at N. T. P. adsorbed by one gram of gel and H is the number of calories evolved per gram of gel.

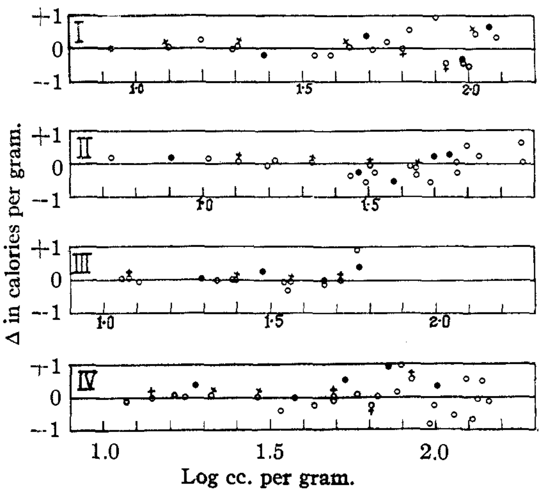

Fig. 2.—Deviation chart: I, methylamine; II, dimethylamine; III, trimethylamine; IV, ammonia; 10-14 mesh gel at 25°, ○; 20-30 mesh gel at 25°, ●; 10-14 mesh gel at 40°, ♀; $\Delta = H_{\text{calculated}}$ minus H_{observed}. $H_{\text{calculated}}$ was obtained by means of the equations:

$$\left.\begin{array}{l}(NH_3)\text{ at }25°\text{: } H = 0.9538Q^{0.9036}\\ (NH_3)\text{ at }40°\text{: } H = 0.9544Q^{0.9047}\end{array}\right\}\begin{array}{l}(\text{up to } Q = 78);\ H = 1.663Q^{0.7787}\\ \quad (Q > 78)\end{array}$$

$$\left.\begin{array}{l}CH_3NH_2\text{ at }25°\text{: } H = 1.100Q^{0.9258}\\ CH_3NH_2\text{ at }40°\text{: } H = 1.179Q^{0.9101}\end{array}\right\}\begin{array}{l}(\text{up to } Q = 80);\ H = 2.302Q^{0.7538}\\ \quad (Q > 80)\end{array}$$

$$\left.\begin{array}{l}(CH_3)_2NH\text{ at }25°\text{: } H = 1.065Q^{0.9539}\\ (CH_2)_3N\text{ at }25°\text{: } H = 1.176Q^{0.9188}\\ (CH_3)_3N\text{ at }40°\text{: } H = 1.232Q^{0.9037}\end{array}\right\}\begin{array}{l}(\text{up to } Q = 68);\ H = 2.286Q^{0.7700}\\ \quad (Q > 68)\end{array}$$

In Fig. 3 the log of cc./g: is plotted against the log of calories/g. The data were plotted to large scale and the equations given under Fig. 2 were determined from the curves. The curves are straight lines up to a certain point, then the slope changes and another straight line appears to result. A possible explanation of this change of slope is that the surface of the gel has become covered with a monomolecular layer of gas at this point. Using Langmuir's[11] method to calculate the area covered by one molecule of a gas, the area covered by the adsorbed gas at the point where the slope of a curve changes may be calculated. The results of such calculations are summarized in Table X.

TABLE X

AREA COVERED AT CHANGE OF SLOPE POINT OF CURVES

Gas	Q in cc./g. at change point	Area covered in sq. cm.
NH_3	78	2.7×10^6
CH_3NH_2	80	4×10^6
$(CH_3)_2NH$	68	4×10^6
$(CH_3)_3N$	76	3.2×10^6

Bartell and Ying Fu,[12] by a method based on the heat of wetting, found the specific area of silica gel to be 4.5×10^6 sq. cm./g. This is in fairly good agreement with the values given in Table X.

In order to compare the heats of adsorption of the gases investigated we have calculated by the method of Lamb and Coolidge[13] the molecular heats of adsorption, that is, the amount of heat, in kilogram calories, that would be evolved when one gram mole of the gas is adsorbed by 500 g. of silica gel. The values of H_m thus calculated are in the increasing order: ammonia, monomethylamine, trimethylamine and dimethylamine. Other constants of these gases are in this order as shown by Table XI.

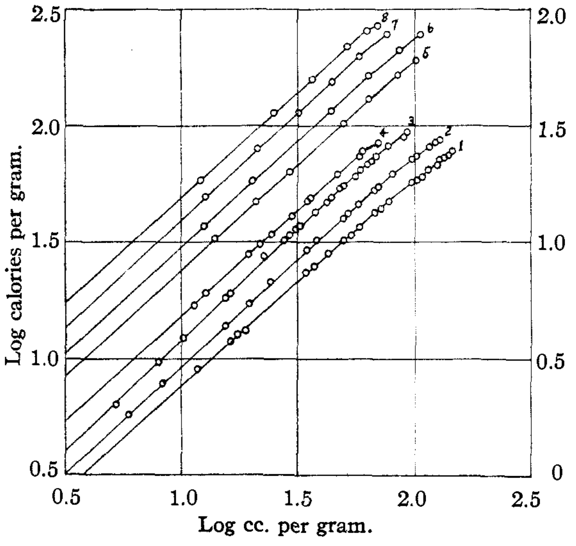

Fig. 3.—Heats of adsorption of ammonia and the methylamines on silica gel: Curves 1, 2, 3 and 4 at 25°, use left-hand scale; Curves 5, 6, 7 and 8 at 40°, use right-hand scale. Curves 1 and 5, ammonia; Curves 2 and 6, monomethylamine; Curves 3 and 7, dimethylamine, displaced upward 0.1 unit; Curves 4 and 8, trimethylamine, displaced upward 0.2 unit.

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[11] Langmuir, THIS JOURNAL, **40**, 136 (1918).

[12] Bartell and Ying Fu, "Colloid Symposium Annual," 1927, Vol. I, p. 135.

[13] Lamb and Coolidge, THIS JOURNAL, **42**, 1146 (1920).

TABLE XI

PHYSICAL CONSTANTS AND MOLAL HEATS OF ADSORPTION OF AMMONIA AND THE METHYLAMINES

Gas	T, °C.	C_p/C_v	B. p. in °K. at 1 atm.	H_m at 25°, kg.-cal.	H_m at 40°, kg.-cal.
NH_3	132.4	1.317	234.6	14.8	14.9
CH_3NH_2	156.9	1.202	266.4	18.7	18.8
$(CH_3)_3N$	161.0	1.184	276.6	19.0	19.1
$(CH_3)_2NH$	164.6	1.149	280.3	20.1	20.0

Table XI shows that H_m for these gases does not change to any great extent with temperature over the range investigated.

Relation of Heat of Adsorption to Mesh Size and Previous History of Adsorbent.—The points obtained using 20–30 mesh silica gel fall on the curves obtained when 10–14 mesh gel was used. The previous use of the gel as an adsorbent for the gases investigated had no effect on the heat of adsorption provided the gel was degassed at 300° before it was used.

Summary

1. The adsorption isotherms of methylamine on alumina gel, silica gel and activated coconut charcoal have been determined at 0, 30 and 40°.
2. The heats of adsorption of ammonia, methylamine, dimethylamine and trimethylamine on silica gel at 25 and 40° have been determined.
3. It has been shown that the heat of adsorption does not change with mesh size nor the previous use of the gel as an adsorbent provided it is degassed at 300°.
4. It has been shown that the heat of adsorption does not change with temperature over the range investigated.
5. The heats of adsorption of these gases have been shown to be definite and reproducible.

AUSTIN, TEXAS RECEIVED JUNE 18, 1934

[CONTRIBUTION FROM THE RANDAL MORGAN LABORATORY OF PHYSICS, UNIVERSITY OF PENNSYLVANIA]

Specific Heat, Entropy and Free Energy of Gaseous Nitric Oxide Computed from the Spectroscopic Data

BY ENOS E. WITMER

In 1927 the writer[1] computed the specific heat of nitric oxide from the spectroscopic data of Jenkins, Barton and Mulliken[2] from 1 to 500°K. This was regarded as being of special interest because nitric oxide has a doublet normal level. Recently the entropy and the free energy were computed from the values of the partition sum and its derivatives (the P_1, P_2, P_3 used below) used in the computation of the specific heat. In the meantime, Johnston and Chapman[3] have published calculations of the thermodynamic properties of nitric oxide from the spectroscopic data. They, however, misinterpreted the data of Jenkins, Barton and Mulliken in regard to the value of the doublet separation of the $^2\Pi_{1/2}$ and $^2\Pi_{3/2}$ states. Jenkins, Barton and Mulliken state on p. 171 of their article that the doublet separation is 124.4 cm.$^{-1}$. According to their footnote 38 this value was calculated from the figure 120.9 cm.$^{-1}$ obtained from Miss Guillery's[4] data (p. 144 of her paper) by adding on $9/4\ B''_2 - 1/4\ B''_1$ in the notation of Jenkins, Barton and Mulliken.

In order to understand the nature of the error made by Johnston and Chapman, it is necessary to write down the formulas for the energy levels of the two Π states which constitute the normal level of the nitric oxide molecule.

For the $^2\Pi_{1/2}$ state, the energy levels in cm.$^{-1}$ are

$$\begin{aligned}F'_1(v,J) = {} & (1.6754 - 0.01783v \pm 0.0011)(J + 1/2)^2 + \\ & (0.106 \pm 0.064)10^{-3}(J + 1/2)^3 - \\ & (0.506 \pm 0.137)10^{-5}(J + 1/2)^4 + \\ & 1892.119v - 14.4243v^2 + 0.04021v^3 - \\ & 0.001351v^4\end{aligned} \tag{1}$$

Here J takes on the values $^1/_2$, $^3/_2$, . . . etc.

For the $^2\Pi_{3/2}$ state, we have

$$\begin{aligned}F'_2(v,J) = {} & (1.7239 - 0.01866v \pm 0.0015)(J + 1/2)^2 \\ & + (0.010 \pm 0.069)10^{-3}\ (J + 1/2)^3 - \\ & (0.871 \pm 0.135)10^{-5}\ (J + 1/2)^4 + \\ & 120.9 + 1891.976v - 14.4543v^2 + 0.04229v^3 \\ & - 0.001423v^4\end{aligned} \tag{2}$$

Here J takes on the values 3/2, 5/2, . . . etc. The ± signs in the coefficients of the powers of $(J + 1/2)$ indicate the probable error. The

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(1) E. E. Witmer, *Phys. Rev.*, **29**, 918 (1927). The complete results for the specific heat were presented at a meeting of a section of the German Physical Society held in Goettingen in the winter of 1927–1928.

(2) F. A. Jenkins, H. A. Barton and R. S. Mulliken, *ibid.*, **30**, 150 (1927).

(3) H. L. Johnston and A. T. Chapman, THIS JOURNAL, **55**, 153 (1933).

(4) M. Guillery, *Z. Physik*, **42**, 121 (1927).