

### Summary

1. General methods of establishing the thermodynamic scale of temperature to  $-193^{\circ}$  by means of platinum-resistance thermometers as proposed by Henning are discussed.

2. An experimental method is outlined which will enable us to decide between the results of Henning and those of Keyes, Townshend and Young regarding the validity of the proposed methods of calibration.

3. Our results using the flat-coil calorimetric type of platinum-resistance thermometer entirely corroborate those of Henning and of Van Dusen for the strain-free type of thermometer.

4. It is concluded that Henning's proposed methods of establishing the thermodynamic scale of temperature in terms of platinum-resistance thermometers, using thermometers of pure platinum and entirely strain-free, are entirely valid and reproducible.

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## INFRA-RED ABSORPTION SPECTRA. SOLUTIONS OF NITROGEN PENTOXIDE AND NITROGEN TETROXIDE IN ORGANIC LIQUIDS

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This investigation was undertaken originally, for the purpose of testing relations between reaction velocity and absorption spectra predicted on the basis of the "radiation hypothesis."<sup>1</sup> The unimolecular decomposition of nitrogen pentoxide in the gas phase and in various solvents has been measured,<sup>2</sup> and it seemed important to ascertain whether a change in the temperature coefficient of reaction rate is accompanied by a shift in the position of the significant absorption band, in agreement with this hypothesis. Confirmation of such a shift has been reported in the decomposition of triethylsulfonium bromide in solutions.<sup>3</sup>

Of more interest, however, than the testing of this hypothesis has been the study of the relationship between near infra-red absorption spectra and the structure of molecules. Furthermore, the study of solutions is rather new in the field of infra-red spectroscopy and nitrogen pentoxide and tetroxide with their distinctive spectra and high solubility offered unusually good systems for generalization.

<sup>1</sup> A good statement of this hypothesis may be found in papers by Perrin and by W. C. McC. Lewis, *Trans. Faraday Soc.*, **17**, 500, 550 (1922).

<sup>2</sup> (a) Daniels and Johnston, *THIS JOURNAL*, **43**, 53 (1921). (b) Lueck, *ibid.*, **44**, 757 (1922). (c) Forthcoming publication.

<sup>3</sup> Taylor and Lewis, *J. Chem. Soc.*, **121**, 665 (1922).

### Experimental Procedure

The spectrometer, made in part by Schmidt and Haensch was very kindly loaned by the Department of Physics of the University of Wisconsin. A Nernst lamp glower, shielded from air currents, was operated on a storage battery at 110 volts and 0.8 ampere. Fluctuations in current were balanced by hand regulation of a rheostat. The 60° prism of rock salt had faces of 20 sq. cm. The thermopile of five junctions was connected with a Leeds and Northrup galvanometer which gave a deflection of 15 mm. per microvolt with a period of five seconds. The transparent scale located in front of the operator was easily adjusted to give frequent zero settings. The operation was simple and rapid and the results were reproducible, but the precision was not great.

Absorption cells were made of clear plates of rock salt which had been sawed from a large crystal and polished by the Brashear method with water and rouge on a flat surface of rosin and Venetian turpentine. The final polishing was accomplished by rubbing with a smear of rouge on flat chamois skin, a procedure which resulted in a considerable saving of time. The problem of cementing the plates was a difficult one, since the rock salt could not be heated and the cement had to withstand nitrogen oxides and organic solvents. Nothing better was found than LePage's fish glue, suggested by Coblenz.<sup>4</sup> For gases the plates were glued to the ends of a glass tube about 80 mm. long, provided with inlet and outlet stopcocks. For thin layers of liquids the two plates were separated by a nearly closed circle of platinum wire, 0.4 mm. in diameter. The evaporation from this cell was objectionable. Most of the determinations were made with the cell shown in Fig. 1, which was made by cutting in two a glass plate 1.5 mm. thick, through which a hole 30 mm. in diameter had been bored. The two halves were glued together with cross pieces so as to leave square, vertical channels. Small, bent capillaries were inserted and the rock-salt plates glued to the front and back, so as to cover the hole.

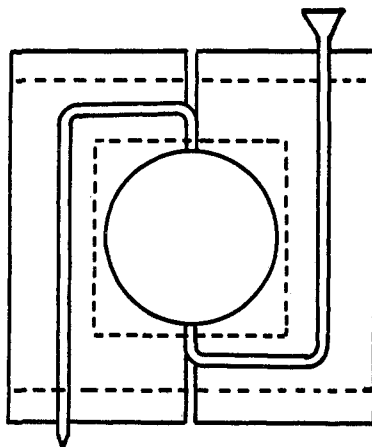


Fig. 1.

In order to prevent fogging, the glue was allowed to dry, partially, before the plates were attached and the cell was not touched with the warm fingers.

It was impossible to avoid slight action of the nitrogen oxides on the glue, and the action doubtless resulted in the formation of traces of nitric acid. No difficulty resulted from this action as far as absorption spectra were concerned, but the rock-salt windows became etched. It was necessary after the examination of every solution to split off the plates, repolish them and rebuild the cell.

The nitrogen pentoxide was prepared in a manner described before.<sup>5</sup> The nitrogen peroxide was obtained by heating lead nitrate, drying the gas with phosphorus pentoxide and condensing it in a tube surrounded by ice and salt. The organic solvents were carefully purified and distilled within 0.1° or less just before using. The same solvents were used in a previous research and their purification has been described.<sup>2b,2c</sup> A high state of purity is not so essential when thin absorption cells are used. Thick cells (several

<sup>4</sup> Coblenz, "Investigation of Infra Red Spectra. I," 41, *Carnegie Inst. Publ.*, 1905.

<sup>5</sup> Daniels and Bright, *THIS JOURNAL*, 42, 1133 (1920).

millimeters), however, contain so much material that even traces of impurities cannot be tolerated.

The spectrometer readings were converted into wave lengths by the method of Langley<sup>6</sup> using the principle of minimum deviation and the setting with sodium light. The deviations of light of different wave lengths were taken from Paaschen's work.<sup>7</sup>

The calibration of the spectrometer scale in wave lengths was checked with the emission band of the Bunsen burner at  $4.40\mu$ , and with absorption maxima of carbon tetrachloride at  $6.45\mu$ , carbon disulfide at  $4.6\mu$  and the different bands of chloroform. The correct setting of the spectrometer was assured in each experiment by determining the galvanometer deflections in the region of  $4.29$  and  $2.75\mu$ , with the empty cell. The carbon dioxide of the air was sufficient to register a sharp minimum in the deflection at these points. If the setting did not agree with the calibration, the thermopile slit was moved until it did agree. In this way the spectrometer readings were always convertible directly into wave lengths by reference to a single table.

In carrying out the experiments the spectrometer was moved each time so as to give exact settings, every  $0.05\mu$ . One series was made with the empty cell, a second with the solvent and a third with the solution, the galvanometer deflections at each  $0.05\mu$  being recorded in successive columns. When an absorption maximum was suspected, deflections were taken at fractions of the  $0.05\mu$ . Dividing the figures of the second column by those of the first with a slide rule gave the percentage transmission of the solvent. This transmission was plotted directly, each division along the abscissa corresponding to  $0.05\mu$ . Dividing the figures of the third column by those of the second gave the percentage transmission of the solute, with certain reservations to be discussed later.

In some cases the light intensity was greater with the liquid than with the empty cell and the percentage transmission was greater than 100%. The empty cell reflected light internally, especially when the plates were somewhat fogged from moisture, and when the plates were wet with the liquid this reflection was diminished. In plotting the curves any transmission greater than 100% was indicated by a location just above the 100% ordinate. The error amounted to about 10% of the deflections and the absorption curves may be incorrect to this extent. The experiments showed that the effect was practically independent of the wave length and no error was introduced in the location of the absorption maxima nor in the general conclusions.<sup>8</sup>

<sup>6</sup> Langley, *Phil. Mag.*, 17, 194 (1884). Kayser, "Handbuch der Spektroskopie," S. Hirzel, Leipzig, 1900, vol. 1, p. 752.

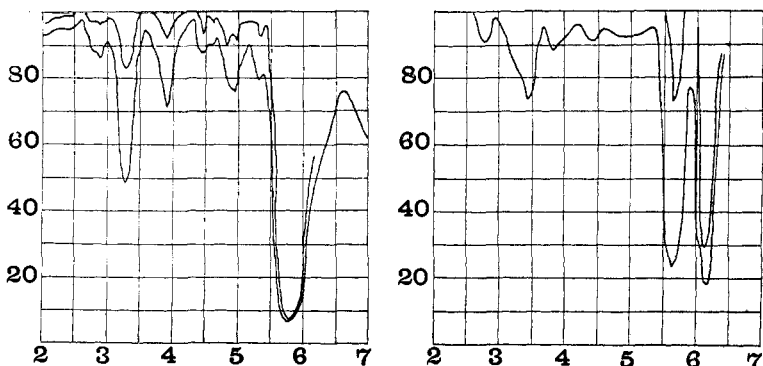
<sup>7</sup> Paaschen, *Ann. Physik*, 4, 299 (1901).

<sup>8</sup> See H. A. Taylor's discussion of this error and its elimination. [Taylor, "Treatise on Physical Chemistry," D. Van Nostrand Co., New York, 1924, p. 1261.]

The slit width for most of the experiments was 0.1 mm., corresponding to an arc of one minute on the spectrometer table. At  $6\mu$  this corresponded to  $0.1\mu$  and at  $2\mu$  to  $0.15\mu$ . The correction for slit width<sup>9</sup> was not introduced because it made but a slight difference in the location of the maxima and because it tended to cancel out in a comparison of different solutions. Runge's correction is of doubtful value in absorption spectra because the spectra are discontinuous.<sup>10</sup>

### Experimental Results

Typical examples of the absorption spectra are shown in Figs. 2-11 in which the dotted lines represent the solvent and the full lines the nitrogen oxides. The positions of maximum absorption (that is, minimum



Infra-red absorption spectra of gases (8cm. cell). Abscissas, wave lengths in  $\mu$ ; ordinates, transmission in percentages.

Fig. 2.—Gaseous nitrogen pentoxide. Fig. 3.—Gaseous nitrogen tetroxide and nitrogen dioxide.  
Upper line, 51 mm. partial pressure; lower line, 279 mm. partial pressure.

transmission) are given in Tables I and II. Wherever possible, they are compared with the results of other investigators. Apparent differences in spectra may often be due to differences in cell thickness or concentration. Since the position of maximum absorption appears in many cases to change, with the concentration, sometimes by as much as  $0.1\mu$ , and since the absorption spectrum of the solvent may give rise to complications in the spectrum of the solute, considerable care is necessary in arriving at the true position of a band. The tables were made after a critical survey of more than 100 detailed graphs.

It was necessary to examine solutions of different concentrations. For example, a solution which was sufficiently concentrated to show the band at  $4.8\mu$  was so concentrated that the  $5.8$  band was too wide to give a fair estimate of its true position; a solution sufficiently dilute to give a narrow

<sup>9</sup> Runge and Paaschen, *Ann. Physik*, **60**, 712 (1897).

<sup>10</sup> Kemble, *Phys. Rev.*, **8**, 699 (1916).

TABLE I  
 SUMMARY OF ABSORPTION MAXIMA IN ORGANIC LIQUIDS

Solvent	Wave lengths, $\mu$							
Carbon tetrachloride.....	..	..	..	..	..	..	..	6.50
“ “ (Coblentz) ..	..	..	..	..	..	..	..	6.50
Chloroform.....	2.35	2.70	3.30	4.15	..	..	..	6.60
“ (Coblentz) ..	2.38	2.75	3.33	3.80	4.40	5.60	5.90	6.80
Tetrachloro-ethane.....	2.30	2.65	3.25	4.10	4.85	5.45	..	6.15
Dichloro-ethane.....	2.35	2.70	3.35	..	..	5.35	5.90	—
Carbon disulfide.....	..	..	3.55	..	4.60	..	..	6.50
“ “ (Coblentz) ..	..	..	3.20	..	4.60	..	..	6.80
Nitromethane.....	2.25	2.75	3.40	3.95	4.95	5.35	5.80	—
“ “ (Coblentz) ..	2.26	2.65	3.41	4.10	5.09	..	5.80	6.35
<i>iso</i> Propyl bromide.....	2.30	..	3.40	4.30	4.85	5.25	5.7	—
Butyl ether.....	2.35	..	3.40	4.25	4.80	..	5.65	—

 TABLE II  
 ABSORPTION MAXIMA OF NITROGEN PENTOXIDE IN SOLUTION

Solvent	Wave lengths, $\mu$							
Gas phase.....	..	2.90	3.30	3.90	4.30	4.90	5.80	
“ “ (Warburg and Leithauser) ..	2.82	2.91	3.39	3.89	4.29	4.83	5.81	
Carbon tetrachloride.....	..	2.85	3.30	3.80	4.30	4.90	5.80	
Chloroform.....	..	2.95	..	..	..	..	5.75	
Tetrachloro-ethane.....	..	2.85	..	..	..	..	5.85	
Dichloro-ethane.....	..	..	..	..	..	..	5.85	
Carbon disulfide.....	..	2.85	3.25	3.80	4.35	4.90	5.75	
Nitromethane.....	..	2.85	..	..	..	..	5.75	
<i>iso</i> Propyl bromide.....	..	2.90	3.25	..	4.35	..	5.75	
Butyl ether.....	..	2.90	3.30	..	..	..	5.85	

band at  $5.8\mu$  did not show absorption at  $4.8\mu$ . The correct position was taken as the maximum in the most dilute solution which registered the band with certainty. When these precautions were taken it became evident that the absorption bands of nitrogen pentoxide are not shifted by the process of solution. Uncertainties amounting to as much as  $0.05\mu$  may be attributed to concentration effects.

A shift with a change in the quantity of absorbing material has been observed before. For example, Ellis<sup>11</sup> noted a tendency for an absorption maximum to be displaced toward a longer wave length when a thicker cell was used. To test further the influence of concentration on the position of absorption bands, chloroform was dissolved in carbon tetrachloride to give 10, 50, 90 and 100% chloroform, but the positions of the transmission minima from 2 to  $4\mu$  were identical in all cases within the limit of accuracy of the measurements ( $0.02$  to  $0.03\mu$ ). A full interpretation of the shift with changes of concentration cannot be given on the basis of the data which are available at present.<sup>12</sup> It is possible that the

<sup>11</sup> Ellis, *Phys. Rev.*, **23**, 48 (1924).

<sup>12</sup> See also Bonino, *Gazz. chim. ital.*, **53**, 555, 591 (1923).

shift may be due to the presence of smaller independent absorption bands which are too narrow to be resolved. In case the slit is too wide a shift is to be expected unless the absorption band is symmetrical.

No difficulty was experienced from temperature changes, although Lewis and Taylor<sup>13</sup> found that temperature had a considerable influence on the position of a transmission minimum, under the conditions of their experiments.

In the cases of the distinctive bands at 2.9 and 5.8 $\mu$ , and the band of nitrogen tetroxide at 5.7 to 5.3 $\mu$ , special care was taken to measure ac-

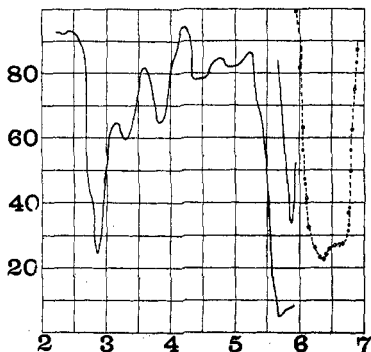


Fig. 4.—Carbon tetrachloride.

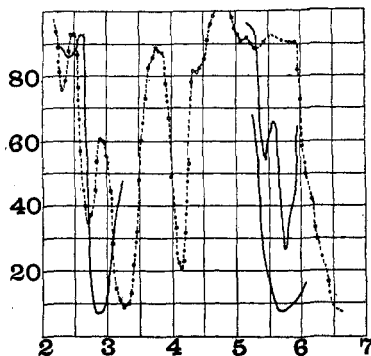


Fig. 5.—Chloroform.

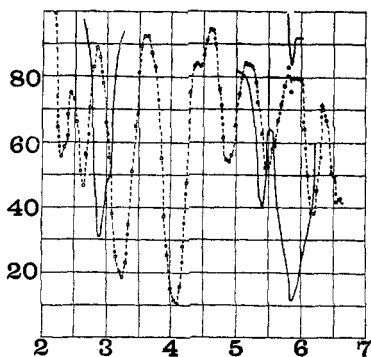


Fig. 6.—Tetrachloro-ethane.

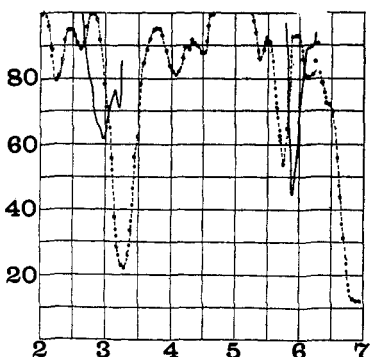


Fig. 7.—Dichloro-ethane.

Figs. 4-7.—Infra-red absorption spectra of solutions of  $N_2O_5$ . Abscissas, wave lengths in  $\mu$ ; ordinates, transmission in percentages; full lines, nitrogen pentoxide; dotted lines, solvent.

curately any shifts. With this end in view a series of determinations in a limited region was made without changing the prism or cell, merely changing the solutions in quick succession.

The method of representing the absorption of the solute by dividing the thermopile readings of the solution by those of the solvent is not adequate. It is correct only when the cell thickness is changed in such a way as to

<sup>13</sup> Ref. 3, p. 667.

include the same number of molecules of solvent in the path of the light in the two cases. This procedure has not been followed in the past and care was necessary in the interpretation of false absorption bands. If the solvent shows a region of greater transparency, and a somewhat opaque solute replaces part of the solvent the ratio of transmission of the solution to that of the solvent will be low not because of low transmission of the solute in this region but because of high transparency of the solvent.

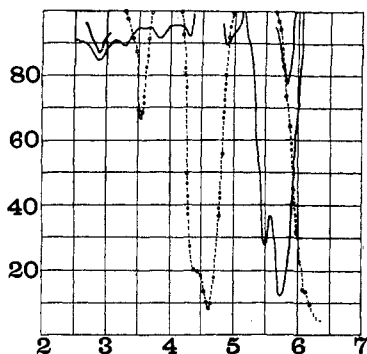


Fig. 8.—Carbon disulfide.

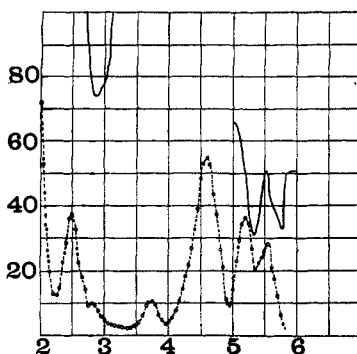


Fig. 9.—Nitromethane.

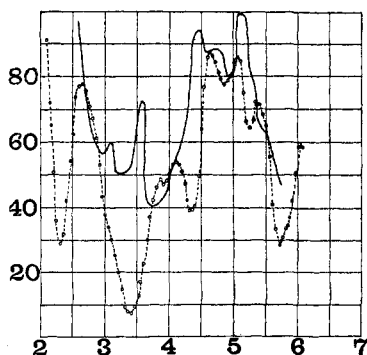
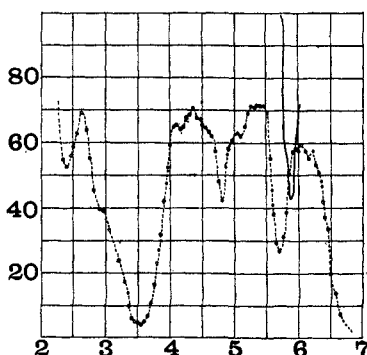
Fig. 10.—*iso*-Propyl-bromide.

Fig. 11.—Butyl ether.

Figs. 8-11.—Infra-red absorption spectra of solutions of  $N_2O_5$ . Abscissas, wave lengths in  $\mu$ ; ordinates, transmission, in percentages; full lines, nitro-pentoxide; dotted lines, solvent.

In the same way, false transmission peaks in the solute are apt to occur at positions corresponding to transmission troughs in the solvent. Where the absorption bands of the solvent happen to overlap those of the solute the exact position of the latter cannot be determined with certainty. It is for this reason that certain bands of the solute are left out of the graphs and tables. Although this method of representing absorption spectra is unsatisfactory, it appears to be the best available, with absorption cells of fixed thickness.

TABLE III  
ABSORPTION MAXIMA OF NITROGEN TETROXIDE IN SOLUTION

	Wave lengths, $\mu$				Wave lengths, $\mu$	
	NO <sub>2</sub>	N <sub>2</sub> O <sub>4</sub>	NO <sub>2</sub>		NO <sub>2</sub>	N <sub>2</sub> O <sub>4</sub>
Gas phase	3.40	5.65	6.15	Tetrachloro-ethane...	3.40	..
(Warburg and Leithäuser)	3.43	5.70	6.12	Dichloro-ethane.....	3.40	5.35
(E. von Bahr)	..	5.70	6.10	Carbon disulfide.....	..	5.45
Solvents				Nitromethane.....	..	5.30
Carbon tetrachloride.....	3.40	5.45	6.2	<i>iso</i> Propyl bromide...	..	5.45
Chloroform.....	3.35	5.40	..	Butyl ether.....	..	5.40

The absorption spectra of the nitrogen tetroxide and dioxide are shown in Table III and typical graphs given in Fig. 3, and as an impurity in some of the nitrogen pentoxide spectra. The fact that the  $5.65\mu$  band is deepened much more than the others by an increase in pressure (Fig. 3) shows that it belongs to the nitrogen tetroxide and that the 3.4 and 6.1 bands belong to the nitrogen dioxide. This conclusion agrees with observations at low temperatures.<sup>14</sup> The fact that the  $5.65\mu$  band is much more prominent in solution shows that the equilibrium is shifted toward nitrogen tetroxide in solution.

Cundall<sup>15</sup> has determined quantitatively the equilibrium constants in solution by measuring the fading of the brown color (nitrogen dioxide). The most striking observation, however, is an unmistakable shift in this band from  $5.65$  in the gas phase to values between  $5.35$  and  $5.45\mu$  in solution.

A further check was made on the shift of nitrogen tetroxide in solution, after several improvements had been made in the spectrometer. The gas cell, filled with nitrogen tetroxide and dioxide, showed absorption at  $5.7\mu$ . Without changing the spectrometer some of the gas was bubbled through carbon tetrachloride in a thin cell. The absorption maximum, which was less intense than before, was at  $5.55\mu$ . When more nitrogen tetroxide was bubbled through the cell the absorption became more intense than in the gas phase, but the maximum remained exactly at  $5.55\mu$ .

In comparing the various spectra it must be remembered that the nitrogen pentoxide may be contaminated by its decomposition products, nitrogen tetroxide and nitrogen dioxide. The extent of this decomposition varies with the age of the solution and its temperature. It results in a deepening of the band at  $3.30$ , where both nitrogen dioxide and pentoxide have bands, and in the formation of a band at  $5.4\mu$  in solution or at  $5.65\mu$  in the gas. At very high concentrations the latter band may merge with the  $5.8$  band of nitrogen pentoxide and give an apparent displacement toward the shorter wave length. Also the nitrogen tetroxide may combine with moisture to give a trace of nitric acid which is sufficient to cause absorption at the intense band of nitrogen pentoxide at  $5.8\mu$ .

<sup>14</sup> Warburg and Leithäuser, *Ann. Physik*, **28**, 315 (1909).

<sup>15</sup> Cundall, *J. Chem. Soc.*, **59**, 1076 (1891); **67**, 794 (1895).



### The Radiation Hypothesis

According to the radiation hypothesis the temperature coefficient of reaction velocity should permit a calculation of the effective radiation which is supposed to bring about the reaction. From the experiments on the decomposition rates of gaseous nitrogen pentoxide it has been calculated that the significant absorption band should lie at  $1.16\mu$ , and it has been pointed out that although there is no absorption in this region, there is absorption at  $3.3$  and  $5.8\mu$ , which are multiples of the  $1.16$  band.<sup>16</sup> If these bands are really significant they should show a shift in the solvents which give different temperature coefficients of decomposition. The theoretical absorption bands and their multiples<sup>2b</sup> are compared with the actually determined values in Table IV. There is no evidence of a shift of any of the nitrogen pentoxide bands in any of the solvents. It is true that the absolute precision of the spectrometer was not high and that concentration changes affect the position of the absorption maxima, but it is believed that a shift of  $0.05\mu$  could have been detected with certainty.

TABLE IV  
COMPARISON OF ACTUAL ABSORPTION BANDS OF NITROGEN PENTOXIDE WITH  
CALCULATED VALUES

Solvent	Critical increment, calcd. <sup>2b,10</sup> $\bar{\nu}$	Absorption bands of $N_2O_5$ —Calcd.—		
		1	3	5
<i>iso</i> Propyl bromide.....	26,500	$1.07\mu$	$3.21\mu$	$5.35\mu$
Carbon disulfide.....	26,400	1.08	3.24	5.40
Carbon tetrachloride.....	25,470	1.12	3.36	5.60
Tetrachloro-ethane.....	25,150	1.14	3.42	5.70
Gas phase.....	24,700	1.16	3.48	5.80
Chloroform.....	24,450	1.17	3.52	5.85
Nitromethane.....	24,200	1.18	3.54	5.90
		—————Observed—————		
All solvents		$3.30 \pm 0.05$	$5.80 \pm 0.05$	

The shift in the nitrogen tetroxide band from  $5.65$  to  $5.45$  or  $5.3\mu$  may possibly prove to be in accord with the radiation hypothesis, but unfortunately the decomposition of nitrogen tetroxide into nitrogen dioxide is so rapid that nothing is known of its rate. According to this hypothesis it would be predicted that the temperature coefficient of decomposition would be greatest in the solvents in which the absorption band is shifted farthest to the shorter wave lengths. If the nitrogen dioxide bands were unchanged it might follow also that in these liquids the temperature coefficient of the change in equilibrium toward nitrogen dioxide would be greatest.

### The Chemical Significance of Infra-red Absorption Bands

Since the near infra-red bands are tracks left by the atomic nuclei as they are displaced within the molecule, their examination should lead ultimately

<sup>16</sup> Ref. 2 a, p. 79. Ref. 1, p. 585.

to an increased knowledge of molecular structure and hence to a prediction of chemical and physical properties.

Twenty years ago, Coblenz<sup>4</sup> wrote, "there is something, call it 'particle,' group of 'atoms,' 'ion' or 'nucleus' in common with many of the compounds studied which causes absorption bands that are characteristic of the great groups of organic compounds, but we do not know what that 'something' is."

It is possible now to interpret this "something," with the help of G. N. Lewis' conception of the electron pair,<sup>17</sup> according to which the positive and negative character of the molecule is determined by the relative position of the electron pair between the atoms. This position of the electron pair determines also the extent to which the atomic nuclei may be displaced, relative to each other, and determines, therefore, the infra-red absorption. It should be possible eventually to connect molecular structure and polarity with absorption spectra in the near infra-red.

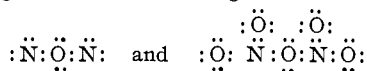
A few examples will serve to emphasize this relation.

The diatomic elements, such as hydrogen, oxygen and nitrogen, have no absorption bands in the near infra-red, and they are classed as non-polar. The molecule must be perfectly symmetrical, the atoms being alike and at equal distances from the electron pair.

A similarity in the infra-red spectra of acetylene and hydrocyanic acid has been pointed out.<sup>18</sup> An examination of the molecular structures  $\text{H:C}::\text{N:}$  and  $\text{H:C}::\text{C:H}$  shows that such a similarity is to be expected.

The absorption bands of the various methyl derivatives are all alike, and the C:H linkage is found in each.

The spectrum of nitrous oxide<sup>19</sup> with bands at 2.9, 3.6, 3.9, 4.05 and 4.3 $\mu$  bears a close resemblance to the spectrum of nitrogen pentoxide. This fact is explainable in the light of the structure given these substances by Lewis.<sup>20</sup>



### Summary

1. Absorption spectra between 2 $\mu$  and 7 $\mu$  have been determined in the case of the following liquids: carbon tetrachloride, chloroform, dichloroethane, tetrachloro-ethane, carbon disulfide, nitromethane, *isopropyl* bromide, butyl ether.

2. The absorption spectrum of nitrogen pentoxide in each of these solvents has been determined. No shift of absorption maxima could be detected in the different solvents.

<sup>17</sup> Lewis, "Valence and the Structure of Atoms and Molecules," Chemical Catalog Co., New York, 1923, p. 79.

<sup>18</sup> Burmeister, *Verb. Deut. Phys. Geo.*, 15, 589 (1913).

<sup>19</sup> Ref. 14, p. 317.

<sup>20</sup> Ref. 17, p. 129.

3. These measurements fail to confirm the predictions of the radiation hypothesis.

4. The absorption spectrum of nitrogen tetroxide has been determined in each of these solvents. The absorption maximum of nitrogen tetroxide showed an appreciable shift from  $5.65\mu$  in the gas phase to  $5.45$ – $5.30\mu$  in solution.

5. Relations between molecular structure and infra-red absorption spectra have been interpreted in the light of the G. N. Lewis theory of valence, based on the electron pair.

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[CONTRIBUTION FROM THE GEOPHYSICAL LABORATORY, CARNEGIE INSTITUTION OF WASHINGTON AND THE FIXED NITROGEN RESEARCH LABORATORY, UNITED STATES DEPARTMENT OF AGRICULTURE]

## AN X-RAY EXAMINATION OF SOME AMMONIA CATALYSTS

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### Introduction

The study of a large number of heterogeneous catalytic reactions has brought to light many cases which show the extreme sensitivity of catalysts to the presence of relatively small concentrations of foreign materials. In some cases these foreign materials exert an inhibiting influence on the catalyst and are called "poisons;" in other cases, the added materials enhance the activity of the catalyst and are called "promoters."<sup>1</sup> The mechanism by which a promoter functions is one of the most interesting phases of catalytic action and has been the subject of much speculation. It seems highly improbable that a single explanation of promoter action, applicable to all cases, will ever be found; nevertheless, certain general suggestions have been made as to the function of promoters. These have attributed to a promoter such effects as the favorable adjustment and orientation of the adsorbed gaseous reactants, the rapid desorption of the reaction product, and the production and maintenance of a desirable physical structure.

For many catalysts, at least, the effect of the promoters on the physical structure is of primary importance. This type of effect is directly amenable to study by X-ray diffraction methods. These methods can give information regarding the atomic positions in solids, the probable limits of crystal size, and the existence of solid solutions. They can, however, yield no knowledge of the conditions existing at the surface where catalytic action undoubtedly takes place.

The extensive study of iron catalysts for ammonia synthesis at the

<sup>1</sup> See Pease and Taylor, *J. Phys. Chem.*, **24**, 241 (1920), for a review of the literature.