Infrared Spectral Evidence for Complex Formation between Ammonia and Halogen-Containing Compounds[1]

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Infrared spectra have been obtained for solutions of ammonia in a variety of solvents, primarily halogen-containing compounds, and in solutions of these materials in pentane. The frequency of the symmetric (ν_2) bending mode of ammonia is shown to be a useful index of association involving the nonbonding pair of electrons. Measurements of the frequency of this band show that ammonia forms complexes with a variety of halogen-containing compounds. Infrared spectral evidence, furthermore, indicates that such association is through the nonbonding electrons rather than through hydrogen bonds involving the N–H hydrogens. Such infrared spectral measurements of solutions of ammonia provide additional methods for the investigation of charge-transfer type interactions.

Introduction

Investigations of complex formation, such as in charge-transfer complexes or hydrogen-bonded complexes, involving amines generally depend on spectral measurements of electronic transitions involving the nonbonding pair of electrons of the nitrogen atom or on changes in the spectral properties, infrared or visible-ultraviolet, of the complexing agent.[2] Here it will be shown that the symmetric bending vibration of the ammonia molecule, for which the potential energy function of the free molecule is the double-minimum curve of Figure 1a, is sensitive to any involvement of the nonbonding electrons in complex formation and, therefore, that the frequency of this vibration can be used to investigate amine interactions that are not generally easily studied.

In the vapor phase, the ν_2 band is split by inversion doubling and exhibits two overlapping parallel bands separated from one another by 36 cm.$^{-1}$.[3] It is clear that association of ammonia molecules in the gas phase through the nonbonding pair of electrons would, if the lifetime of the complex were greater than vibrational frequencies, remove the equivalence of the two inversion positions and would be expected to remove, or greatly alter, the inversion doubling. Thus the ν_2 band shape and position should indicate any such association. In solution, even in a relatively inert solvent, as will be shown, the inversion splitting of this vibrational band is not observed. The potential function for the vibration will, however, still be relatively

easily altered by interactions and thus the frequency of the vibration will be sensitive to such interactions.

Here the use, in an analytical way, of this vibration and other spectral features of the ammonia molecule to study hydrogen bonding and a charge-transfer type of interaction will be presented.

Experimental

All spectra were obtained using double-beam operation with a Beckman IR-7 prism-grating spectrophotometer.

The sample cell was of a demountable type with rock salt windows, a Teflon spacer, and a stainless steel body. Solutions of ammonia under pressure in a variety of solvents, including mixed solvents, were obtained by filling a mixing compartment, which is attached to the cell by means of a stainless steel valve, first with the solvent and then with ammonia at a pressure of up to 80 p.s.i. Repeated filling of the mixing compartment with ammonia, shaking to attain equilibrium, and refilling with ammonia followed finally by admitting the solution to the cell gave solutions with enough ammonia to show appreciable absorptions in the regions studied, even with relatively thin cells. The concentrations of ammonia were, as a result of this procedure, unknown but, for the purposes of this study, such information is not required.

For the reference cell, a variable thickness cell was used. Since the effective thickness of the sample cell proved to be somewhat dependent on the pressure, this cell was adjusted to compensate for various absorptions due to the solvent or solvent mixture. The ammonia ν_2 band, at about 1000 cm.$^{-1}$, occurs, however, in a region where, with the solvents used here, many absorption bands occur, and the compensation is not in all cases reliable enough to reveal the shape of the entire absorption band.

The ammonia gas was Matheson anhydrous ammonia and was used without further purification. No evidence of interfering impurities were observed in the spectra.

The hydrocarbon solvents were dried over sodium wire and the carbon tetrachloride (spectrograde) was dried over P_2O_5. Spectrograde chloroform was washed with water and dried with Drierite immediately before use. Most of the other solvent materials, shown in Table I, were spectrograde and were used without treatment.

Results and Discussion

1. Band Shapes of NH_3 in Solution with Inert Solvents. It is now recognized[4] that the infrared absorp-

(1) This work was supported in part by a grant from the National Science Foundation.

(2) See, for example, H. Tsubomura, *J. Am. Chem. Soc.*, **82**, 40 (1960), and preceding papers of the series; C. Reid and R. S. Mulliken, *ibid.*, **76**, 3869 (1954), for charge-transfer studies; and G. C. Pimentel and A. L. McClellan, "The Hydrogen Bond," W. H. Freeman and Co., San Francisco, Calif., 1960, for hydrogen-bonding studies.

(3) G. Herzberg, "Infrared and Raman Spectra of Polyatomic Molecules," D. Van Nostrand Co., Inc., New York, N. Y., 1945, pp. 222, 257, 295.

(4) M. O. Bulanin and M. D. Orlava, *Opt. Spectry.* (USSR), 4, 569 (1958); J. Lascombe, P. Van Huong, and M. L. Josien, *Bull. soc. chim. France*, 1175 (1959); W. J. Jones and N. Sheppard, *Trans. Faraday Soc.*, **56**, 625 (1960); G. E. Ewing, *J. Chem. Phys.*, 37, 2250 (1962); M. O. Bulanin and M. V. Tonkov, *Opt. Spectry.* (USSR), 16, 234 (1964).
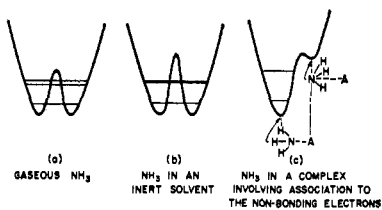
Figure 1. The potential energy diagrams (schematic) for the ν_2 symmetrical bending vibration of NH_3 in different systems.

Table I. The Positions (in cm.$^{-1}$) of the ν_2 Symmetric Bending Absorption Band of NH_3 Complexed with Various Compounds[a]

Complexing agent	$\bar{\nu}^a$	$\Delta\bar{\nu}_1{}^b$	$\bar{\nu}^c$	$\Delta\bar{\nu}_2{}^d$
Pentane	(961)	(0)	961	(0)
t-Butyl chloride	974	13	1005	31
CCl_4	980	19	996	16
CCl_3CH_3	982	21	1011	29
C_2H_5I	993	32	1010	17
CCl_3Br	994	33	1014	20
CBr_4	995	34	...	..
CH_2I_2	996	35	1030	34
CH_2Br_2	999	38	1033	34
CH_2Cl_2	999	38	1034	35
$CHBr_3$	1011	50	1036	25
$CHCl_3$	1013	52	1036	23
Pyridine	...[e]	..	1026	..
CH_3NO_2	...[f]	..	1040	..

[a] For the complex in pentane. [b] $\Delta\bar{\nu}_1 = \bar{\nu}$ (column 2) $-$ 961. [c] With complexing agent as solvent. [d] $\Delta\bar{\nu}_2 = \bar{\nu}$ (column 4) $-$ $\bar{\nu}$ (column 2). [e] No evidence from the ν_2 band of complex formation. [f] Insolubility of CH_3NO_2 in pentane prevented studies of complex formation.

Figure 2. The ν_2 band of ammonia dissolved in a variety of hydrocarbons (ammonia pressure 60 p.s.i., cell thickness 0.025 mm.).

tion bands of molecules with small moments of inertia tend to show, even in the case of solution spectra, a contour that has some of the features of the gas phase rotation–vibration band. For ammonia dissolved in an inert solvent, this implies the additional possibility of observing the inversion splitting which is part of the gas-phase band structure of the ν_2 band, and such a splitting has in fact been reported by Cannon[5] for ammonia in CCl_4. This result, obtained with ammonia at 1 atm. pressure, is, as Cannon recognized, unreliable because of the strong CCl_4 band that also occurs at the position (about 1000 cm.$^{-1}$) of the NH_3 band. Using ammonia at a higher pressure it is possible to obtain solution spectra not only in CCl_4, which will be shown to interact with NH_3, but also in the more inert hydrocarbon solvents and, as shown in Figure 2, no inversion doubling appears.

The absence of an observable inversion doubling for NH_3 in solution even though the equivalence of the two inversion positions is maintained, as must be the case in a noninteracting solvent, is readily accounted for by the dielectric effect of the medium. The two pyramidal forms of the molecule have dipole moments, whereas the planar form to which the maximum in the potential curve corresponds must have a zero dipole moment. The dielectric effect of the surrounding solvent will act to stabilize the polar forms relative to the nonpolar form,[6] and the result will be a potential

curve for this vibration of the molecule of the same double-minimum shape, shown in Figure 1b, but with a higher barrier to inversion.

Since appreciable energy-level splitting occurs only for energy levels that lie near the top of the barrier and a splitting of 10 or more cm.$^{-1}$ would be needed to be detected in solution spectra, no such splitting would be expected for NH_3 in solution.

Wide wings on the ν_2 band as reported by Cannon[5] do show up, however, and, although the detailed shape of the various absorption bands (shown in Figure 2 and as the top curves in Figures 5 and 7) are different, they all give evidence for the rotation of the NH_3 molecules in these solvents. In the investigations to be reported below on the nature of various complexes that are formed, it will be important to recognize that the shape of the symmetric vibrations ν_1 and ν_2, at 3320 and 961 cm.$^{-1}$ in pentane, are dependent on rotation of the molecule about the axes perpendicular to the figure axis of the molecule, whereas the degenerate modes ν_3 and ν_4, at 3400 and 1620 cm.$^{-1}$ in pentane, owe their contour primarily to rotation about the figure axis of the molecule.[7]

Finally, the possibility that there is sufficient self-association of ammonia in these systems to affect the spectra must be considered. The ν_2 bending band was investigated in various hydrocarbon solvents over an ammonia pressure range of 15 to 80 p.s.i. No change in the position of the band maximum or in the shape of the entire band was detected. Similar measurements were made on the N–H stretching region and, again, in inert solvents no evidence was obtained for association. (Here, it can also be mentioned that in chloroform evidence is obtained for self-association at the higher pressures. The results to be reported were therefore obtained for solvents such as chloroform in which ammonia is more soluble at lower pressures than those at which self-association is appreciable.)

2. Spectral Effect of Hydrogen Bond Formation to NH$_3$. The addition of NH_3 to solutions of compounds like $CHCl_3$ and $CHBr_3$ that enter into hydrogen bond formation with bases leads, as the spectra in the C–H stretching region of Figure 3 show, to such association.

(5) C. G. Cannon, *Spectrochim. Acta*, 10, 426 (1958).
(6) See, for example, C. J. F. Böttcher, "Theory of Electric Polarization," Elsevier Publishing Co., Inc., New York, N. Y., 1945, pp. 414–440.
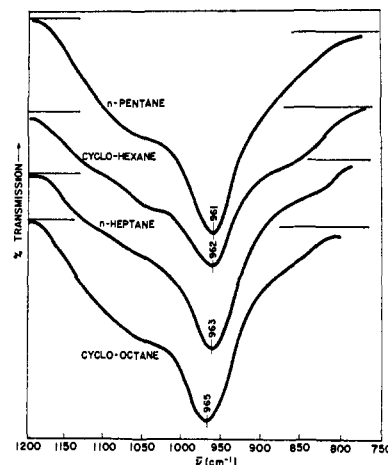(7) G. Herzberg, "Infrared and Raman Spectra of Polyatomic Molecules," D. Van Nostrand Co., Inc., New York, N. Y., 1945, pp. 414–440.

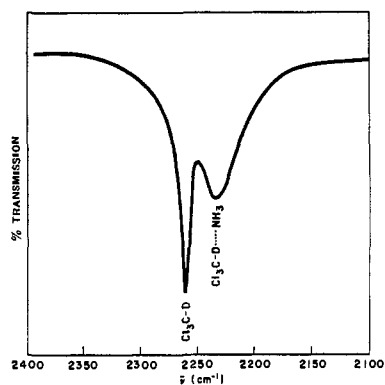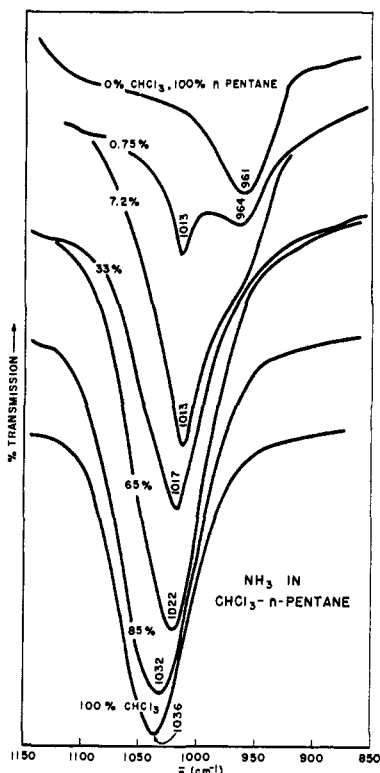Figure 3. The C–D absorption band of a solution of NH_3 in $CDCl_3$.

Figure 4. Absorption due to the v_2 symmetric bending mode of NH_3 in chloroform–pentane solutions. The spectra are identified by the mole per cent of chloroform. Pressures of ammonia ranging from 60 p.s.i. for the pure pentane solutions to atmospheric pressure for the pure chloroform solutions were used. The cell thickness was about 0.025 mm. throughout for the mixed solvent and 0.1 mm. for pure $CHCl_3$.

The frequency shifts of 26 cm.$^{-1}$ for the C–D stretching mode of $CDCl_3$ with ammonia is to be compared with the values of 77 cm.$^{-1}$ obtained for triethylamine.

The v_2 bending mode also reveals this association and some spectral evidence is given in Figure 4 for chloroform–pentane solutions. Similar results are obtained for $CHBr_3$ with the new band, due to the hydrogen-bonded complex, coming in at 1012 cm.$^{-1}$. Such results show that the frequency of the symmetric bending mode of ammonia can be used in much the same way as is, for example, the C–H frequency of $CHCl_3$ to investigate interactions. The NH_3 vibration has the advantage, as we will see, of allowing types of association to lone-pair sites other than by hydrogen bonding also to be studied.
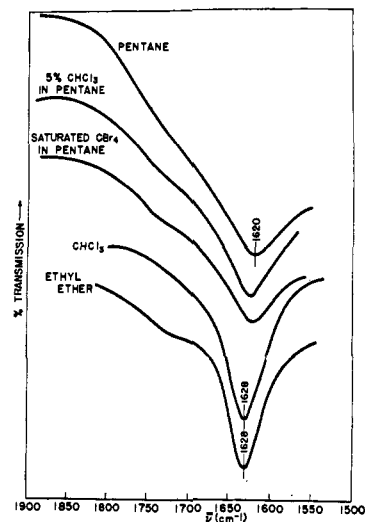

Figure 5. Absorption due to the degenerate bend mode v_4 of ammonia in different solvent systems. Ammonia pressures of about 50 p.s.i. and cell lengths from about 0.05 to 0.1 mm. were used. (The low-frequency side of the band is obscured by solvent absorption.)

The shift of the v_2 band to higher frequencies as a result of complex formation follows from a change in the potential energy function for the vibration from the symmetric double-minimum well to an asymmetric function with, as shown in Figure 1c, a single, narrower well which will have correspondingly wider spaced energy levels.

The other qualitative feature of the band due to the symmetric bending of the ammonia in the complex, the narrowness of the band compared to that due to the free ammonia, is also the reverse of the effect found in C–H or O–H stretching vibrations where the band due to the complexes is characterized by great width.

The removal by the association of the rotational freedom of the ammonia molecule about the axes perpendicular to the figure axis, which is responsible for some of the breadth of this band of free NH_3, can account for the sharpening up that accompanies the formation of the complex. By contrast, as Figure 5 shows, the absorption due to the degenerate bending mode v_4 at 1620 cm.$^{-1}$ shows no significant change in position or shape. It follows that the hydrogen-bonding association, as would be expected, does not interfere appreciably with rotation of the NH_3 molecule about its figure axis.

3. Complex Formation between NH_3 and Halogen-Containing Compounds. With the background provided by the hydrogen-bonding studies, the v_2 band can be used to investigate other interactions with lone-pair electrons. Results such as those obtained for CBr_4 and CCl_4, which are shown in Figure 6, were also obtained for the compounds listed in Table I.

The v_4 bending mode, as illustrated in Figure 5, for CBr_4 shows, as in the hydrogen-bonding cases, no significant change in position or shape. A similar lack of spectral change occurs in the N–H stretching region but there, as shown in Figure 7, the bands overlap seriously and their shapes are not easily recognized.

The appearance of a new, narrow, high-frequency band alongside the v_2 band of free ammonia, along with the other spectral features, is strong evidence for
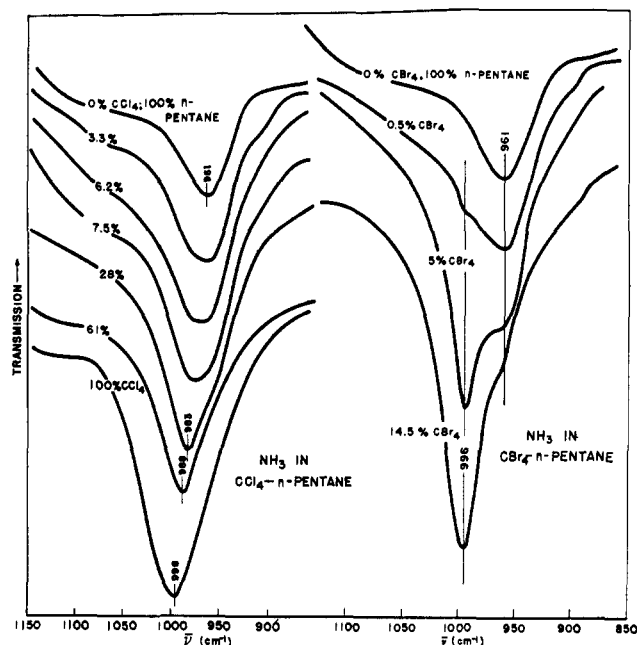
Figure 6. Absorption due to the ν_2 symmetric bending mode of NH_3 in CCl_4–C_5H_{12} and CBr_4–C_5H_{12} solutions. The spectra are identified by the mole per cent of CCl_4 or CBr_4. Ammonia pressures from 60 to 40 p.s.i. were used with cell lengths of 0.025 mm.
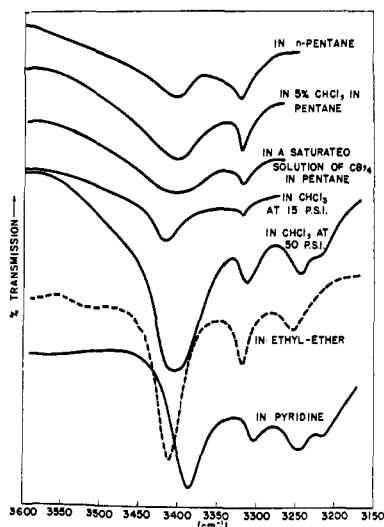

Figure 7. The N–H stretching region for NH_3 in a variety of solutions. (In the gas phase NH_3 has absorption bands centered at 3414 cm.$^{-1}$ due to the ν_3 degenerate stretching mode and at 3337 cm.$^{-1}$ due to the ν_1 symmetric stretching mode.) The lower three spectra show evidence of association through the N–H bond.

the formation of complexes that perturb the ammonia molecule in a way that is comparable to a hydrogen bond. The conclusion that such specific interaction occurs is strengthened by the spectral data for NH_3 in CCl_3Br–C_5H_{12} solutions. Although the new bands that develop badly overlap, it appears that two new bands, corresponding to two different sites of association for NH_3 on CCl_3Br show up in the spectra of intermediate solutions, as shown in Figure 8.

The possibility that the frequency shifts of the ν_2 band with these halogen-containing compounds are due to hydrogen bond formation between the hydrogens of the ammonia molecule and the halogens acting as proton acceptors in hydrogen bond formation must be
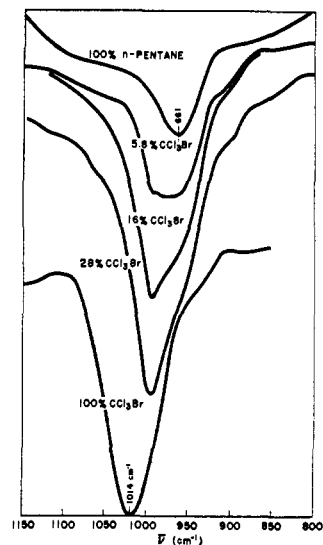

Figure 8. Absorption due to the ν_2 symmetric bending mode of NH_3 in CCl_3Br–C_5H_{12} solutions with ammonia pressures of about 60 p.s.i. and cell lengths of 0.025 mm. used throughout. Percentages are mole per cent of CCl_3Br.

considered. The N–H stretching frequencies, in the 3400-cm.$^{-1}$ region, would be expected to reveal any such association, and the spectra of Figure 7 show this region for pentane and a variety of interacting solvents. The expected hydrogen-bonding shift is observed to some extent with pyridine, but with ether, where hydrogen bonding might also be expected, the only indication of an interaction is a marked change of shape of the ν_3 bond. The removal of the broad wings can, however, be taken as evidence for an interaction that is sufficient to remove the rotational freedom about the molecular axis and a weak $H_2N–H \cdots O<$ bond would accomplish this. By contrast, the spectra in the solvents $CHBr_3$ and CBr_4 show no appreciable change in position or shape of these bands, and therefore the evidence indicates no N–H hydrogen-bond interaction in these systems.

The suggestion that amines form complexes through the nonbonding nitrogen electrons with halomethanes has already been put forward by Stevenson and Coppinger[8] on the basis of an ultraviolet absorption band that could be attributed to the complex. The infrared experiments reported here, therefore, confirm this result. Furthermore, the existence of such complexes is extended to other halogen-containing species.

The nature of the complexes formed between ammonia, and, presumably, other amines and halogen-containing molecules needs to be considered. The existence of a well-defined vibrational spectrum for these complexes implies that these species have a particular structure and an appreciable lifetime. They cannot, therefore, be properly treated in terms of "contact charge-transfer complexes."[9] The infrared spectral evidence points to association through the amine nonbonding electrons, and this feature implies that complexes be viewed as the more familiar charge-transfer complexes such as formed, for example, by pyridine and iodine.

(8) D. P. Stevenson and G. M. Coppinger, J. Am. Chem. Soc., 84, 149 (1962).
(9) L. E. Orgel and R. S. Mulliken, ibid., 79, 4839 (1957).

The extension to the type of systems that form complexes such as revealed by the bending mode of NH_3 leads one to expect that such association might occur between halogen-containing molecules and atoms, other than nitrogen, that contain nonbonding electrons. It has already been pointed out by Heald and Thompson[10] that, as in their study of the frequencies of the CO_2 bands and carbonyl bands in a variety of solvents, specific interactions must be taken into account when a polar group, such as the carbonyl group, exists in halogen-containing solvent. Similar conclusions had been reached earlier from considerations of solvent effects on frequencies by Bellamy.[11] More recently, Allerhand and Schleyer[12] have pointed out, in a study of specific and general solvent interactions, that the OH band of phenol shows two closely spaced bands in mixtures of hexane and perfluorocarbon and mixtures of perfluorocarbon and carbon tetrachloride. Although the cause of this splitting is not known for certainty and solvent clusters are suggested as a cause, it may well be another example of lone pair-to-halogen

interactions such as that revealed by the ammonia solution spectra.

4. Frequency Shifts as a Function of Solvent Concentration. One remaining feature that is very evident in the spectra of Figures 4 and 6 and the results of the final two columns of Table I needs comment. It is clear that even after the new and presumably 1:1 complex is formed between NH_3 and a solvent molecule, the position of the band due to this species shifts gradually but markedly to higher frequencies as the concentration of the interacting species is increased relative to the pentane in the solution. The shift, moreover, is in the direction that would be expected if the added, active solvent component tended to increase the strength of the interaction. Although, the values of $\Delta\bar{\nu}$ of Table I indicate a general solvent effect, there seems to be no simple correlation of these data with the empirical relations such as that recently proposed by Allerhand and Schleyer[12] to correlate frequency shifts of, for example, the hydrogen-bonded OH band. Thus, the present study clearly indicates both specific interactions and general solvent effects, as emphasized by Allerhand and Schleyer. The data for the general solvent effect on the 1:1 species formed in the ammonia systems do not, however, seem to follow suggested empirical correlations.

(10) C. Heald and H. W. Thompson, *Proc. Roy. Soc.* (London), A268, 89 (1962).
(11) L. J. Bellamy, *Spectrochim. Acta*, 14, 192 (1959).
(12) A. Allerhand and P. von R. Schleyer, *J. Am. Chem. Soc.*, 85, 37 (1963).

Adsorption of Carbon Monoxide on Alumina at High Pressures[1]

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Contribution from the van der Waals Laboratory, University of Amsterdam, Amsterdam, The Netherlands. Received March 19, 1965

The glass-piezometer technique developed earlier for adsorption measurements at pressures up to 3000 atm. has been applied for measuring the adsorption of CO on alumina at 0, 25, and 50° and pressures up to 2160, 2940, and 1415 atm., respectively. The adsorption isotherms exhibit a maximum in the gas density range 150–170 amagats (pressure 140–220 atm.). In the range 550–640 amagats they level off instead of intersecting and taking the upward course observed earlier for N_2 adsorption on alumina. The adsorption of CO is found to be fully reversible. The alumina does not undergo any permanent change due to the applied pressure.

Introduction

In a recent publication from this laboratory an experimental technique has been described for the measurement of adsorption of gases on solids in the temperature range −7 to 100° and at pressures from 6 to 3000 atm.[3] The results obtained for adsorption of nitrogen

on alumina at −7.6, 0, 25, 50, 75, and 100° and a preliminary discussion of the results are also given in that paper. The second ascending and apparently endothermic part of the nitrogen adsorption isotherms in the gas density range 450–640 amagats (pressure 1500–3000 atm.) motivated further investigation in this field. Hence the adsorption of carbon monoxide on alumina was measured. The results obtained at 0, 25, and 50° are given in this paper.

Experimental

Full details of the glass-piezometer technique for high-precision measurements of the compressibility of gases at pressures up to 3000 atm. are given in the earlier papers of Michels, *et al.*[4] Adaptation of this technique for high-pressure adsorption measurements, the assumptions involved in the method of measurement and in the calculation of the apparent adsorption, ΔG, etc., have all been given elsewhere.[3] However, two distinctive features of this method over almost all the earlier measurements in the field of high-pressure adsorption may be pointed out here: (1) the adsorbent and the adsorbate gas are enclosed in glass and not in metal even at a pressure of 3000 atm.; (2) the use of the

(1) Taken in part from the author's doctorate thesis, Technological University, Delft, 1961. Copies of the thesis are available from the author.
(2) Regional Research Laboratory, Hyderabad-9, India.
(3) A. Michels, P. G. Menon, and C. A. ten Seldam, *Rec. trav. chim.*, 80, 483 (1961).
(4) A. Michels and C. Michels, *Phil. Trans. Roy. Soc.* (London), A231, 409 (1933); *Proc. Roy. Soc.* (London), A153, 201 (1935); A. Michels, C. Michels, and H. Wouters, *ibid.*, A153, 214 (1935).