

The extension to the type of systems that form complexes such as revealed by the bending mode of  $\text{NH}_3$  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<sup>10</sup> that, as in their study of the frequencies of the  $\text{CO}_2$  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.<sup>11</sup> More recently, Allerhand and Schleyer<sup>12</sup> 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

(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).

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  $\text{NH}_3$  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<sup>12</sup> 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.

## Adsorption of Carbon Monoxide on Alumina at High Pressures<sup>1</sup>

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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<sub>2</sub> 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  $100^\circ$  and at pressures from 6 to 3000 atm.<sup>3</sup> The results obtained for adsorption of nitrogen

on alumina at  $-7.6$ ,  $0$ ,  $25$ ,  $50$ ,  $75$ , and  $100^\circ$  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  $50^\circ$  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.*<sup>4</sup> 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,  $\Delta G$ , etc., have all been given elsewhere.<sup>3</sup> 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).

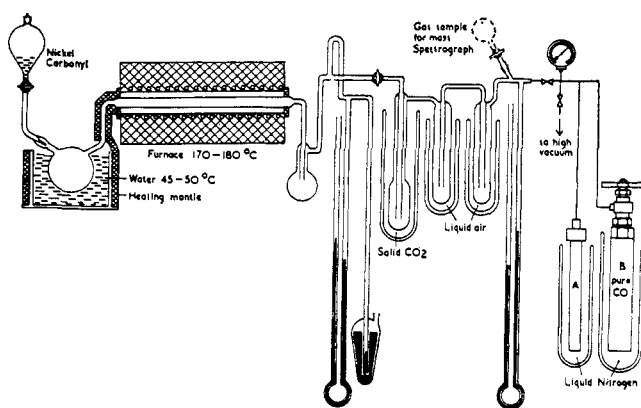


Figure 1. Apparatus for the preparation of pure CO.

free-piston-type Michels pressure balance<sup>5</sup> not only ensures an accuracy of 1 in 10,000 or better in pressure measurements, but maintains the pressure constant even if the amount of gas adsorbed varies with time during any particular measurement.

The alumina sample used as adsorbent was prepared in a way identical with that for alumina-A used for nitrogen adsorption isotherms<sup>3</sup> (Peter Spence Type-H alumina, dehydrated under high vacuum for 6 hr. at 300°; helium density 3.359 g./cc.; B.E.T. surface area 120 m.<sup>2</sup>/g., using 16.2 Å.<sup>2</sup> as the molecular area for nitrogen; X-ray analysis showed it to be a mixture of  $\gamma$ - and  $\chi$ -alumina; dehydration at 1200° removed 1.29% by weight of water). The weight of alumina taken in the evacuated capsule in the top bulb of the piezometer was 4.7881 g.

Four fillings of gas in the piezometer were used to cover the pressure range up to 3000 atm. The total gas in the piezometer ("normal volume") at these fillings were: (a) 666.07, (b) 1699.88, (c) 2671.06, and (d) 5900.14 cc. STP. The total volumes of the piezometer above the platinum contacts 1 to 9 at 25° and 1 atm. pressure were as follows: (1) 82.4110, (2) 50.6819, (3) 12.7191, (4) 11.8221, (5) 11.0329, (6) 10.3285, (7) 9.7322, (8) 9.2358, and (9) 8.8412 cc. The free volume inside the capsule was 3.635 cc. The gas densities at high pressures were calculated from the compressibility isotherm data for CO measured earlier<sup>6</sup> in this laboratory.

Adsorption measurements at 0 and 25° were completed. During the last stage of the measurements at 50°, owing to an accident, the pressure in the apparatus fell from 2000 to 300 atm. within a few seconds. The alumina in the top bulb of the piezometer was blown out of the capsule and fell down into the lower bulbs thereby making any further measurement impossible. On opening the apparatus, some of the platinum contacts between the bulbs of the piezometer were found to be damaged and two of them broken by the sudden rush-down of mercury. The volume calibrations were thus altered. Hence the experiment could not be continued further with the present piezometer.

**Adsorbate.** Pure CO was prepared by the thermal decomposition of nickel carbonyl in the apparatus

(5) A. Michels, *Ann. Phys. (Leipzig)*, **72**, 285 (1923); **73**, 577 (1924); *Proc. Roy. Acad. Sci. (Amsterdam)*, **26**, 805 (1923); **27**, 930 (1924).

(6) L. Jansen, A. Michels, and J. M. Lupton, *Physica*, **20**, 1215, 1235, 1244 (1954); J. M. Lupton, Doctoral Thesis, Amsterdam, 1954.

shown in Figure 1. Because of the toxic nature of CO and even more so that of nickel carbonyl, the entire apparatus was set up in a fume cupboard provided with a powerful exhaust fan. The apparatus was thoroughly evacuated before letting the carbonyl into the distillation flask and subsequently flushed out a few times with CO. Nickel in the form of fine powder was caught in the first trap. Unreacted carbonyl (or that freshly formed from the nickel powder) and possibly traces of moisture and carbon dioxide were trapped in a condenser cooled by solid carbon dioxide and two others in series cooled in liquid air. The CO formed was condensed in a stainless steel bomb cooled in liquid nitrogen and finally distilled over into a brass bomb. A mass spectrometric check showed no trace of impurities in the CO prepared.

## Results

The results of the adsorption measurements of CO on alumina-A are given in Table I. The following symbols have been used: filling, gas filling in the piezometer;  $n$ , piezometer contact at which the measurement is made;  $P$ , gas pressure in international atmospheres;  $\rho$ , gas density in amagat units (1 amagat unit of density = the density of the gas at 0° and 1 international atm. pressure);  $\Delta G$ , apparent adsorption in cm.<sup>3</sup> (STP)/g. of alumina. The exact temperatures, measured with a calibrated platinum resistance thermometer, are also given in the table. In Figure 2 the high-pressure adsorption isotherms ( $\Delta G$  vs.  $\rho$ ) of CO on alumina are shown; the results for N<sub>2</sub> on the same adsorbent at the same temperatures<sup>3</sup> are also given there for comparison.

## Discussion

The  $\Delta G$ - $\rho$  adsorption isotherms of both the gases show a maximum in the density range 150-200 amagats. Such maxima in high-pressure adsorption isotherms have also been observed by earlier workers.<sup>7</sup> After the maximum, the apparent adsorption gradually decreases until it levels off at about 450-550 amagats for both the gases. Above 550 amagats the nitrogen adsorption isotherms (at -7.6, 0, 25, 50, 75, and 100°)<sup>3</sup> take a rather steep upward course with a complete reversal of the temperature dependence of adsorption. This new phenomenon is seen only in the case of N<sub>2</sub>. The CO isotherms show only a very slight tendency, if at all, to ascend again after the leveling off; they do not intersect within the experimental pressure range used.

The adsorption and desorption pressures at any contact of the piezometer always agree to at least 1 in 10,000 and very often much better than that. This corresponds to the accuracy of the Michels pressure balance and the temperature control of the thermostat ( $\pm 0.01^\circ$  or better). The higher pressure series (filling d) also reveal that the alumina in the piezometer does not undergo any plastic deformation or permanent set even at the highest pressure employed in these measurements. (In the case of high-pressure N<sub>2</sub> adsorption,

(7) A. S. Coolidge and H. J. Fornwalt, *J. Am. Chem. Soc.*, **56**, 561 (1934); V. V. Khodot, *Izv. Akad. Nauk SSSR, Otd. Tekhn. Nauk*, **733** (1948); **991** (1949); **1085** (1951); A. von Antropoff, *Kolloid-Z.*, **129**, **11** (1952); **137**, **105** (1955); J. van der Sommen, P. Zwietering, B. J. M. Eillebrecht, and D. W. van Krevelen, *Fuel*, **34**, 444 (1955); D. H. Moffat and K. E. Weale, *ibid.*, **34**, 449 (1955).

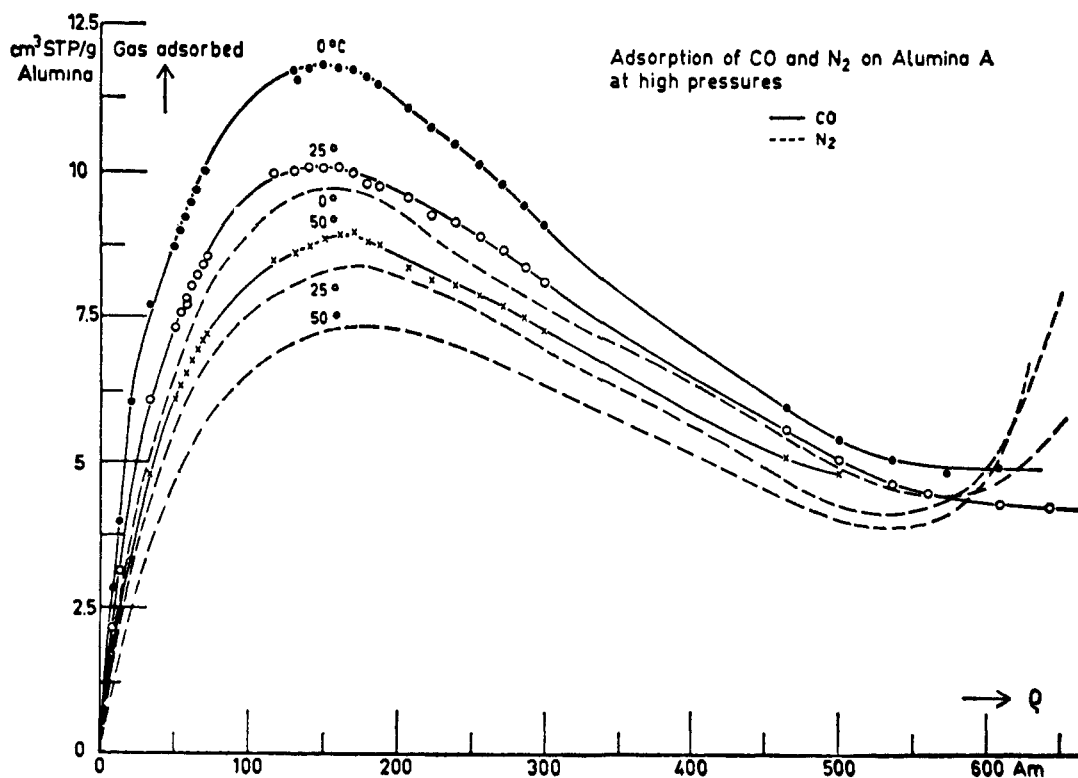


Figure 2. Adsorption of CO and N<sub>2</sub> on alumina at high gas densities (pressures up to 3000 atm.).

Table I. Adsorption of CO on Alumina at High Pressures

Filling	n	-0.769°			24.996°			49.945°		
		P	$\rho$	$\Delta G$	P	$\rho$	$\Delta G$	P	$\rho$	$\Delta G$
a	1	7.8691	7.9243	2.81	8.6674	7.9574	2.15	9.4421	7.9857	1.59
	2	12.6516	12.7763	3.97	13.9731	12.8475	3.12	15.2578	12.9103	2.39
	3	47.9036	49.1369	8.65	53.6535	49.6291	7.29	59.2977	50.0842	6.03
	4	51.3638	52.7441	8.95	57.6010	53.2884	7.55	63.7198	53.7847	6.27
	5	54.8817	56.4145	9.18	61.6055	56.9967	7.79	68.2175	57.5379	6.49
	6	58.4540	60.1465	9.43	65.7063	60.7896	8.00	72.8208	61.3693	6.70
	7	61.8791	63.7252	9.65	69.6336	64.4159	8.20	77.2417	65.0374	6.89
	8	65.1484	67.1391	9.67	73.2992	67.7949	8.36	81.3647	68.4485	7.06
	9	67.8631	69.9721	9.97	76.5064	70.7436	8.50	84.9918	71.4403	7.17
b	1	20.0136	20.2922	6.00	22.1067	20.3664	4.38	24.1321	20.4264	3.27
	2	32.2079	32.8424	7.65	35.7033	32.9713	6.05	39.0849	33.0751	4.76
	3	125.8973	129.3416	11.68	143.1318	129.9355	9.97	159.7860	130.4151	8.56
	4	135.8952	139.1399	11.72	154.8516	139.770	10.04	173.1683	140.2683	8.68
	5	146.2151	149.0652	11.79	167.0388	149.7783	10.03	187.0466	150.2515	8.81
	6	157.0610	159.2571	11.74	179.7715	159.987	10.05	201.6663	160.4703	8.89
	7	167.7007	169.0360	11.70	192.3554	169.841	9.96	216.111	170.3613	8.94
	8	177.9058	178.1837	11.59	204.4397	179.066	9.78	230.0105	179.540	8.76
	9	187.0910	186.2028	11.47	215.3286	187.089	9.73	242.5443	187.5898	8.70
c	1	31.3941	32.0034	7.42	34.7587	32.0942	5.85	37.9909	32.1504	4.23
	2	50.5085	51.8546	9.42	56.2166	52.0052	7.42	61.7216	52.1134	6.01
	3	210.8707	206.027	11.06	243.0531	206.527	9.53	274.0755	206.913	8.32
	4	231.0193	221.803	10.72	267.0024	222.332	9.23	301.6250	222.715	8.10
	5	252.7793	237.796	10.45	292.8035	238.300	9.12	331.3643	238.704	8.02
	6	276.7153	254.186	10.10	321.2153	254.692	8.85	364.0362	255.081	7.85
	7	301.5235	269.943	9.76	350.6165	270.437	8.61	397.8377	270.828	7.66
	8	326.5136	284.650	9.40	380.1844	285.139	8.32	431.7521	285.513	7.46
	9	350.1001	297.555	9.06	407.9952	298.024	8.07	463.6371	298.406	7.23
d	1	68.8855	71.0403	9.94	76.9093	71.1135	8.48	84.6405	71.1522	7.17
	2	111.9408	115.3993	11.91	126.3628	115.5095	9.93	140.2690	115.593	8.43
	3	891.2552	462.793	5.91	1026.6666	462.882	5.52	1155.2169	463.000	5.05
	4	1104.7746	498.360	5.37	1264.3307	498.474	5.03	1415.3623	498.542	4.78
	5	1378.4727	534.480	5.04	1566.2982	534.677	4.62			
	6	1733.0072	571.487	4.82	1952.2136	571.720	4.47			
	7	2161.1942	607.046	4.92	2414.1072	607.486	4.29			
	8				2940.3956	640.934	4.24			

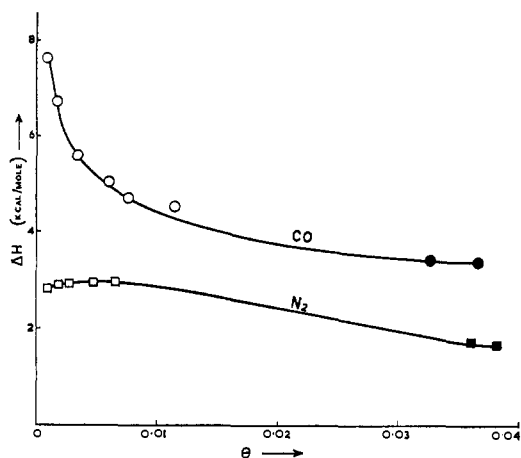


Figure 3. Heat of adsorption of CO and N<sub>2</sub> on alumina: open points are from low-pressure adsorption data and solid points from high-pressure data.

it was confirmed that there was no change in the helium density, surface area, or X-ray structure of the alumina sample taken out of the piezometer after finishing all high-pressure measurements.<sup>3</sup>) The full reversibility of the adsorption and the quickness with which adsorption equilibrium is established, as indicated by steady pressure within 1 hr. of changing to a new contact of the piezometer, indicate that only physical adsorption, and no chemisorption or any such slow activated process is involved in this case.

The adsorption of CO on alumina at pressures below atmospheric, however, involves much stronger adsorbent-adsorbate interactions. A conventional volumetric adsorption apparatus has been used to measure the adsorption at -78, 0, and 20° for both CO and N<sub>2</sub> on the alumina sample. The isosteric heats of adsorption as a function of surface coverage by the two gases from the 0 and 20° low-pressure isotherms and from the

0 and 25° high-pressure isotherms ( $\Delta G$  vs.  $P$ ) are plotted together in Figure 3, which shows the high heat of adsorption for the first amounts of CO adsorbed.

Calculation of entropy change on adsorption of CO and N<sub>2</sub> on alumina both at low pressures and at high pressures gives an idea of the thermodynamic behavior of the gases in the adsorbed state, in particular the mobility of the adsorbed molecules.<sup>8</sup> Until the surface coverage  $\theta$  reaches about 0.003, the adsorption of CO seems to involve strong interactions with the surface with the consequence that the adsorbed molecules seem to be quite immobile and fixed to definite sites on the surface. The small dipole moment of CO, its larger quadrupole moment, and greater polarizability, as compared to N<sub>2</sub>, apparently seem to have a profound influence on the first amounts of CO adsorbed on alumina, making it a case of stronger physical adsorption. But at about  $\theta = 0.011$ , the CO adsorption conforms more to the mobile than to the fixed-site type. At high pressure it shows supermobile adsorption, just as for N<sub>2</sub> on alumina at the same coverage and temperature. When the total number of molecules on the surface (the amount adsorbed together with the amount present in a surface layer due to the applied high gas density only) reaches about 60-65% of the  $v_m$  value from the B.E.T. equation, restrictions on the mobility of the adsorbed CO molecules become gradually noticeable.

A detailed analysis of these results and a tentative explanation for the second ascending and endothermic part of the high-pressure N<sub>2</sub> adsorption isotherms will be published separately.

*Acknowledgment.* The author is highly indebted to Professor A. Michels for providing all the experimental facilities for carrying out this work and his constant encouragement, and to Professor J. H. de Boer for many stimulating discussions.

(8) J. H. de Boer and P. G. Menon, *Proc. Roy. Acad. Sci. (Amsterdam)*, B65, 17 (1962).

## The Direct Measurement of Centroids of High-Resolution Nuclear Magnetic Resonance Spectra

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*Contribution from Union Carbide Research Institute, Tarrytown, New York.*

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*The direct measurement of the average chemical shift from the centroid of a high-resolution n.m.r. spectrum is accomplished by a simple extrapolation of the double integral. The technique is justified, described, tested, and applied.*

Anderson and McConnell have shown how the lower moments of high-resolution magnetic resonance spectra are expressly related to the magnetic parameters, particularly the chemical shifts, which are involved.<sup>1</sup>

(1) W. A. Anderson and H. M. McConnell, *J. Chem. Phys.*, 26, 1496

In the simplest instance the centroid, or normalized first moment, was equated to the average value of the chemical shifts regardless of complications in the spectrum due to spin couplings. In addition to being thereby an accessible quantity, the mean chemical shift is in several ways a useful one. It serves as a convenient starting point for the assignment of transitions in complex spectra,<sup>2</sup> gives a direct way of measur-

(1957); see also, J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High Resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., Inc., New York, N. Y., 1959, pp. 156-160.

(2) E. B. Whipple and Y. Chiang, *J. Chem. Phys.*, 40, 713 (1964).