addition for neutral equivalent by potentiometric titration with the standard base. All of the hexacyanoferrates(III) on drying underwent reductive decomposition, yielding a mixture of ferrous ions, cyanogen, ferricyanide and other by-products.

Results

The results of the analyses of the various hexacyanocobaltates(III) are given in Table I, those on the hexacyanoferrates(III) in Table II.

TABLE I

SUMMARY OF ANALYSIS OF TETRAALKYLAMMONIUM HEXACYANOCOBALTATES(III)

Empirical formula	Mol. wt. Calcd.	Neut. equiv.	Co, % Found	Co, % Theor.	H_2O,[b] %
$(Bu_4N)_3Co(CN)_6$	941	..	6.22	6.26	..
$(Pr_4N)_3Co(CN)_6$	773	..	7.57	7.62	..
$(Et_4N)_3Co(CN)_6$[a]	635	..	9.23	9.28	..
$(Me_4N)_3Co(CN)_6$[a]	437	..	13.41	13.49	..
$(Bu_4N)H_2Co(CN)_6 \cdot 2H_2O$	495	248	11.82	11.91	7.25
$(Pr_4N)H_2Co(CN)_6 \cdot 2H_2O$	439	221	13.38	13.42	8.19
$(Et_4N)_2HCo(CN)_6 \cdot 2H_2O$	542	543	10.81	10.87	6.60
$(Me_4N)_2HCo(CN)_6 \cdot 2H_2O$	400	399	14.70	14.73	8.96

[a] Analyses are based on samples dried at 80° *in vacuo*. All other samples were analyzed on the air-dried basis. [b] Losing weight on heating at 80° *in vacuo*.

The results are in good agreement with the calculated molecular weights based on the empirical formulas proposed in the first column of these tables.

The analyses of the thermal decomposition products of hexacyanocobaltates(III) in a qualitative sense indicated the presence of $Co(CN)_3$, and those of hexacyanoferrates(III) suggested the presence of $Fe_3Fe(CN)_6$.

Tetraalkylammonium hexacyanocobaltates(III) have no major advantages as supporting electrolytes in aqueous solution polarography over the tetraalkylammonium halides or potassium hexacyanocobaltate(III). Freshly prepared hexacyanocobaltate(III) supporting electrolytes permit polarography as far as +0.35 v. and up to −2.3 v. (45° tangent potential) toward S.C.E. Inasmuch as the hexacyanocobaltate(III) ion hydrolyses in aqueous solution yields aquopentacyanocobaltate(III) and hydrogen cyanide, the solutions cannot be stored for any length of time. However, the tetraalkylammonium hexacyanocobaltates(III) can be used as supporting electrolytes in organic solvents because of their solubility and their greater stability rather than in aqueous solutions. In addition, it is felt that uses for the acid salts of tetraalkylammonium hexacyanocobaltates(III) and hexacyanoferrates(III) may be found in neutralization and oxidation–reduction reactions in nonaqueous solutions.

TABLE II

SUMMARY OF ANALYSIS OF TETRAALKYLAMMONIUM HEXACYANOFERRATES(III)

Empirical formula	Mol. wt. calcd.	Neut. equiv.	Oxidation equiv.
$(Bu_4N)_3Fe(CN)_6$	938	..	943
$(Pr_4N)_3Fe(CN)_6$	770	..	774
$(Et_4N)_3Fe(CN)_6$	632	..	634
$(Me_4N)_3Fe(CN)_6 \cdot 2H_2O$[a]	470	..	472
$(Bu_4N)H_2Fe(CN)_6 \cdot 2H_2O$[a]	493	245	491
$(Pr_4N)HFe(CN)_6 \cdot 2H_2O$[a]	436	217	435
$(Et_4N)_2HFe(CN)_6 \cdot 2H_2O$[a]	539	539	541
$(Me_4N)_2HFe(CN)_6 \cdot 2H_2O$[a]	397	398	395

[a] Tetramethylammonium hexacyanoferrate(III) and all acid salts were analyzed on the air-dried basis.

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The Mechanism of Chemisorption: Nitrogen on Nickel

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RECEIVED JANUARY 2, 1958

The adsorption of nitrogen on nickel–silica catalyst samples at moderately low temperatures in the neighborhood of −78° produces a small reversible loss of magnetization as measured by the low frequency a.c. permeameter method. This effect is also observed with argon and with krypton. It is shown that the effects described cannot be due to molecular chemisorption and that they may be due to polarization of physically adsorbed molecules or to the dimensional changes caused by the adsorbed gases, or to both.

Introduction

It often has been stated that nitrogen is chemisorbed on nickel at low temperatures.[1–6]

The work of Schuit and DeBoer is of special significance to the present investigation because the nickel–silica catalyst samples used were prepared, in some cases, by quite similar methods. Their conclusion that nitrogen is chemisorbed appears to be based primarily on the fact that the quantity of nitrogen adsorbed at −78° depends on the amount of nickel present and not on the total surface as determined by nitrogen adsorption at −196°. This work carries the implication that there is no chemisorption of nitrogen on nickel at −196°.

Some further evidence is given by Suhrmann and Schulz[7] who found that nitrogen is adsorbed, in part irreversibly, on nickel films at −183° and that this causes an increase of electrical resistance of about 0.6%. It is, however, to be noted that

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[1] O. Beeck and A. Wheeler, *J. Chem. Phys.*, **7**, 631 (1939).

[2] O. Beeck, A. E. Smith and A. Wheeler, *Proc. Roy. Soc.* (*London*), **A177**, 62 (1940).

[3] O. Beeck, W. A. Cole and A. Wheeler, *Disc. Faraday Soc.*, **8**, 314 (1950).

[4] O. Beeck, "Advances in Catalysis," Vol. II, Edited by W. Frankenburg, Academic Press, New York, N. Y., 1950, p. 151.

[5] B. M. W. Trapnell, *Proc. Roy. Soc.* (*London*), **A218**, 566 (1953).

[6] G. C. A. Schuit and N. H. DeBoer, *J. chim. phys.*, **51**, 482 (1954).

[7] R. Suhrmann and K. Schulz, *Z. Naturforsch.*, **10a**, 517 (1955).

the change of resistance seems to be related more to the reversibly adsorbed nitrogen than to that which is irreversibly adsorbed. Furthermore, Suhrmann[8] has reported that while argon causes no change of resistance at −183°, yet xenon causes a change comparable to that of nitrous oxide which, as is well known, is strongly chemisorbed on nickel, generally dissociatively, to yield molecular nitrogen and adsorbed oxygen.

The surface potentials associated with adsorbed nitrogen, and other gases, on nickel have been studied by Mignolet.[9] The appearance of an appreciable surface potential for nitrogen on nickel at −196° has been mentioned in support of the view that chemisorption of nitrogen can occur under these conditions. But Mignolet himself makes no such claim. He has shown that the surface potential observed for xenon on nickel is actually larger than that for nitrogen, and he points out that the "surface potential appears to afford a criterion of limited applicability for distinguishing between van der Waals adsorption and chemisorption." The effects are attributed, following a suggestion of Frost,[10] to induced polarization.

In an earlier paper[11] we reported some changes of magnetization in nickel–silica which we thought might be attributed to nitrogen chemisorbed at moderately elevated temperatures. These observations were made, before development of the permeameter[12] for the study of chemisorption, on apparatus which did not permit evacuation of the sample. The results have since been found in our own laboratory, and elsewhere,[13] to have been due to a failure to remove all the hydrogen introduced during the reduction step.

The purpose of the present work was to apply the magnetic method to the problem of the supposed chemisorption of nitrogen at low temperatures.

Experimental Part

Magnetization.—All magnetic measurements were made on the low frequency a.c. permeameter previously described and improved.[12,14]

Preparation of Materials.—Catalyst samples were identical with those previously described,[14] namely, Universal Oil Products Company nickel-kieselguhr hydrogenation catalyst containing 52.8% nickel, and coprecipitated nickel–silica containing 37.5% nickel. These were reduced for 12 hours at 360° and cooled to the temperature of measurement. A trace of helium was added over each sample to hasten attainment of thermal equilibrium.

Hydrogen and helium were purified as previously described. Nitrogen and argon were purified by passage over reduced copper–asbestos at 600°, then over silica gel at −78°. Krypton was The Air Reduction Co. Reagent grade and was used without further purification.

Results

The data consist of magnetizations *vs.* volumes adsorbed at 1 atm. for nitrogen on nickel–silica from −78 to 25°. To these data are added some measurements at 2 mm. and −196°. There are also presented pressure–volume and magnetization–volume isotherms at −78°. These data were extended by determination of the magnetization changes occurring during desorption of nitrogen at several temperatures, and of adsorption occurring up to 300°.

Data also are given for helium, for argon and for krypton.

All adsorption data are given in cc. (S.C.) of gas adsorbed per g. of nickel–silica sample, rather than per g. of nickel. This departure from our previous custom in this work is due to realization that most of the adsorption reported in this paper is on the silica support. Magnetizations given in Table I show per cent. loss at the temperature of measurement, but the isotherm shown in Fig. 1 gives the magnetizations in the manner used in our earlier papers, namely, the fraction of the magnetization remaining at the temperature of measurement, after adsorption had taken place. All magnetization changes found were negative. Measurements on coprecipitated catalyst gave results similar to those for the UOP sample, although the total adsorption of nitrogen was somewhat larger, owing, no doubt, to the moderately larger specific surface.

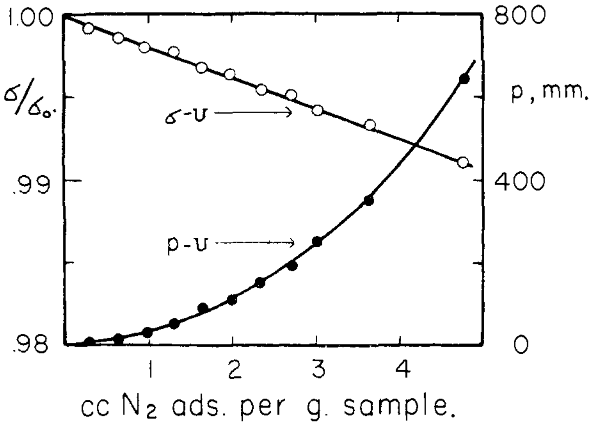

Fig. 1.—Magnetization–volume and pressure–volume isotherms for nitrogen on nickel–silica at −78°.

TABLE I

NITROGEN ADSORBED AT 1 ATM. ON UOP CATALYST

Temp., °C.	Vol., cc.	Mag. % loss
25	0.6	0.0
−20	1.5	.3
−50	2.4	.9
−78	3.3	.5
−196	14.3[a]	.2[a]

[a] Pressure 2 mm.

The incremental addition of nitrogen to a bare UOP surface at −196° produced negative thermal transients. The height of these proved to be directly proportional to the volume of nitrogen admitted to the system, in sharp contrast to the diminishing transients observed for the incremental addition of hydrogen to nickel–silica at room temperature.[15] The thermal transients were per-

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[8] R. Suhrmann, E. A. Dierk, B. Engelke, H. Hermann and K. Schulz, *J. chim. phys.*, **54**, 15 (1957).

[9] J. C. P. Mignolet, *Disc. Faraday Soc.*, **8**, 105, 326 (1950).

[10] A. A. Frost, *Trans. Electrochem. Soc.*, **82**, 259 (1942).

[11] P. W. Selwood, S. Adler and T. R. Phillips, THIS JOURNAL, **77**, 1462 (1955).

[12] P. W. Selwood, *ibid.*, **78**, 3893 (1956).

[13] J. J. Broeder, L. L. Van Reijen and A. R. Korswagen, *J. chim. phys.*, 37 (1947).

[14] P. W. Selwood, THIS JOURNAL, **79**, 4637 (1957).

[15] E. L. Lee, J. A. Sabatka and P. W. Selwood, *ibid.*, **79**, 5391 (1957).

ceptible for nitrogen admission over UOP at −78°, were fairly large and observed both for adsorption and for desorption on coppt. at −78° and were not observed for any sample on admission of nitrogen at room temperature.

Isotherms for nitrogen on copptd. nickel–silica at −78° are shown in Fig. 1.

In view of several reports to the effect that some of the nitrogen adsorbed at low temperature is difficult to remove, it was decided to see whether this could be confirmed for the two samples under study. A sample of coppt. was re-reduced and evacuated as described above, then exposed to nitrogen at −78°. The total N_2 taken up was 4.9 cc. per g. of sample to 1 atm. Of this amount 0.8 cc. proved difficult to remove. After 2 hr. pumping the pressure was still 10^{-2} mm. All the remaining gas was released readily when the sample was warmed at room temperature.

This experiment was repeated with UOP. The total adsorption to 1 atm. at −78° was 3.3 cc., and of this all but 0.3 was pumped off readily at −78°, with the pressure down to about 10^{-4} mm. after 1 hr.; as before, all the remaining nitrogen came off readily at 25°. In each of these runs the small negative change of magnetization reported in Table I was observed.

A final experiment at −78° on UOP was done to determine if the observed magnetic change was related to all the adsorbed nitrogen or merely to that fraction of the nitrogen shown to be less readily released. On a sample weighing 5.22 g. the total nitrogen admitted to the sample chamber was 41.4 cc. (S.C.) which included 21.6 cc. in the dead space. Of the 41.4 cc. admitted, 29.0 cc. was recovered on the first Toepler cycle and the magnetization, which had fallen 0.5%, rose at once to within 0.1% of the original value. Further pumping recovered all the nitrogen in about 2 hr., with recovery of all the magnetization. The loss of magnetization observed on admission of nitrogen at −78° is, therefore, not caused primarily by the nitrogen which is less readily pumped off.

At −50° the magnetic effect for adsorbed nitrogen was slightly larger than that at −78°. At −20° the effect was slightly smaller, and no effect could be detected at room temperature.

Above room temperature it was hardly expected that any significant adsorption would be found. On coppt. at 25° the adsorption to 1 atm. was about 0.7 cc. per g. of sample and this diminished as the temperature was raised to 300°. As stated above, no change of magnetization on admission of nitrogen was observed at room temperature or higher. Similarly, a sample of UOP exposed to nitrogen at 1 atm. and 60° for 5 days showed no magnetic change and no additional adsorption after the trifling volume taken up in the first second or two after exposure.

The possible effect of helium on the magnetization was studied for coppt. at −78°, and for UOP at −196° and at 25°. No adsorption and no magnetic effect could be detected to 1 atm. pressure. This is consistent with the results already published on helium[16] to 140 atm. at 25°.

On the other hand, an effect with argon was observed. At room temperature on UOP the volume adsorbed was 0.6 cc. per g. of sample, but no magnetization change took place. At −78° to 1 atm. the adsorbed volume was 1.3 cc. per g. of sample and this produced a loss of magnetization of about 0.6%. The effect was readily reversible on pumping, although no thermal transients were observed. About 5% of the argon proved to be a little difficult to remove at −78°.

In view of the results obtained with argon it seemed desirable to try krypton. When krypton was flushed onto a UOP sample at −78° the volume of gas adsorbed to 1 atm. was 5.5 cc. (S.C.) per g. of sample, and this was accompanied by a 2.3% loss of magnetization. This was completely and repeatedly reversible on pumping for a few minutes. There were slight suggestions of negative and positive transients on admission and evacuation, respectively.

Discussion

The results presented above show that nitrogen on nickel shows no true chemisorption, in the sense in which that term is generally used. The maximum change of magnetization is only a few per cent. of that observed for hydrogen chemisorbed on nickel. This in itself is not proof that a small fraction of the nitrogen taken up may not be chemisorbed, but it has been shown above that the magnetic change is associated with *all* the nitrogen adsorbed and not merely with that fraction most strongly held. Furthermore, the magnetization change caused by adsorbed argon is almost identical with that caused by nitrogen. It has never been seriously suggested that any inert gas could be chemisorbed. On the other hand it is mildly disturbing to find that the effect of nitrogen reaches a low maximum in the neighborhood of −50°. The magnetization effect appears to be linear with volume of gas adsorbed at any one temperature at which any effect is observed. But the magnetization change is not linear with volume adsorbed at different temperatures. This behavior is characteristic of chemisorbed gases. But all these effects are so trifling in comparison with those produced by a gas such as hydrogen, which is truly chemisorbed, that it seems quite safe to say that the supposed chemisorption of molecular nitrogen on nickel at low temperature is without significance in heterogeneous catalysis.

It remains to inquire the reason for the slight magnetic effect observed. Two reasons suggest themselves. The first is that molecules of nitrogen are polarized on the nickel surface and thereby induce some slight change of electron concentration in the conductivity band, with consequently some redistribution of electrons in the d-band This view of induced polarization is supported by the observation that adsorbed argon causes about the same effect as nitrogen. The polarizability of argon is nearly the same as that of nitrogen. Evidence that the effect is related to polarization of physically adsorbed molecules is provided by the results on krypton, which has a considerably higher polarizability than argon.

In view of the fairly large magnetic effect pro-

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[16] L. Vaska and P. W. Selwood, THIS JOURNAL, **80**, 1331 (1958).

duced by krypton, it may be wondered if some part of the magnetic effect previously reported[17] for such gases as ethane and benzene may not similarly be due to physical adsorption. But if the data are calculated in the same way, it will be seen that the magnetic change produced by benzene vapor is about 20 times greater than that produced by the same volume of krypton. The "physical" effect is, therefore, barely significant in comparison with the "chemical" effect. This does not mean that the effect produced by krypton would not be an interesting area for further investigation.

Another possible explanation for the effect of adsorbed nitrogen on the magnetization of nickel, and one which may not be mutually exclusive with the polarization idea, is based on the observations of Yates on the dimensional changes in unsintered Vycor glass caused by adsorbed gases. Yates[18,19] finds that non-polar gases, such as nitrogen and argon, cause a more or less linear expansion when adsorbed on unsintered Vycor. The nickel–silica catalyst samples bear some resemblance structurally to unsintered Vycor and, except for complications caused by the presence of the nickel, might be expected to behave in a somewhat similar manner. Any expansion of the silica network would increase the distance between adjacent nickel particles and this would be expected to lower the observed magnetization, insofar as it reduced any coöperative interaction between adjacent nickel particles. The failure of Broeder, *et al.*,[13] to observe the effects described in this paper is attributable to the fact that none of their measurements was made below room temperature.

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(17) P. W. Selwood, THIS JOURNAL, **79**, 3346 (1957).

(18) D. J. C. Yates, *Proc. Roy. Soc. (London)*, **A224**, 526 (1954).

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, AMHERST COLLEGE]

Components of Charge and Potential in the Non-diffuse Region of the Electrical Double Layer: Potassium Iodide Solutions in Contact with Mercury at 25° [1]

BY DAVID C. GRAHAME

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The differential capacity on mercury of aqueous potassium iodide solutions of 17 different concentrations has been measured and the components of charge and potential computed from the results. It is found that the differential capacity of the non-diffuse region of the electrical double layer, when measured at constant n^i (n^i = superficial density of adsorbed anions), is independent of n^i within the limits of accuracy of the measurements. The capacity does depend upon the electronic charge, however, in a manner resembling that found previously for unadsorbed electrolytes. It is also found that ψ^u, the potential generated across the non-diffuse region by specifically adsorbed anions, is proportional to n^i, the constant of proportionality being nearly independent of the surface charge density q. These results must be considered anomalous in relation to presently accepted concepts of the nature of the electrical double layer. A formal description of the electric fields within the non-diffuse region of the double layer requires the simultaneous use of two different values of the dielectric constant of that region, which is another expression of the same anomaly. The measurements permit a formal calculation of the relative distances from the interface of the inner and outer Helmholtz planes. The ratio varies with the surface charge density q in about the expected manner, though perhaps more rapidly. The measurements also permit the calculation of a specific adsorption potential, and this likewise varies with surface charge density in a reasonable manner.

Introduction

A theory of the non-diffuse part of the double layer (the inner region) has been presented elsewhere.[2] Methods of obtaining the components of charge in the diffuse and non-diffuse parts of the double layer from differential capacity measurements also have been described[3] and have been applied to a number of tenth-normal solutions of potassium and barium salts.[4] Measurements which might have been suitable for testing the theory outlined in ref. 2 have been reported by Esin and Markov,[5] by Devanathan and Peries[6] and by Anderson and Parsons,[7] but for one reason or another none of these investigations was entirely suitable for our objective. In particular it was desired to ascertain whether or not the theory described in ref. 2 is contradicted by experiment and, if not, whether an analysis along the lines indicated yields any new and significant information about the properties of the inner region of the double layer.

Experimental Details and Methods of Calculation

The experiment consisted in the measurement at 25° of the differential capacity of mercury in contact with aqueous solutions of potassium iodide of 17 different concentrations ranging from 0.015 to 1.2 *N*. The technique has been described in the literature many times[8,9] and was not modified in any essential detail. The solutions of potassium iodide were made up in conductivity water from twice recrystallized reagent grade salt. Measurements of potential were made relative to a normal calomel electrode, and no correction was or should have been made for liquid junction potentials. What was done, rather, was to compute the potential relative to a hypothetical electrode reversible to the iodide ion and kept always at the concentration of the salt

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(1) Reproduction in whole or in part permitted for any purpose of the U. S. Government.

(2) D. C. Grahame, *Z. Elektrochem.*, **62**, 264 (1958).

(3) D. C. Grahame, *Chem. Revs.*, **41**, 441 (1947).

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(6) M. A. V. Devanathan and P. Peries, *Trans. Faraday Soc.*, **50**, 1236 (1954).

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