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The Effect of Adsorbed Gases on Contact Electrification*

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The magnitude of the electrification produced on contact of quartz and of sodium chloride on nickel in atmospheres of air, oxygen, and nitrogen has been measured. Reproducible pressure-dependent results were obtained that indicate the contact electrification is a surface phenomenon and depends greatly on the nature of the surfaces involved. At least two layers of adsorbed gas play an important part in the phenomenon of contact electrification. In the pressure range from 760 to 30 mm at least one layer of adsorbed gas is removed. In this pressure range the surface covered with adsorbed gas makes the major contribution to the charge separation. At pressures below 0.1 mm at least a second layer of adsorbed gas is removed. In this pressure range the major contribution to the charge separation is made by the surface from which the second layer of gas has been removed. A fit of the data to Langmuir adsorption isotherms was obtained. Water vapor and perhaps hydrogen act as surface poisons in the phenomenon of contact electrification.

CONTACT or frictional electrification and contact potential difference are two "solid to solid" contact phenomena that lead to the electrical charging of the solids involved. Contact potentials are observed only when both of the solids are metals. This effect may be readily explained in terms of the electron theory of metals. The magnitude of the contact potential may either be measured directly or computed from the work functions of the metals. The results thus obtained are consistent and reproducible.

When one or both of the solids is a non-conductor, the measurement of contact potential is not possible or rather meaningless. Non-conductors do not accept or give up electrons readily. Such bodies do not have the free electrons which are necessary for the phenomenon of contact potential difference. Therefore the theory which explains contact potentials cannot explain contact electrification. Nor has there yet been published a theory which satisfactorily explains this phenomenon.

The charging of two non-conductors by friction was the first form of electrical charging discovered. The phenomenon of charging by impact or contact is a very widespread one encountered in dust storms and in many industrial processes where there is friction between non-conductors. The control and applications of contact electrification in industry would be of greater importance if the phenomenon were better understood. While a great deal of work has been done, very little satisfactory information has been obtained. Nearly all the published data are qualitative and often are contradictory and not reproducible.[1–5] In fact the very nature of the phenomenon is obscure. It was suggested by Professor Loeb that this phenomenon be further investigated and that great care be taken to work with reproducible surfaces in a reproducible environment with particular reference to the nature and pressure of the gases in contact with the surfaces.

Nearly every man who has worked on the contact potentials of metals has noticed and remarked on the effect of adsorbed gases on the potentials measured. It is now customary to take great pains to remove all traces of gas, to prepare clean surfaces, before making a measurement of contact potential.

Recently the importance of adsorbed gas in another contact phenomena, friction, has been shown.[6,7] It therefore seems strange that the few men who have studied contact electrification

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[1] P. E. Shew and C. S. Jex, Proc. Roy. Soc. London **A118**, 97–113 (1928).
[2] A. Fleming, Proc. Roy. Soc. London **53**, 51–3 (1941).
[3] R. Schnurman, Proc. Phys. Soc. London **53**, 547–53 (1941).
[4] P. Boning, Zeits. f. tech. Physik **8**, 385–98 (1927).
[5] H. Israel, Zeits. f. tech. Physik **9**, 289–93 (1928).
[6] R. Schnurman, Proc. Phys. Soc. **53**, 538–46 (1941).
[7] H. Donandt, Chem. Abs. **36**, 3466 (1942).

recently have paid little or no attention to the gases adsorbed by the solids used.

I have attempted to study quantitatively the charge separation produced on the contact of two dissimilar solids, one of them a non-metallic, and the effect of gas pressure on this charge separation.

APPARATUS

The apparatus consists of two nickel flasks mounted coaxially and separated by a cylindrical insulator made of quartz. One of the flasks is filled with small particles of the non-metallic solid. The end plates of the flasks are perforated so that equilibrium gas pressure may be quickly established. The whole is enclosed in a glass envelope connected to a vacuum system through a ground glass joint. (See Fig. 1 for a cross section of the apparatus.)

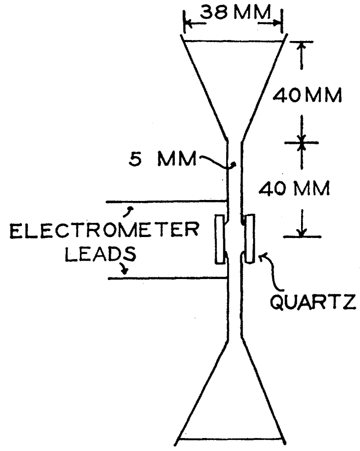

FIG. 1. Cross section of the apparatus.

When the envelope is inverted, the non-metallic particles fall from one flask to the other, carrying with them a charge. The potential built up between the flasks is measured with a quadrant electrometer. From this potential and from the known capacity of the apparatus the charge separation is computed.

The total capacity of the system, flasks, electrometer, and parallel capacitor is $750\mu\mu f$.

MATERIALS

The quartz particles used were prepared by crushing amorphous quartz in an agate mortar. The NaCl was prepared from commercial salt. A hot saturated solution of commercial salt was filtered and then heated until about one-fourth of the water had evaporated. The crystals formed were recovered, dried, and crushed in the agate mortar.

TABLE I. Physical constants of the particles used.

	Quartz	Quartz	Quartz	NaCl
Weight	7.02 g	4.74 g	7.81 g	8.10 g
Density	1.55	1.55	1.55	2.17
Total vol. (cc) of non-metallic used	4.52	3.05	5.03	3.73
Av. vol. (cc) of individual particle	3.2×10^{-5}	3.2×10^{-5}	3.2×10^{-5}	3.2×10^{-5}
Number of particles	1.41×10^{5}	0.95×10^{5}	1.57×10^{5}	1.16×10^{5}

TABLE II. Quartz on nickel with air in the chamber. 7.0 grams of quartz.

		Electrometer reading							
Date	Pressure	1	2	3	4	5	6	Av.	Volts
4/26/43	30	26.7	25.2	25.9	25.8	26.2		26.0	53.3
4/27/43	31	25.7	25.8	26.6	26.3	25.4	26.1	26.0	53.3
7/ 2/43	30	25.3	24.6	24.7	24.0	24.1		24.5	49.4
5/ 6/43	7×10^{-5}	36.6	35.1	36.5	36.1	35.2	36.2	36.0	104
5/ 6/43	264	36.7	35.9	36.8	36.3	36.1		36.4	107
4/26/43	42	25.4	24.7	24.9	25.1	24.6	25.0	24.9	50.5

Particles of nearly uniform size were segregated by differential screening. The average particle radius was 0.02 cm. The volume of an average particle was computed from the diameter by assuming that the particles were spherical. An approximate figure for the number of particles used was then computed (Table I).

The gases used were air, oxygen, nitrogen, and hydrogen. No attempt was made to purify the gases other than to remove water vapor, mercury vapor, oil particles, and dust particles.

EXPERIMENTAL PROCEDURE AND RESULTS

In order that data taken on different runs be comparable, it was necessary that the surfaces

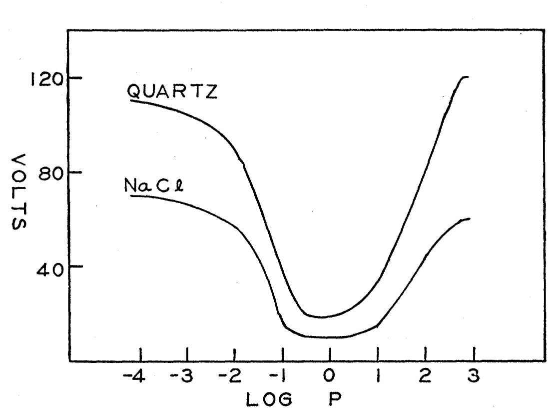

FIG. 2. Potential-pressure dependence for the entire range studied.

used be reproducible. I found that baking the apparatus for several days at 200°C in vacuum produced nickel, quartz, and NaCl surfaces with characteristics that were sufficiently reproducible for the needs of this experiment. The apparatus was given this treatment before each run.

For both quartz and NaCl a large number of measurements of potential were made at various pressures ranging from 7×10^{-5} to 760 mm of Hg. The rate of increase of pressure between measurements was slow so that the water vapor and dust traps could work efficiently. The rate of decrease of pressure between measurements was rapid.

At any single pressure from five to eight measurements of the potential were made from a similar number of inversions of the apparatus. In Table II are listed typical sets of measurements taken on different days and at different pressures. The difference between the highest and lowest reading of a set varies between 2 and 6 percent of the average of the set. The differences between average values taken for the same pressure on different days are of the same order of magnitude.

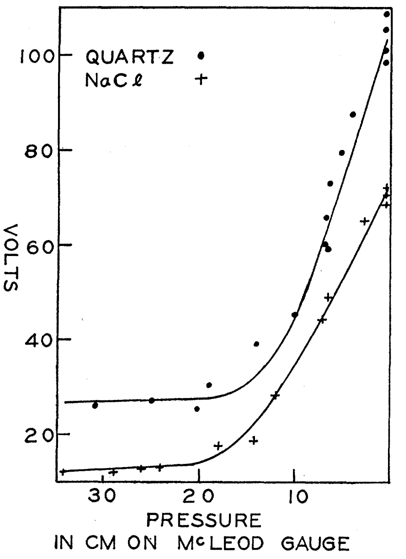

FIG. 3. Potential as a function of pressure—the low pressure range.

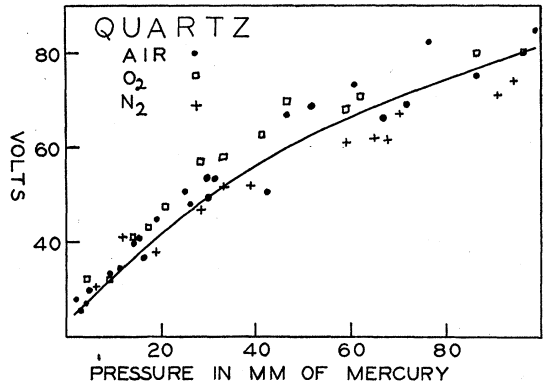

FIG. 4. Quartz: dependence of potential on gas in the chamber.

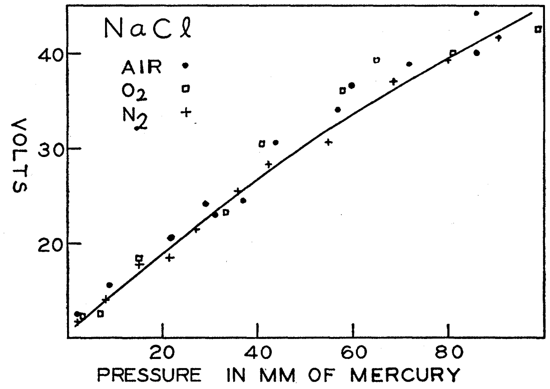

FIG. 5. NaCl: dependence of potential on gas in the chamber.

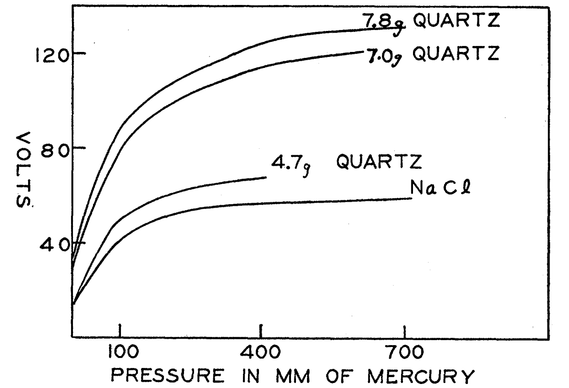

FIG. 6. Potential as a function of pressure—the high pressure range.

The sets of measurements were averaged and plotted (Figs. 2 to 6). In all, four sets of runs were made. The first run was made with 7.0 g of quartz particles in the apparatus. In the second run 8.1 g of NaCl were used and in the third run 4.7 g of quartz was used. The nickel flasks were then cleaned in dilute nitric acid and washed in distilled water. The fourth run was made with 7.8 g of freshly ground quartz.

In Fig. 2 potential is plotted against the logarithm of the pressure in order to give an over-all picture of the experimental results. The low

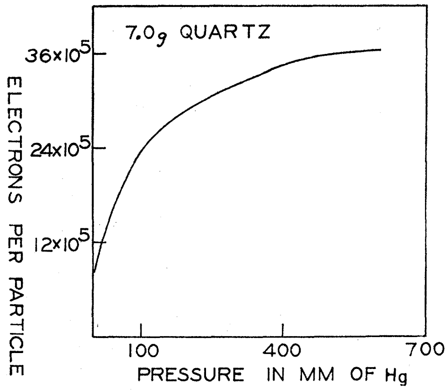

FIG. 7. Charge separation in terms of electrons per particle as a function of pressure.

pressure data are plotted in Fig. 3. For convenience the potential is plotted against McLeod gauge readings and thus against a quantity proportional to the square root of the pressure. In Figs. 4–6 the potential is plotted as a function of pressure in mm of Hg.

On the whole the quartz and NaCl behave quite similarly in the apparatus. But there was one very striking difference. After electrification the quartz particles were always negative while the NaCl particles were always positive.

From the capacity of the system and the measured potential, I computed the total charge separation, and the charge separation in terms of electrons per particle (Table III and Fig. 7). Although I have given the charge separation in terms of the electrons per particle, I do not wish to intimate that the mechanism of charging is that of a transfer of electrons as such. A possible mechanism will be discussed later.

DISCUSSION OF EXPERIMENTAL RESULTS

Air, Oxygen, and Nitrogen

On examining Figs. 4 and 5, we see that for the middle pressure range there is no significant difference in the behavior of oxygen, nitrogen, and their mixture air in this experiment. An examination of all of the data available shows that there is no real difference in their behavior at any pressure that I have studied.

The high pressure portion of the curve (Fig. 6) has a shape similar to that of the Langmuir adsorption isotherm.[8] The analytic expression for the adsorption isotherm is

$$x=aP/(1+aP), \qquad (1)$$

where x represents the fraction of the surface covered by the adsorbed gas or rather the fraction of completion of an adsorbed layer. P represents the pressure of the gas being adsorbed and a is a constant depending on the gas and the surface. If the charge separation depends on the presence of adsorbed gas, we may thus postulate that the potential measured will be proportional to the fractional completion of the adsorbed layer. That is,

$$V=bx \qquad (2)$$

or

$$V=baP/(1+aP). \qquad (3)$$

TABLE III. Charge separation.

Non-metal	Pressure in mm of mercury	Volts	E.s.u.	Electrons per particle
Quartz	0.97	24.8	55.8	1.21×10^6
Quartz	47	67.2	151	3.28×10^6
Quartz	649	122	273	5.95×10^6
NaCl	0.81	12.1	27.2	0.72×10^6
NaCl	60	36.5	82.2	2.16×10^6
NaCl	701	60.5	136	3.59×10^6

On rearranging, Eq. (3) becomes

$$\frac{1}{V}=\frac{1}{abP}+\frac{1}{b}. \qquad (4)$$

Then $1/V$ plotted against $1/P$ should be a straight line with slope $1/ab$ and intercept $1/b$. The reciprocal values of V and P are plotted in Figs. 8–11. The results approximate fairly well to

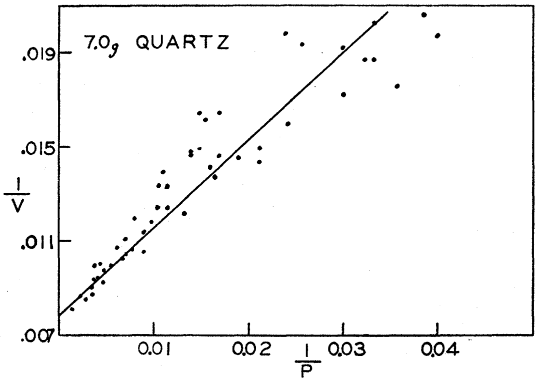

FIG. 8. 7.0 g quartz: plot of the reciprocal of the data for determination of adsorption isotherm constants.

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[8] I. Langmuir, J. Am. Chem. Soc. **38**, 2267 (1916); **40**, 1361 (1918).

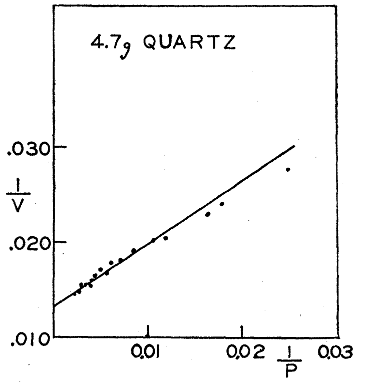

Fig. 9. 4.7 g quartz: plot of the reciprocal of the data for determination of adsorption isotherm constants.

a straight line. The constants obtained by fitting straight lines to the points are listed in Table IV.

These constants may be checked by comparing computed and observed values of the potential. Such a comparison is made in Tables V and VI. The data used for the comparison were selected at random from the available data. The differences between the observed and the computed values of the potential are of the same order of magnitude as the differences between individual values of the potential for a given pressure. We may safely say that Eq. (3) fits the experimental data within the uncertainty of the experiment.

Let us now inquire into the dependence of the constants of Eq. (3) on physical factors. The magnitude of the constant a should depend on the nature of the gas adsorbed and on the nature of the adsorbing surface, and should be independent of the nature of the other solid surface involved. Since the magnitude of a did not change when NaCl was substituted for quartz (Table IV), it seems likely that the gas involved in the contact electrification had been adsorbed by the nickel. The other possible but less likely conclusion is that the adsorption behavior of quartz and NaCl toward the gases used is nearly identical.

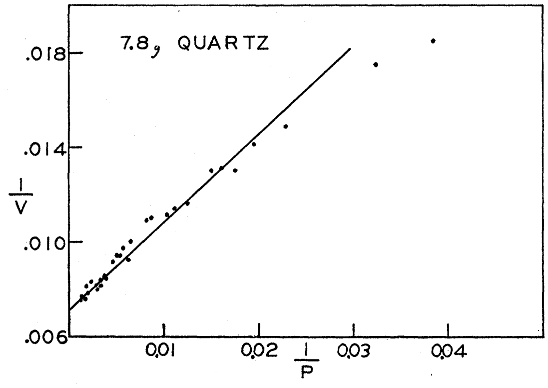

Fig. 10. 7.8 g quartz: plot of the reciprocal of the data for determination of adsorption isotherm constants.

The magnitude of the constant b should depend on the nature of both solids involved and on the number of particles that can make contact. We may assume that the charge separation is proportional to the area of contact and therefore to the number of similar particles that can make contact. In the last row of Table IV are listed the values for b adjusted to 10^5 particles. The values for the three quartz runs are of the same order of magnitude while the value for NaCl is quite different.

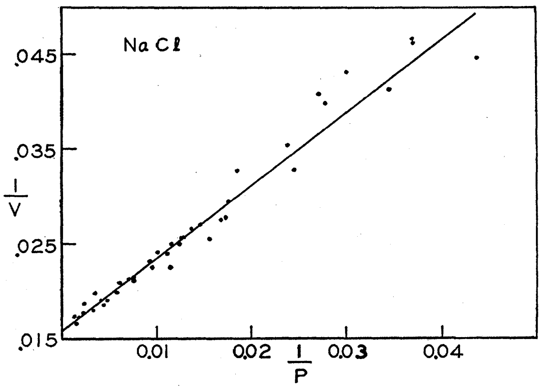

Fig. 11. NaCl: plot of the reciprocal of the data for determination of adsorption isotherm constants.

The action of NaCl is different from that of quartz not only in that the sign of the charge produced is different but also in the magnitude of the electrification per particle.

In arriving at Eq. (3), I assumed that the magnitude of the charge separation depended only on the portion of the surface covered with adsorbed gas. If the uncovered portion of the surface also makes a contribution to the charge separation, Eq. (3) must be changed to read

$$V=b\frac{aP}{1+ab}+c\left(1-\frac{dP}{1+dP}\right). \qquad (5)$$

If the uncovered portion of the surface does make such a contribution in this pressure range, it was so small as to have been obscured by the random variations in the results obtained.

TABLE IV. Adsorption isotherm constants—the high pressure range.

	Quartz			
	7.02 g	4.74 g	7.81 g	NaCl
Slope	0.375	0.64	0.37	0.80
Intercept	0.0078	0.0133	0.0070	0.0158
ab	2.67	1.56	2.70	1.25
b	128.0	76.0	143.0	63.3
a	0.021	0.021	0.019	0.020
Number of particles	1.41×10^5	0.95×10^5	1.57×10^5	1.16×10^5
b adjusted to 10^5 particles	90.9	80.0	91.2	54.4

At pressures below 30 mm the data no longer fit Eq. (3), and at pressures below 0.1 mm the magnitude of the charge separation increases with decrease in pressure (Figs. 2 and 3). The potentials computed from Eq. (3) for pressures below 30 mm are lower than the observed potential. This difference is probably the contribution of the surface uncovered by the removal of the layer of adsorbed gas. The rapid increase in potential below 0.1 mm cannot be assigned to changes in the first layer of gas, for even at 1.0 mm but 2 percent of the surface is covered by this layer. This increase in potential must be caused by further changes in the surfaces making contact. Since the change in potential is still pressure dependent, it is reasonable to assume that the change involved is the removal of a second layer of adsorbed gas. Since the potential increases with decrease in pressure, we may assume that the surface uncovered by the removal of this second layer is making the major contribution to this potential. If this be the case, the dependence of potential on pressure should have the form of Eq. (6),

$$V=c/(1+dP). \tag{6}$$

For pressures below 0.1 mm a decent fit of the data of Eq. (6) was obtained. The constants for the two runs with sufficient low pressure data to be so analyzed are listed in Table VII.

There are then at least two layers of adsorbed gas involved in the pressure range studied. At atmospheric pressure both layers are essentially complete and the charge transfer is large. As the pressure is decreased, one of these adsorbed layers is removed and the amount of charge transferred is reduced. The surface uncovered by the removal of the first layer of gas is then of lower activity than the same surface covered by the gas. The dependence of potential on pressure in this range is given by Eq. (3). At a pressure of 1 mm the first layer has been nearly removed but the second layer has not yet been touched. It is in this region that the charge transfer is a minimum. As the pressure is further reduced, the second layer of adsorbed gas is removed uncovering a surface of higher activity than that of the same surface covered by the adsorbed gas. The dependence of potential on pressure in this range is given by Eq. (6). It is probably a coincidence that the charge transfer obtained when both of the layers are complete is of the same order of magnitude as the charge transfer obtained when both layers have been removed.

We have not sufficient data to assign the second layer to one of the surfaces making contact. It may even be that what appears to be the removal of a single layer of adsorbed gas in each of the pressure ranges studied may be the nearly coincident removal of a layer of adsorbed gas from each of the surfaces.

Judging from the consistency of the results obtained with air, oxygen, and nitrogen, I believe that I have succeeded in reproducing the solid surfaces used by consistent treatment. I cannot, however, definitely state the exact nature of the surfaces used. It is probable that even at the lowest pressures used one or both of the surfaces were covered with a layer of adsorbed oxygen or nitrogen or both. The work of Roberts[9] indicates

TABLE V. Comparison of computed and experimental values of the potential. 7.0 g quartz.

P	$2.67\,P$	$1+0.021\,P$	Computed V	Observed V	V_0-V_c
4	10.7	1.084	9.9	27.2	+17.3
11	29.4	1.23	23.9	34.7	+10.8
25	66.8	1.53	43.6	50.6	+ 7.0
30	80.1	1.63	49.3	53.3	+ 4.0
42	112	1.88	59.4	50.5	− 8.9
61	163	2.28	71.5	73.0	+ 1.5
86	229	2.81	81.0	75.0	− 6.0
101	269	3.12	86.3	85.0	− 1.3
128	342	3.79	90.4	94.0	+ 3.6
147	393	4.09	96.5	96.0	− 0.5
208	555	5.37	103	103	0.0
251	670	6.27	106	101	− 5.0
375	993	8.81	112	118	+ 6.0
463	1235	10.71	115	116	+ 1.0
699	1731	14.61	118	122	+ 3.0

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[9] J. K. Roberts, *Some Problems in Adsorption* (Cambridge University Press, 1939).

that at pressures below 10^{-5} a metal surface can be covered by more than one strongly held layer of adsorbed gas.

Hydrogen and Water Vapor

In an attempt to use hydrogen in the apparatus with quartz, I ran into many difficulties. I was unable to obtain any reproducible data in the hydrogen atmosphere. The charge collected was first of the same order of magnitude, then much lower than in the case of the other gases. I also had considerable difficulty in removing the hydrogen. Baking the apparatus at 200°C for three days while it was being evacuated by a mercury pump removed only some of the surface hydrogen. A run made in air after this treatment gave results that were much too low and which decreased with each inversion of the apparatus. It was only after the apparatus had been baked at 200°C and 20 mm of air for six days that reproducible results were again obtained.

The effect of hydrogen on the NaCl-nickel system was much the same as its effect on the quartz-nickel system.

The apparatus as it comes from the glass blower has been in contact with moist air. In this condition extremely low results are obtained for the charge separation. The charge separation can be returned to the higher reproducible values by baking out the apparatus at 200°C and a pressure of 7×10^{-5} mm of mercury.

Apparently water vapor and hydrogen act as poisons for the phenomena of contact electrification. The poisoning by hydrogen may have been a water vapor effect. It is probable that oxygen was never completely removed from the apparatus before the hydrogen runs. Then the processes involved in contact electrification may have catalyzed the chemical combination of hydrogen and oxygen to form a poisoning water layer on one of the surfaces. This mechanism would also account for the inconsistent results obtained with air when there was some residual hydrogen in the apparatus.

Mechanism of Contact Electrification

We do not have sufficient data to state definitely the mechanism of contact electrification of quartz or sodium chloride on nickel. The results indicate that the adsorbed gas molecules play an important part in the mechanism of charge transfer.

TABLE VI. Comparison of computed and experimental values of the potential. 8.1 g NaCl.

P	1.25 P	$1+0.020\,P$	Computed V	Observed V	V_0-V_c
2	2.50	1.04	2.4	12.4	+10.0
5	6.25	1.10	5.7	14.1	+ 8.4
9	11.2	1.18	9.5	15.5	+ 6.0
22	27.5	1.44	19.1	20.5	+ 1.4
37	46.3	1.74	26.6	24.5	− 2.1
57	71.5	2.14	33.2	33.9	+ 0.7
72	90.0	2.42	37.1	37.5	+ 0.4
100	125	3.00	41.7	41.7	0.0
114	142.5	3.28	43.5	47.5	+ 4.0
131	164	3.62	45.4	44.7	− 0.7
172	215	4.44	48.5	49.2	+ 0.7
280	350	6.60	53.0	55.5	+ 2.5
457	572	10.14	56.2	57.0	+ 0.8
701	876	15.02	58.4	60.5	+ 2.1
760	950	16.20	58.6	58.1	− 0.5

TABLE VII. Adsorption isotherm constants—the low pressure range.

	7.0 grams quartz	8.1 grams NaCl
c	105	70
d	17	14

A substance like quartz does not accept or give up electrons easily, and therefore a mechanism involving the transfer of electrons is unlikely. But even amorphous quartz has holes in its short range order system from which ions of oxygen are missing. Some of these holes are on the surface. The presence of these holes should make it easier for negative ions to transfer from the nickel to the quartz. It is possible that the ions of the adsorbed gas molecules, oxygen or nitrogen, are transferred from the nickel to the quartz on contact and carry the charge.

In the case of sodium chloride this mechanism necessitates either the transfer of positive ions from the nickel to the sodium chloride or the transfer of negative ions from the sodium chloride to the nickel. The transfer of positive oxygen ions seems an unlikely process. An alternative process is the transfer of negative ions of gas molecules adsorbed by the sodium chloride or the transfer of chlorine ions from the surface of the sodium chloride. In either case the awkward point is the constancy of the constant a of Eq. (3) in all the experiments. If we accept this latter mechanism and also the constancy of a, we must believe that nickel and sodium chloride behave in much the same way in adsorbing oxygen and nitrogen.

Further study of the phenomenon is needed before even an hypothesis for the mechanism can be made. In spite of the conflicts introduced by the ionic mechanism, it still seems more likely than an electronic mechanism.

ACKNOWLEDGMENTS

The author wishes to express his thanks and appreciation to Professor L. B. Loeb at whose suggestion the problem was undertaken and under whose direction it was carried out. In addition the author wishes to thank W. M. Taylor, Jr., and E. H. Guyon for their aid in the construction of the apparatus.

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The Mechanics of the Condensation of Gases

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An attempt is made to explain the phenomenon of condensation of the gas, on the basis of the classical mechanical model of a gas. The condensation of the gas is connected with a change in the topological structure of the energy surface in the $6N$-dimensional phase space. This occurs when the total energy is zero. The agreement with experiment is satisfactory.

1. INTRODUCTION

THIS paper is based on the assumption of a classical model for a gas: It is composed of N point masses attracting and repelling each other; the force between two molecules is derived from a potential $ar^{-n}-br^{-m}$, where r is the distance between them; a, b, n, m are positive constants (which we will consider as known from experiment) with $n>m$. We neglect internal degrees of freedom of the molecules. The differential equations governing the motions determine a family of trajectories in the $6N$-dimensional phase space. If the total energy of the system is fixed, equal to c, the trajectories are restricted to a $(6N-1)$-dimensional manifold $M(c)$. It is to be remembered that, since in a gas there is never any information as to the initial conditions of the individual molecules, this manifold (and the volume, see Section 5) is the only thing that is physically given.

The structure of $M(c)$ is analyzed for varying c and it is found that, for $c\geqq 0$, $M(c)$ has one type of structure, while for $c<0$ the structure is quite different. Roughly speaking, at $c=0$, $M(c)$ collapses from an infinite manifold ($c\geqq 0$) to a finite manifold ($c<0$). It would seem appropriate to identify the energy value zero (where the structure of the manifold changes) with a state of transition of the whole system. This transition would be of the nature of a phase transition, like condensation, for the gas. Accordingly we could say that a transition will take place when the total energy is zero. This last hypothesis combined with the usual statistical method leads to results which can only partially be checked by experiment. One has to make additional assumptions in order to obtain explicit expressions for the transition temperatures. These computations have been made for a number of gases, and a good agreement with experiment is found.

2. ANALYSIS OF $M(c)$

We consider a gas of N particles (x_i, y_i, z_i), $(i=1, 2, \cdots N)$ in xyz space. All masses are assumed to be equal to m. The distance between particle i and particle j is denoted by r_{ij}. With the mutual interaction between the molecules given by $f(r)=ar^{-n}-br^{-m}$ the total potential energy is

$$V=\sum_{i\neq j}\left(\frac{a}{r^n_{ij}}-\frac{b}{r^m_{ij}}\right). \tag{1}$$