and solid phase when projected practically coincide with the point representing the theoretical composition of primary lead orthophosphate.

The stability of the secondary lead and primary lead phosphates at various acid concentrations is, therefore, quite clearly indicated by the diagram, which also furnishes us a means of predicting what happens when various mixtures are brought to equilibrium. Thus, any mixture whose representative points fall within the area ACE will yield a solution with no solid phase; and similarly one can predict the composition of the compound formed in the preparation of any empirical mixture which fall within the limits of the area ABC. The short branch CE delineates the solubility of primary lead phosphate in phosphoric acid at 25°. Its solubility rapidly decreases with increasing acid concentration.

Summary

The isotherm of the system, lead oxide-phosphoric anhydride-water has been traced at 25°.

The results indicate that secondary lead hydrogen phosphate is capable of existing over a considerable range of concentration of phosphoric acid under equilibrium conditions at 25°.

At equilibrium tertiary lead phosphate cannot exist in the presence of even a small amount of acid.

The product of the reaction between secondary sodium phosphate and a lead salt at room temperature is tertiary lead phosphate. This slowly shifts to the secondary lead salt which is the equilibrium product.

BOSTON 17, MASSACHUSETTS

[CONTRIBUTION FROM THE KENT CHEMICAL LABORATORY OF THE UNIVERSITY OF CHICAGO]

A STUDY OF THE LUMINOUS DISCHARGE IN CHLORINE. THE ELECTRON AFFINITY OF HALOGEN MOLECULES

BY W. ALBERT NOYES, JR.

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In a recent article[1] it was shown that the potential necessary to maintain a luminous discharge in bromine was of the same order as that necessary in the case of iodine,[2] and that the potentials for these two electronegative gases were higher than in the case of electropositive gases such as hydrogen and mercury.[3] It was suggested that one could account for this fact without assuming that the halogen molecules as such possessed an electron affinity. The halogen atoms have definite electron affinities

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[1] Noyes, THIS JOURNAL, **45**, 1192 (1923).

[2] Noyes, *ibid.*, **45**, 337 (1923).

[3] (a) Gibson and Noyes, *ibid.*, **44**, 2091 (1922). (b) McCurdy, *Phil. Mag.*, **46**, 524 (1923).

which have been calculated by several different methods[4] and they increase from iodine to chlorine, as one would predict from the chemical properties of these elements. In the arc, however, we are dealing with conditions which are undoubtedly very far from equilibrium and in which the concentrations of the monatomic halogen atoms are very difficult to estimate. It was pointed out that since the heat of dissociation of bromine was higher than that of iodine, the concentration of the former as monatomic gas might reasonably be expected to be lower than the concentration of monatomic iodine, a fact which would counterbalance, to a certain extent, its larger electron affinity.

In the present article it is desired to present a study of the luminous discharge in chlorine and to study as far as possible any conclusions which may be drawn as to the relative ease with which chlorine, bromine and iodine combine with electrons in the gaseous state.

Experimental Procedure

Fig. 1 shows the apparatus used.

H is connected to the McLeod gage and mercury pumps.[5] Before each run the stopcock at P was closed and the plunger in L raised by means of the solenoid surrounding it. The system was then evacuated to a pressure of about 10^{-5} mm., which was as low as could be obtained with the large amount of sulfuric acid and calcium chloride in the line. The line was tested for leaks by leaving it for several days with a pressure of about 0.001 mm. The change in pressure during this time was inappreciable. The evacuation was continued for several days with frequent flaming out of the various parts of the line, especially of the calcium chloride tubes, and with intermittent heating of the filament. During this time liquid air was placed around the U-tube at Q.

The stopcock at M was then closed and concd. hydrochloric acid was allowed to run into the flask A which contained manganese dioxide. The chlorine generated passed through the tube B, containing potassium permanganate, and then bubbled through Column C, containing beads and concd. sulfuric acid. The tube D was filled with glass wool to prevent any spray from being carried along in the stream of gas. The chlorine next passed over calcium chloride contained in the tube E. Practically the only volatile impurities in the chlorine at this point would be traces of water vapor and hydrochloric acid. Chlorine liquefies at —33.6° and hydrogen chloride at —83.1°. The bulb F was immersed in a mixture of carbon dioxide snow and ether. This condensed the chlorine and left the hydrogen chloride, with the exception of a small amount dissolved in the liquid chlorine, in the vapor state.

P was connected directly to a water pump. The tube N was immersed in carbon dioxide snow and ether to prevent back diffusion of much water vapor. This was further prevented by a calcium chloride tube and the four tubes, K, filled with beads and sulfuric acid to within a millimeter or two of the top, so that the gases necessarily passed close to the acid. The tube J was immersed in carbon dioxide snow and ether to take out vapors of sulfuric acid.

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[4] See, for example, (a) Born, *Verh. deut. physik. Ges.*, **21**, 679 (1919); (b) Fajans, *ibid.*, **21**, 714 (1919); (c) Franck, *Z. Physik*, **5**, 428 (1921).

[5] The author wishes to express his appreciation to Messrs. Hanson and Reppert of this Laboratory who perfected these pumps so that they could be used in connection with a water pump. This was advisable on account of the effect of chlorine on the oil pumps.

The stopcock at P was opened and chlorine was continuously withdrawn by the water pump. Since the vapor pressure of chlorine at —80° is over 6 cm., the water pump gave a pressure sufficiently reduced to accomplish this. In this manner most of the hydrogen chloride and water vapor was swept out of the apparatus. This was continued for ten or fifteen minutes, and then the plunger in L was allowed to fall, thereby shutting off the water pump. The carbon dioxide snow and ether were removed from around F and placed around G and the chlorine distilled. The plunger in L was again raised and chlorine drawn out for a short time. Finally the plunger was again allowed to fall and the chlorine was distilled into the bulb I by immersing the latter in liquid air.

The vapor pressure of solid chlorine has not been measured accurately. During the early experiments with the bulb I immersed in carbon dioxide snow and ether the filaments burned through very readily and it was impossible to start the glow. Liquid air was next tried. The discharge was exceedingly hard to start in this case. The vapor pressure of chlorine at liquid air temperatures was apparently in the neighborhood of 0.001 mm. It was accordingly necessary to find a fixed point between these two temperatures. Ethyl ether at its melting point (—116.2°) was next tried. The ether was frozen by placing it in a test-tube large enough to surround the trap I and then immersing the tube in liquid air. The test-tube was placed in a Dewar flask, and the temperature remained constant for sufficient time to allow a few readings to be taken. The vapor pressure of chlorine at this temperature was apparently about 1 mm. The filament burned through easily, and it was impossible to start the discharge.

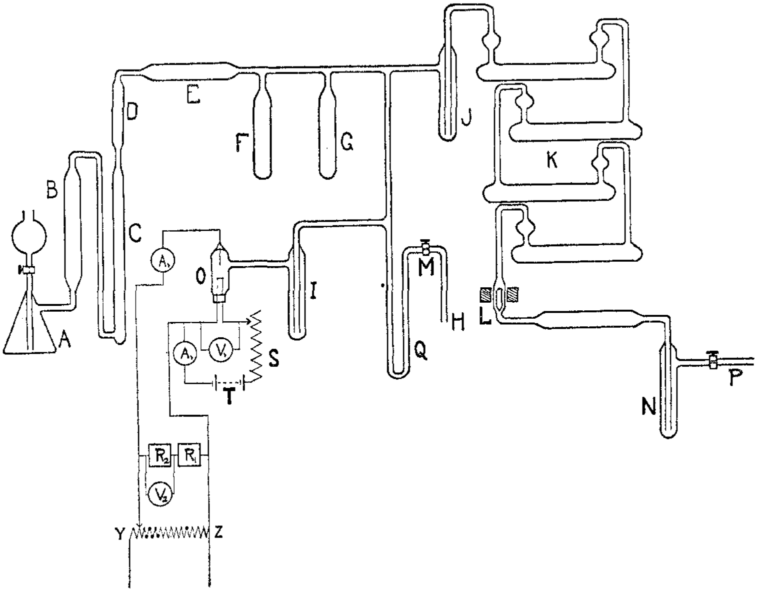

Fig. 1.

The next material tried was acetaldehyde, which was frozen in the same manner as the ether. The temperature was read by means of a pentane thermometer and was found to agree well with the temperature given in the literature (—120.7°). A few points were made in this manner and the chlorine apparently had a vapor pressure of about 0.5 mm. at this temperature. The acetaldehyde oxidized slowly, however, and it was soon impossible to attain the fixed point without freezing it solid.

The bath which was finally chosen for nearly all of the experiments described was one of ethyl chloride at its melting point (—141°). This substance was frozen in the manner described above. After two or three readings had been taken the ethyl chloride was removed from around the tube I and the plunger in L raised. Chlorine was drawn out for several minutes to remove traces of air which might have been given out by the filament or the glass walls of the discharge tube.

The first runs made were extremely erratic and the constancy finally obtained was not nearly as good as that obtained with bromine or iodine. This erratic behavior was probably due to the presence of traces of air. For each tube, however, a minimum value for the potential necessary to maintain the arc was obtained. This point was always more reproducible than the others. In the case of iodine and bromine it was shown that traces of air increased the value of this voltage markedly, and it may be assumed, by analogy, that air would produce a similar effect in chlorine. These minimum values were taken, therefore, as the ones most characteristic of the tubes studied.

The readings were taken in the same manner as for bromine and iodine. To reduce the personal element as much as possible, a series of points was taken in which the resistances R_1 and R_2 were varied at random and the voltage across the tube was calculated by the formula

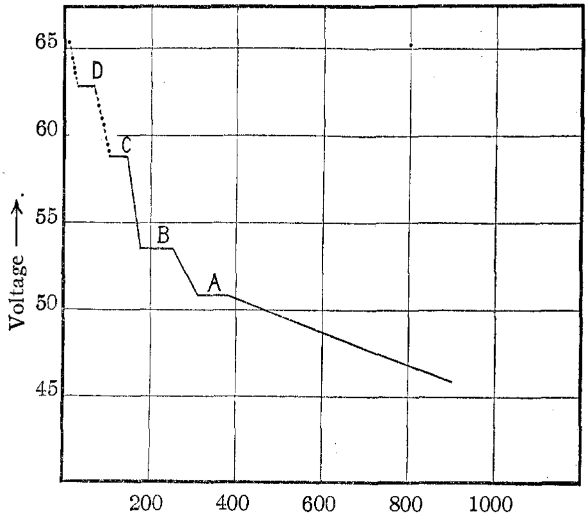

Fig. 2.

$$V_r\left(\frac{R_2R_v}{R_2+R_v}+R_1\right)\Big/\frac{R_2R_v}{R_2+R_v} = V_{\text{total}}$$

where R_2 and R_1 are the values of the resistances, R_v the resistance of the voltmeter, V_2, V_r the voltage as read on the voltmeter and V_{total} the voltage across the tube.

As the slider of the resistance YZ was moved from Y toward Z after the discharge was started, curves of the type shown in Fig. 2 were sometimes obtained when V_{total} was plotted against the current as read by the milliammeter A_2. The increase in voltage as the slider is moved in the direction of Z may be accounted for by the increase in resistance of the gas in the tube as the amount of ionization decreases. The corners, were, of course not as sharp as shown. Some of the points observed in this manner may have a definite meaning. This point will be discussed more fully later.

The chlorine attacked the electrodes rapidly during the first instant or two of discharge due, perhaps, to a layer of adsorbed chlorine on the tungsten. When the chlorine was sufficiently pure the electrodes were very little attacked at the pressures used.

Table I gives the minimum values of E_d for the tubes studied. E_d as here used, is the voltage just before the last large decrease in current as read by the milliammeter, A_2. This probably coincides[1] with the point of disappearance of the glow.

TABLE I

MINIMUM VALUES OF E_d

Dimensions of tubes: Diameter: 2.5 cm. Distance between electrodes: Tube 1, 0.8 cm.; Tube 2, 1.2 cm.; Tube 3, 1.0 cm.; Tube 4, 0.55 cm.; Tube 5, 0.25 cm.; Tube 6, 0.2 cm.; Tube 7, 0.7 cm.; Tube 8; 0.5 cm.

Tube	Temp. Cl_2 °C.	E_d (av.) v.	No. of readings	Max. dev. v.	Av. dev. v.
1	−183	41.9	5	0.6	0.2
2	121	58.7	10	1.0	.2
3	121	75.8	4	0.1	.1
4	141	50.7	3	.8	.6
5	141	34.2	6	.4	.3
6	141	25.5	18	1.2	.6
7	141	74.9	11	1.3	.6
8	141	26.5	8	0.6	.3

It will be noticed that all of these points are approximately multiples of 8 volts. In many cases critical voltages near these values were obtained in other tubes. Table II gives a summary of all of these points which are multiples of about 8 volts.

TABLE II

SUMMARY OF ALL POINTS WHICH ARE APPROXIMATELY MULTIPLES OF EIGHT VOLTS

Voltage (av.)	Voltage (calcd.)	Difference	No. of points
25.8	(25.8)	(0.00)	26
34.2	33.9	.3	6
41.7	42.0	.3	17
50.1	50.1	.0	16
58.7	58.2	.5	10
66.9	66.3	.6	6
75.1	74.4	.7	15

If each of the successive values is subtracted from the one that follows, these critical potentials are obtained: 8.4, 7.5, 8.4, 8.6, 8.2, 8.2; av. 8.2 with a maximum deviation of 0.7 volt. Three times this value gives 24.6. Subtracting from 25.8 gives a correction of 1.2 volts. This is approximately equal to half the voltage drop across the filament, including leads. If this arbitrary correction[6] is subtracted from the various voltages and the result is divided by the proper integer, the following values are obtained: (8.2), 8.3, 8.1, 8.2, 8.2, 8.2, 8.2; av. 8.2 volts. The column marked "Voltage (calcd.)" in Table II is obtained by multiplying 8.2 by the proper integer and adding 1.2 volts. The differences between the values in Col. 1 and Col. 2 are all less than the experimental error.

Other values were frequently found which may have a definite meaning. For example, 23 points were noticed with an average of 54.1 volts. Subtracting 50.1 from this gives 4.0 volts. It was shown by Gibson and Noyes[3a] and more recently by McCurdy[3b] that the potential required to maintain luminosity in mercury vapor may be some multiple of the ionization potential plus the first resonance potential in certain cases. Halban and Siedentopf[7] have observed a maximum in the absorption spectrum of chlorine at 3340 Å. This would correspond to 3.7 volts. It is barely possible that this may correspond to a resonance potential of chlorine.

Discussion of Results

In the work on bromine and iodine it was assumed that the electron affinity of the halogens was the direct cause of the high potential necessary to maintain luminosity as compared with the potential necessary in an electropositive gas. With recent theories of molecular structure,[8] however, it is difficult to see just why a chlorine molecule should have a decided tendency to take up an electron. It seems more probable that the electron affinity is due to reactions of the following type: $Br_2 + 2e = 2Br^-$. The entropy change for this reaction can be calculated from the entropy change of the two reactions, $Br_2 = 2Br$ and $Br + e = Br^-$, by use of the Sackur equation for a monatomic gas[9] which has been shown to apply

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[6] The application of this correction is purely arbitrary. In all of the work the potential is measured from the negative end of the filament which, since the resistance of the leads is not negligible, makes the measured potential slightly greater than the actual potential between cathode and anode. In the work on iodine it was shown that this potential was approximately equal to the correction for thermal emission velocity of the electrons and since the two corrections are of opposite sign no resultant correction was needed. In the present case, for reasons of economy of space, it was found necessary to make the leads much longer which increased the potential drop along them. In this case the algebraic sum of the two corrections was no longer nearly zero but is, approximately, equal to 1.2 volts. If this correction is neglected and the values in Col. 3 of Table I are divided by the proper integer the following values are obtained: 8.4, 8.4, 8.4, 8.4, 8.5, 8.5, 8.3, 8.8; av. 8.5 volts. This is higher than the value (8.2) found by subtracting successive multiples.

[7] Halban and Siedentopf, *Z. physik. Chem.*, **103,** 71 (1922).

[8] See, for example, Lewis, THIS JOURNAL, **38,** 762 (1916).

[9] Lewis and Randall, "Thermodynamics and the Free Energy of Chemical Substances," McGraw-Hill Book Company, **1923,** p. 457.

within experimental error to the entropy of electron gas.[10] The change in entropy for the second of these reactions is equal to $-S_e$, the entropy of the electrons, since by the Sackur equation the entropies of Br^- and Br should be equal. This point may be open to question, especially since the electron acquired by the bromine atom may be in a different state from the remaining seven valence electrons. This will serve as a first approximation, however. For the first reaction the entropy of bromine gas as given by Lewis, Gibson and Latimer[11] was taken, namely, $S(^1/_2Br_2, \text{gas}) = 27.7$. For the reaction Br_2 (g) + 2e (g) = $2Br^-$ (g); $\Delta S^\circ_{298} = 15.6$. The heats of reaction can be calculated from the known heat of dissociation of bromine,[12] 52,400 calories, and the value of the electron affinity of bromine atoms, —87,000 calories, of Fajans.[4b] For the above reaction, therefore, $\Delta H = -121{,}600$ and $\Delta F^\circ_{298} = -126{,}200$.

Similar calculations were carried out for iodine and chlorine. In the case of iodine, the heat of dissociation (36,860) is known[13] and the electron affinity calculated by Fajans[4b] agrees well with the spectroscopic value of Gerlach and Gromann[14] (—81,000 and —81,800, respectively).

Foote and Mohler[15] in interpreting the ionization potential of hydrochloric acid, used 112,000 calories and —119,000 calories as the heat of dissociation and the electron affinity of chlorine, respectively. The heat of dissociation of chlorine as now given is 70,000 calories[16] which is probably more accurate than the older value. However, as pointed out by Latimer,[17] the electron affinity of chlorine according to Franck's interpretation of the spectra of the halogens[18] is now given as —90,000 calories, and these new values lead to the same value of the ionization potential of hydrogen chloride as that calculated by Foote and Mohler. The new values were, accordingly, used in the calculation.

For the three halogens the following values were obtained.

$$Cl_2(g) + 2e(g) = 2Cl^-(g);\ \Delta F^\circ_{298} = -114{,}000$$
$$Br_2(g) + 2e(g) = 2Br^-(g);\ \Delta F^\circ_{298} = -126{,}000$$
$$I_2(g) + 2e(g) = 2I^-(g);\ \Delta F^\circ_{298} = -130{,}000$$

These values are all negative and large. This probably means that an electron must reach ionizing speed in a shorter distance than the mean free path in order to start an arc, since the number of free electrons would be negligible if equilibrium were reached.

[10] Tolman, THIS JOURNAL, **43,** 1592 (1921).

[11] Lewis, Gibson and Latimer, *ibid.*, **44,** 1008 (1922).

[12] Lewis and Randall, *ibid.*, **38,** 2352 (1916).

[13] Lewis and Randall, *ibid.*, **36,** 2259 (1914).

[14] Gerlach and Gromann, *Z. Physik,* **18,** 239 (1923).

[15] Foote and Mohler, THIS JOURNAL, **42,** 1832 (1920).

[16] Ref. 9, p. 500.

[17] Latimer, THIS JOURNAL, **45,** 2803 (1923).

[18] Franck, *Z. Physik,* **5,** 428 (1921).

The interpretation of the ionization potential of chlorine is exceedingly difficult with the data available. Hughes and Dixon[19] have also observed a critical potential in chlorine at 8.2 volts. The ionization potential of iodine as found by several observers is approximately 10 volts. If this corresponds, as indicated, to dissociation and ionization of one of the two atoms, the ionization potential of the atom should be 8.4 volts. For bromine, the value found was 12.5 volts, which would give 10.2 volts as the ionization potential of the atom. The ionization potential of chlorine is apparently lower than that of either iodine or bromine. The electron affinities correspond to 3.4, 3.7 and 3.9 volts, and one would expect the ionization potentials of the atoms to vary in the same direction.

It seems likely, therefore, either that the potential of 8.2 volts does not correspond to an ionization potential or else that the ionization potential of chlorine corresponds to the formation of a molecular ion. It is possible that the chlorine is in a metastable state, either due to the light from the filament or to radiation in the arc or to successive electron impacts. It has been shown by Compton and Smyth[20] that the ionization potential of fluorescing iodine is lower than the ionization potential of normal iodine. Wendt, Landauer and Ewing[21] have shown that chlorine which has previously been exposed to sunlight reacts more readily with hydrogen than ordinary chlorine for some time afterwards. They ascribe this to the destruction of inhibiting impurities. It is barely possible that in our case we are dealing with some such phenomenon and that the "activated" chlorine is more easily ionized than normal chlorine. However, this "activated" state would necessarily differ in energy from ordinary chlorine by an amount corresponding to about 5.0 volts in order to make the ionization potential of the chlorine atom greater than that of the bromine atom. This does not seem probable. It is more reasonable to explain the low ionization potential on the basis of the formation of a molecular ion.

The potentials necessary to maintain luminosity in iodine, bromine and chlorine are of the same order, which agrees with the work of Gibson and Noyes[22] on the sparking potentials in these gases. These were found to be 4, 4 and 3 (air = 1), respectively.

Summary

1. The luminous discharge in chlorine usually disappears at some multiple of 8.2 volts plus a small correction.

2. It is shown by thermodynamic reasoning that the halogen molecules may take up electrons according to the reaction $X_2 + 2e = 2X^-$. The free-energy change is large and negative, which probably means that the

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[19] Hughes and Dixon, *Phys. Rev.*, **10,** 495 (1917).

[20] Compton and Smyth, *ibid.*, **16,** 501 (1920).

[21] Wendt, Landauer and Ewing, THIS JOURNAL, **44,** 2377 (1922).

[22] Gibson and Noyes, *ibid.*, **43,** 1255 (1921).

electrons must attain ionizing speed in a shorter distance than the mean free path.

3. Certain points were obtained at some multiple of the ionization potential plus 4.0 volts. This corresponds to a strong absorption band in chlorine and it is suggested that this may be one resonance potential of chlorine.

4. The relation of the ionization potentials of iodine, bromine and chlorine to one another is discussed.

5. It is suggested that the point at 8.2 volts in the case of chlorine corresponds to the formation of a molecular ion.

CHICAGO, ILLINOIS

[CONTRIBUTION FROM THE DEPARTMENT OF PHYSICAL CHEMISTRY OF THE UNIVERSITY OF LIVERPOOL]

STUDIES IN CHEMICAL REACTIVITY

II. THE ANTHRACENE ⇆ DIANTHRACENE REACTIONS, PHOTOCHEMICAL AND THERMAL

BY H. AUSTIN TAYLOR AND W. C. M. LEWIS

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On exposure to sunlight a solution of anthracene in benzene produces dianthracene, as was first shown by Fritzsche in 1866.

The photo-polymerization and thermal depolymerization processes have been examined in considerable detail by Luther and Weigert,[1] the investigation being continued by Weigert as well as by Byk,[2] the latter from the theoretical standpoint only. Earlier work is cited in the papers referred to. The considerations involved in these modes of treatment belong to a period at which the possibility of viewing the processes from the point of view of the quantum theory had not yet been recognized. It is of interest, therefore, to see to what conclusions a quantum treatment, as expressed in the radiation hypothesis of thermal change, leads.

Luther and Weigert used in general the mercury vapor lamp as a source of illumination, the anthracene solutions being enclosed in glass vessels so that presumably the ultraviolet region was cut off and the effects (such as the polymerization) are to be attributed, in agreement with Luther and Weigert themselves, to the violet end of the visible spectrum.

It is stated by Perrin[3] that while photo-polymerization is going on the solution fluoresces in the "indigo-violet." This would correspond approximately to a wave length of about $450\mu\mu$.

Incidentally, the velocity of thermal depolymerization of dianthracene at more than one temperature has been more completely investigated

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[1] Luther and Weigert, *Z. physik. Chem.*, **51**, 297 (1905); **53**, 385 (1905).

[2] Byk, *ibid.*, **62**, 454 (1908).

[3] Perrin, *Ann. phys. chim.*, **10**, 133 (1918); **11**, 1 (1919).