the fact observed by Posnjak and Merwin[12] that the compound present in the product of the cyanide process of nitrogen fixation is crystallographically different from ordinary sodium cyanide.

Acknowledgment.—The authors desire to express their indebtedness to Dr. J. M. Braham for suggestions and criticisms during the progress of this investigation.

Summary

The formation of sodium cyanide in a mixture of sodium carbonate, carbon and iron catalyst when heated in nitrogen takes place through (1) the reduction of sodium carbonate to metallic sodium, (2) the formation of sodium carbide from the elements, and (3) the absorption of nitrogen by (gaseous) sodium carbide to form sodium cyanide.

Iron has been shown to exert a marked catalytic effect on the absorption of nitrogen by sodium carbide, but does not appear to be essential for the reduction of sodium carbonate or for the formation of sodium carbide.

WASHINGTON, D. C.

NOTES

Rapid Corrosion of Metals by Acids within Capillaries.—About eight years ago the writer observed an interesting effect of hydrochloric acid upon iron surfaces in capillary spaces. So far as he is aware, this effect has not been previously described, so he feels that it may be well to present it at this time. The following simple experiment, which has been several times repeated, shows the nature of the effect. A rubber band is wrapped rather tightly about a piece of soft iron. The iron is immersed in dil. hydrochloric acid for a week or two. At the end of this time, the iron will be found to have been eaten away or pitted beneath the rubber. The acid has acted more rapidly within the capillary spaces between the rubber and the metal than it has upon the exposed surfaces. The experiment was modified, with the same result, by clamping two flat pieces of iron together and immersing them in acid. Also, the action was observed visually by using a glass slide attached to a flat piece of iron. Beneath the glass the capillary space was seen to be largely filled with greatly flattened bubbles, the boundaries of which were in slow but constant motion. The bubbles would extend till the edges of the slide were ap-

Original surface.

After pickling in HCl, showing pitting effected beneath a rubber band.

Fig. 1.

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[12] Posnjak and Merwin, *J. Wash. Acad. Sci.*, **9**, 282 (1919).

proached, when suddenly a break to the edge would occur, and small bubbles would be ejected with violence into the outer liquid. The contracted bubble would then resume its growth as before. There was thus a continual washing of the capillary surfaces, which may be partly responsible for the more rapid action there.

There is, however, a more important reason for this more rapid attack of the metal in the capillaries. This explanation is based on the belief that the rate of solution of a metal in a non-oxidizing acid is limited partly by the concentration of dissolved hydrogen at the metal surface. Solution of the metal may occur no faster than the hydrogen can escape from its surface. Now if the pressure of dissolved hydrogen is too low to cause bubbles to form, the escape of hydrogen must take place by diffusion and convection through the liquid into the atmosphere above, and will in general be very slow. When, however, a bubble lies upon the metal surface, an easy way of escape is offered the hydrogen, and the pressure in the solution is relieved at this point. This permits the metal beneath and about the bubble to dissolve at an increased rate, leaving a pit into which the bubble or its successors will sink. This may then be the explanation for the more rapid corrosion within the capillary spaces. The capillaries become filled with flattened or lengthened bubbles, while over the external surfaces small, round bubbles are scattered only here and there. The capillary surfaces are for this reason the more rapidly corroded.

This explanation is that of MacInnes and Adler[1] for hydrogen overvoltage, which they attribute to supersaturation of the surface with hydrogen, finding that a fall in overvoltage occurs when a bubble appears upon the cathode surface. Minute bubbles retained in capillaries may be the principal nuclei at which bubbles of hydrogen are liberated. A porous metal will then have a lower overvoltage than the same metal having a perfectly continuous surface.[2]

For this effect of acids in capillaries to be well observed two conditions are essential. First, the acid must not attack the metal with too great ease, else the solution within the capillaries will become rapidly exhausted, and the outer metal will be the more rapidly corroded. Second, the metallic product formed within the capillary must be soluble, else the capillaries will become clogged and the action cease from this cause, as is the case with dil. phosphoric acid and iron.

Such a capillary effect is encountered in the deep etching and pickling

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[1] MacInnes and Adler, THIS JOURNAL, **41,** 194, 2019 (1919).

[2] By this means also Whitman and others [*Ind. Eng. Chem.*, **15**, 672 (1923)] account for the greatly decreased rate of corrosion of a steel shaft in sulfuric acid when rotated rapidly. The evolution of hydrogen is rendered more difficult because the metal surface is washed free from hydrogen bubbles.

of metals with non-oxidizing acids. The pores and intergranular spaces of the metal may be enlarged, the action proceeding deep within the interior of apparently sound metals. Capillaries probably play their part, also, in the ordinary corrosion of unsound metals. Even when metals are apparently sound, pores too small to be detected with the microscope may be the obscure cause of deep penetration and pitting. This type of corrosion may be looked for in the case of metals submerged in the absence of oxygen. Wherever bubbles can be retained there may be more rapid action.[3]

It is believed that this type of corrosion is quite important and worthy of further study.

CONTRIBUTION FROM THE
RESEARCH DEPARTMENT OF THE
WESTINGHOUSE ELECTRIC AND MANUFACTURING COMPANY
EAST PITTSBURGH, PENNSYLVANIA
LEON McCULLOCH

RECEIVED APRIL 22, 1925
PUBLISHED JULY 3, 1925

A Simple Differential Air Thermometer for Use at Low Temperatures.—Having occasion recently to separate mixtures of nitric oxide, nitrous oxide, hydrogen chloride and nitrosyl chloride and to examine the mixtures for other possible gases boiling at intermediate temperatures, I have devised a simple air thermometer for the approximate determination of temperatures between the boiling point of liquid air and zero.

A bulb with a capacity of 2.5 to 5 cc. is blown at the end of a capillary tube 50 cm. in length and with an internal diameter of about 0.8 mm. A small globule of mercury, enough to occupy a length of about 5 mm. of the capillary, was introduced and, by cooling the bulb slightly, this was brought to a position about 100 mm. from the end, and the end was sealed. It is evident that if the temperature of the air in the capillary above the globule remains constant, and we disregard the small change in the volume of the air below the mercury and the transfer of air from the capillary to the bulb, the pressure in the bulb will vary directly as the absolute temperature. Taking the length of the column of air above the mercury as 1 at 0°, the length at any other temperature may be calculated, approximately, by the formula $273 \times 1/T$, in which T is the absolute temperature. The calculation gives the following values.

Temp., °C.	0	−10	−20	−30	−40	−50	−60	−70	−78.5	−80	−90
$273 \times 1/T$	1	1.039	1.079	1.123	1.172	1.224	1.282	1.345	1.404	1.414	1.492
Temp., °C.	−100	−110	−120	−130	−140	−150	−160	−170	−180	−190	−191.6
$273 \times 1/T$	1.578	1.674	1.784	1.908	2.052	2.219	2.415	2.649	2.936	3.286	3.351

With the temperature of the room at 25°, three points are fixed on the stem for the top of the mercury when the bulb is immersed in melting ice,

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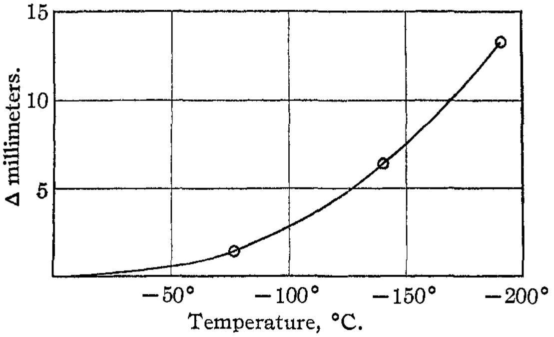
[3] Shipley, McHaffie and Clare, *Ind. Eng. Chem.*, **17**, 381 (1925).

in a mixture of carbon dioxide snow with ordinary alcohol, and in fresh liquid air. The carbon dioxide snow in alcohol is quite accurately —78.5° at 760mm. pressure, with a change of 0.1° for 10 mm. That of liquid air is —191.62°.[1]

By measuring the length of the column of air from the zero point to the end and multiplying this by the numbers given in the table, the approximate locations on the stem of the several temperatures given in the table have been calculated. The differences between these observed and calculated values for —78.5° and for —191.6° are then plotted as ordinates with temperatures as abscissas. If the portion of the curve from 0° to —78.5° is practically a continuation in a straight line of that from —78.5° to —191.6°, the differences for each 10° may be read from the graph and used to correct the calculated values to true values. If the line is not straight, the coefficients a and b may be calculated for the empirical equation, $at^{\circ} + bt^{\circ 2} = \Delta$, using for Δ the differences at —78.5° and —191.6°. With these coefficients Δ may be calculated at —140° and a more accurate graph may be drawn. The accompanying figure illustrates a graph prepared as described.



After fixing points at 10° intervals by means of the graph, single degrees may be marked at equal intervals between these points with a maximum error of about 0.3° in the lower part of the scale and less above that.

It can be seen from the table that the thermometer is most sensitive at low temperatures, the interval for 1° being about eight times as great at —190° as at —40°. Also, a difference of 1° from the standard temperature of 25° for the air above the mercury will cause an error of only 0.3° at —190°, while the error is 0.93° at 0° and 0.67° at —80°.

By using hydrogen in the bulb and careful calibration, a thermometer of this type could be made quite accurate even down to the temperature of liquid hydrogen.

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[1] These values are given me by Professor Rodebush, who has checked them rather accurately.

After using for some weeks a thermometer constructed as described, the points at 0° and at —78.5° were found to be unchanged, indicating that there had been no leakage of air past the mercury.

CONTRIBUTION FROM THE
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Possible Limits for the Heat of Dissociation of Oxygen.—The ionization of oxygen to form singly charged oxygen molecules has been found to occur at about 16 v. by Lockrow and Duffendack[1] and by Smyth.[2] In their study of the low-voltage arc in oxygen, Lockrow and Duffendack find a marked strengthening of lines and the appearance of new lines at 19.5 v.,[3] and they ascribe this to dissociation and simultaneous ionization of one atom.[1] Smyth, working at low pressures and using his method of positive-ray analysis, did not find oxygen atom ions below 23.0 v.

For the similar process in hydrogen Smyth showed that the appearance of atom ions depended on a secondary process involving collisions, since by changing the pressure in the impact region, the voltage at which atom ions appeared could be greatly altered, this voltage decreasing as the pressure increased, until atom ions appeared at the same point as molecule ions.

Returning to the case of oxygen, in view of the fact that at very low pressure, oxygen atom ions do not appear until a considerably higher voltage is reached than that at which they appear at the relatively large pressures used in the low-voltage arc, it would seem probable that excited oxygen molecule ion can dissociate into oxygen atom and oxygen atom ion upon collision with some neutral particle, provided that its energy is greater than, or equal to, the energy change represented in such a process of dissociation. Now, atom ions are not found to occur at 16 v. and, therefore, unless the state of the molecule ion corresponding to 16 v. is metastable, for some special reason not being able to dissociate upon collision, the 16 v. molecule ion does not possess the energy necessary for the dissociation. The molecule must possess more energy than that represented by 16 v. to be able to dissociate upon collision. It appears that at 19.5 v. the excited molecule ion has sufficient energy to undergo this change upon collision. It may well be, however, that the energy increase represented in the dissociation is less than that corresponding to 19.5 v., but that under 19.5 v.

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[1] Lockrow and Duffendack, *Phys. Rev.*, **25**, 110 (1925).

[2] Smyth, *Proc. Roy. Soc.* (London) **105A**, 116 (1924).

[3] Communicated by Dr. Duffendack in a letter to the author.

there is no state of the molecule ion the energy of which is greater than that corresponding to the dissociation. Again, there may be such a state, but it may be metastable, one which upon collision will not undergo dissociation. Considering, then, that this value may be somewhat greater than that strictly required in the change alone, a maximum value can be calculated for the heat of dissociation of oxygen; and a minimum value can be determined, since no atom ions occur at 16 v.

These calculations can be made in the familiar way from the following simple thermochemical considerations. The reactions in question can be represented by the following equations.

$$O_2 = O + O^+ + E^- \qquad (1)$$
$$O = O^+ + E^- \qquad (2)$$

Subtracting (2) from (1) there results

$$O_2 = 2O \qquad (3)$$

The heat of ionization corresponding to Equation 2 can be found from the ionization potential of the atom, which has been determined spectroscopically by Hopfield[4] to be 13.56 v. This corresponds to a heat of ionization of 312,600 cal. per mole. The heat of dissociation and simultaneous ionization of one atom corresponding to Equation 1 is not greater than the energy corresponding to 19.5 v. which is 450,000 cal. per mole, and not less than that corresponding to 16.0 v. which is 369,000 cal. per mole, for the reasons given above. The difference in the first case is 137,400 cal. and in the second 56,400 cal. Therefore, the heat of dissociation of molecular oxygen into atomic oxygen is not less than 56,400 cal. per mole and not greater than 137,400 cal. per mole. While these limits are wide, it is believed that they are narrower than could be given heretofore.

The writer wishes to express his acknowledgment to Professor Richard C. Tolman and to Dr. George Glockler for helpful discussion of these matters.

CONTRIBUTION FROM THE
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OLIVER R. WULF

RECEIVED APRIL 16, 1925
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Germanium. XI. Germanium Glasses. Preliminary Note.—The positions of silicon and germanium in Mendeléeff's Periodic Table make it evident that close analogies between the compounds of the two elements are to be expected. The compounds of germanium which have thus far been isolated and studied, in particular the hydrides, the halides, germanium tetra-ethyl and germanium chloroform, bear out this view,

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[4] Hopfield, *Nature*, **112**, 437 (1923).

although in some cases germanium shows a closer resemblance to tin, the element below it in Group IV, than to silicon.

It therefore seemed reasonable to suppose that glasses similar to the silicate glasses, but in which the silicon dioxide is replaced by germanium dioxide, could be prepared. This has been found to be the case, and thus far four different germanium glasses, a very dense flint, a flint, a borate crown and a barium crown have been made and superficially studied. To render it possible to compare these glasses definitely with similar silicate glasses, identical mixtures were used in the preparation of the corresponding samples except that the silica in the one was replaced by an equimolecular quantity of germanium dioxide in the other.

Table I gives the composition of the "mix" in parts by weight and the refractive index of the resulting glass for each of the four kinds mentioned above, with the corresponding silicate glass in the adjacent column.

TABLE I

COMPARISON OF GERMANIUM AND SILICATE GLASSES

	Very dense flint		Flint		Borate crown		Barium crown	
	Si No. 1	Ge No. 2	Si No. 3	Ge No. 4	Si No. 5	Ge No. 6	Si No. 7	Ge No. 8
Refractive index n_D	1.967	2.068	1.644	1.794	1.5172	1.619	1.5726	1.670
SiO_2	18.0	..	41.3	..	67.850	...	48.323	..
GeO_2	..	31.2	..	71.61	..	117.652	..	83.80
K_2O	..	..	6.8	6.8	8.580	8.580	8.326	8.326
Na_2O	..	..	..	..	8.333	8.333	..	..
BaO	..	..	..	..	3.163	3.163	30.039	30.039
B_2O_3	..	..	..	..	11.869	11.869	3.163	3.163
ZnO	..	..	..	..	..	..	9.665	9.665
PbO	82.0	82.0	51.6	51.6	..	..	..	..
As_2O_3	0.1	0.1	0.3	0.3	0.204	0.204	0.483	0.483

The two germanium flint glasses, Nos. 2 and 4, had a yellowish tinge which was due to the high percentage of lead which they contained. The corresponding silicate glasses showed the same color. The other two germanium glasses were very transparent, free from color and apparently quite stable. Germanium glasses homogeneous in character and free from air bubbles can be prepared much more easily than the corresponding silicate glasses because they melt at considerably lower temperatures than the latter.

As is shown in the table, the replacement of silicon by germanium in the several glasses raises the refractive index in each case.

It is proposed to make a detailed study of germanium glasses in this Laboratory, and to determine the optical, physical and chemical properties of various types.

The preparation of fused, transparent germanium dioxide is also being investigated, and it has already been found to be possible to obtain this in clear, transparent form quite similar in appearance to fused quartz.

Contribution from the
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Filling Mercury Manometers.—The method of filling mercury manometers described by Swan[1] is similar to one which has been found very convenient in this Laboratory. In the latter method, the mercury is distilled into the manometer in a high vacuum. The apparatus is shown in Fig. 1. The bulb A contains the mercury. B is a by-pass for the escape of any gas liberated during the distillation after mercury has sealed off the bottom of the manometer. The vacuum pump is connected at C. After the manometer is filled, the constriction at D is sealed off, air is admitted and a cut made at E.

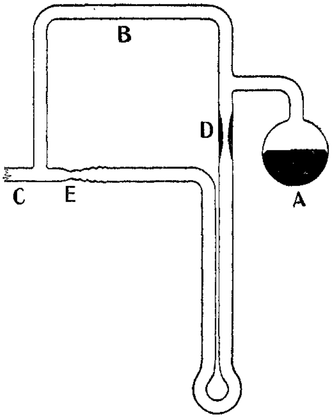

Fig. 1.

The distillation makes it easy to obtain clean mercury surfaces and does away with the necessity of boiling out small tubes. If care is taken to see that all air held by the mercury and the tubes is driven off before the outlet through the manometer is closed by mercury, the by-pass may be found to be unnecessary.

Contribution from the
Chemistry Laboratory
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Philip F. Weatherill

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Published July 3, 1925

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[1] Swan, This Journal, **47**, 1341 (1925).