and Edgar, the addition of chloride ion has no effect on the potential of the nitric acid electrode, but it does result in the more rapid evolution of a gas which the experiment cited above shows is probably nitric oxide. It is possible, therefore, that the chloride ion may act in such a manner that either it tends to displace the equilibrium indicated in equation (1) above to the left, or else it increases the tendency for nitric acid to act as an oxidizing agent in accordance with the equation:

$$4H^+ + NO_3^- — 2H_2O + NO + 3\oplus .$$

These points will be studied more carefully.

Summarizing then, we may say:

1. That it is impossible to get a constant value for the oxidation potential of the tenth-normal nitric acid electrode saturated with nitric oxide, because of the increase in the concentration of nitrous acid due to the direct reduction of nitric acid to nitrous acid by the nitric oxide and by the reduction of nitrate to nitrite ions so that positive charges are available to set up an electromotive force in an oxidation-reduction cell.

2. The chloride ion depresses the potential of the nitric acid electrode, probably because it decreases the tendency toward nitrite ion formation. Where no nitric oxide is introduced externally, this depression is probably permanent instead of temporary.[1]

3. The oxidation potential of tenth-normal nitric acid in equilibrium with nitrous acid and nitric oxide at atmospheric pressure is quite definit. Chloride ion has no effect on this potential, the mean value of which, taken from six separate and distinct experiments, using two different electrodes, is 0.4723 volts measured against a tenth-normal calomel electrode at 25.17±0.02°.

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[CONTRIBUTIONS FROM THE RESEARCH LABORATORY OF PHYSICAL CHEMISTRY OF THE MASSACHUSETTS INSTITUTE OF TECHNOLOGY, NO. 94.]

THE POTENTIAL OF THE LITHIUM ELECTRODE.

BY GILBERT N. LEWIS AND FREDERICK G. KEYES.

Received February 17, 1913.

The method used in measuring the electrode potentials of sodium[2] and potassium[3] has, with some modifications, proved applicable to the determination of the potential of the lithium electrode.

Owing to the extreme solubility of metallic lithium in ethyl amine, this solvent could not be employed. Preliminary measurements had indicated the insolubility of lithium in propyl amine; and, after lithium iodide was found to be soluble in this solvent, it was chosen for our experi-

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[1] THIS JOURNAL, 33, 1091.

[2] Lewis and Kraus, *Ibid.*, 32, 1459 (1910).

[3] Lewis and Keyes, *Ibid.*, 34, 119 (1912).

ments. The propyl amine was dried by prolonged standing over liquid sodium-potassium alloy in a vacuum-tight container with a mercury seal, such as has been described in the previous papers. This proved to be an extremely effective means of drying the amine, and can be strongly recommended in the case of other liquids which are commonly dried by solid sodium. The complete dryness of the amine was sharply indicated by the appearance of a faint blue color, showing doubtless that either sodium or potassium is very slightly soluble in this solvent.

A liquid amalgam of lithium was prepared by electrolyzing lithium chloride solution, and collecting the amalgam in vacuum. This amalgam proved by analysis to contain 0.0350 % lithium by weight.

A cell, consisting of one electrode of metallic lithium, one of lithium amalgam, and an electrolyte of propyl amine nearly saturated with lithium iodide, was set up precisely as in previous experiments, every operation being carried out in vacuum. This proved, however, a much more difficult task than in the other cases; for the melting point of lithium is high (192°), and at this temperature, when the molten metal passes into the cell through the fine capillary, it attacks the glass vigorously. This action could not be altogether avoided; but, by previously heating the capillary in vacuum and treating it once or twice with propyl amine, it was possible to reduce the action. Even under these circumstances several attempts were made before a cell was constructed which remained intact.

When the propyl amine was distilled into the arm of the cell containing the metal, there at once appeared a blue color which increased in intensity until the liquid became opaque. This shows that metallic lithium is far more soluble in propyl amine than was shown in the preliminary experiments. Evidently, therefore, the amine used in the first experiment was not completely dry, or the amine used later contained some impurity in which lithium is soluble. However, as soon as the lithium iodide was dissolved the blue color disappeared and the metal seemed to be no longer attacked rapidly.[1]

Measurements of the electromotive force of the cell were begun at once; and, as soon as the solid salt was all dissolved, the electromotive force

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[1] An interesting explanation of the fact that the lithium is soluble in pure propyl amine, but not in a solution of lithium iodide in propyl amine, suggests itself, and is not altogether lacking in plausibility. The work of Kraus (THIS JOURNAL, **30**, 1323 (1908); *Trans. Amer. Electrochem. Soc.*, 21, 119 (1912)) proves almost conclusively that in a case of this kind the dissolved metal is largely dissociated according to the equation

$$\mathrm{Li} = \mathrm{Li}^+ + \mathrm{X}^-$$

where Li^+ is the same ion which exists in a solution of any lithium salt, and X^- is a more or less solvated electron. If we have a dilute propyl amine solution of lithium in equilibrium with the two ions, then the addition of a considerable quantity of lithium ion through the solution of lithium iodide should diminish the solubility of the lithium just as the solubility of silver chloride is diminished by the addition of Ag^+ or Cl^-.

became nearly constant at potentials which varied between 0.9497 and 0.9507. The contents of the cell were shaken from time to time to avoid differences of concentration on the two sides, and after such shaking the e. m. f. differed from the value 0.9502 by only a few tenths of a millivolt at the most. This value was then taken as the true e. m. f. The cell was, however, studied for several days. During this time the e. m. f. gradually diminished and at the end of four days stood at 0.9457. The e. m. f. on any one day was very nearly constant, even though the cell was subjected to drastic treatment (such as tipping it to remove all solution from the lithium electrode and then distilling the amine from the rest of the cell upon this electrode until it once more gave a blue color). The gradual decrease in the e. m. f. must doubtless be ascribed to an increasing concentration of the lithium amalgam caused by slow transfer of metal from the solid electrode.

Three days after the cell was constructed the temperature coefficient of the e. m. f. was determined by transferring the cell back and forth from a thermostat at 25° to one at 35°. The successive measurements of the e. m. f. beginning at 25° were as follows: 0.9459, 0.9489, 0.9457, 0.9489, 0.9456, 0.9488 and 0.9456. The mean temperature coefficient calculated from these data is +0.000322 volts per degree.

From these data we may calculate the heat of solution of lithium in 0.0350% lithium amalgam with the aid of the Gibbs-Helmholtz equation

$$\mathbf{E} + \Delta\mathbf{H}/\mathbf{F} = \mathbf{T}(d\mathbf{E}/d\mathbf{T})$$

where Δ**H** is the heat absorbed when one equivalent of lithium dissolves in a large quantity of the given amalgam, and **F** is the Faraday equivalent 96,494. Substituting for **E** the value 0.9457, and 0.000322 for $d\mathrm{E}/d\mathrm{T}$, we find Δ**H** to be —81985 joules, or —19605 cal.[1] Strictly speaking, this does not represent the heat of solution in 0.0350% amalgam, but in the slightly more concentrated amalgam which existed in the cell at the time of the measurements. However, the difference between the two heats of solution is probably not appreciable.

Having found the difference in potential between the electrodes of solid lithium and lithium amalgam, it was necessary next to determin the electrode potential of the amalgam in aqueous solution. A cell was set up of the form Li amalgam, LiOH (0.1 *M*), LiCl (0.1 *M*), KCl (0.1 *M*), KCl (1.0 *M*), N. E. The lithium amalgam was contained in a vessel, similar to that used in the previous investigations, which permitted the frequent renewal of the electrode surface. The tube leading from the electrode vessel led into another closed vessel containing the lithium chloride solution which, together with the normal electrode, dipped into

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[1] The mechanical equivalent of heat here employed is given by the equation 1 cal. = 4.182 joules. See Lewis, "The Free Energy of Chemical Substances," THIS JOURNAL, 35, 1 (1913).

an open tube containing the 0.1 M potassium chloride. The electromotive force was not as constant as in the corresponding experiments with sodium and potassium amalgams. Not only the electrode surface, but also the whole contents of the electrode chamber and the intermediate vessels, were renewed repeatedly. These changes caused deviations in the electromotive force averaging 0.0003 or 0.0004 volt. The final value was taken as 2.3952 volts.

This electromotive force includes the liquid potentials, of which that one between the 0.1 M KCl and 1.0 M KCl we shall neglect as usual. In order to evaluate the others by the formula of Lewis and Sargent,[1] it is necessary to know the molecular conductivity of the lithium hydroxide, lithium chloride, and potassium chloride solutions employed. The molecular conductivities of the LiOH and the LiCl were determined for this purpose and found to be 204.4 and 97.9. Kohlrausch gives 128.8 for 0.1 M KCl. Then for the potential LiOH (0.1 M), LiCl (0.1 M), we find $E = -0.0189$, and for the potential LiCl (0.1 M), KCl (0.1 M), $E = -0.0070$. Both these potentials oppose the main electromotive force of the cell, and therefore the electromotive force exclusive of liquid potentials is $2.3952 + 0.0259 = 2.4211$ volts. If now we take the "corrected" degree of dissociation[2] of 0.1 M LiOH as 0.74, we may calculate the electromotive force of a similar cell containing lithium ion at molal concentration. We thus find for the cell Li amalgam, Li^+ (1.0 M) || N. E.; $E = 2.4211 - 0.0669 = 2.3542$ volts.

This is the normal electrode potential of the lithium amalgam against the calomel electrode. In order to find the normal electrode potential of solid lithium we need only to add the difference between the potentials of lithium and lithium amalgam given above, namely, 0.9502 volt. We, therefore, find for Li, Li^+ (1.0 M) || N. E.; $E =$ *3.3044 volts.*[3]

This is the highest electrode potential hitherto measured. It is interesting to compare the electrode potentials of the three alkali metals so far measured, and also the heat of solution of these metals in their dilute amalgams, as in the following table:[4]

	Electrode potential against the calomel electrode.	Heat of solution[5] in mercury (cals.).
Li	3.3044	—19605
Na	2.9981	—19790
K	3.2084	—26050

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[1] Lewis and Sargent, THIS JOURNAL, 31, 363 (1909).

[2] See Lewis, *Ibid.*, 34, 1631 (1912).

[3] All the e. m. f. values here given are in terms of the new international volt. The vertical bars indicate that the liquid potentials have been eliminated.

[4] The electrode potentials of Na and K are those given in the previous papers. These are in terms of the old volt, and calculated assuming a degree of dissociation based on the conductivities.

[5] These are the heats of solution in the several dilute amalgams employed. They undoubtedly differ somewhat from the heats of solution in pure mercury.

It has been currently supposed that the electrode potential of lithium would prove to be smaller even than that of sodium;[1] but as a matter of fact the heats of formation of the three ions might have led us to expect the order in which the electrode potentials actually occur, for the heat of formation of lithium ion is nearly 1000 calories higher than that of potassium ion, and the latter is in turn about 5000 calories higher than the heat of formation of sodium ion.

ON A NEW KIND OF ELECTROMOTIVE FORCE AND SOME POSSIBLE APPLICATIONS TO PHYSICO-CHEMICAL PROBLEMS.

[PRELIMINARY COMMUNICATION.]

By Reinhard Beutner.

Received December 2, 1912.

The phenomena which are described in this paper relate to *galvanic cells composed of water-insoluble organic liquids and aqueous solutions. These cells have e. m. fs.* nearly equal to the well-known galvanic cells composed of metals and aqueous solutions and exhibit many interesting properties.

1. The well-known investigations of Nernst have shown that the single potential differences which compose the e. m. f. of whole cells depend on the concentration of the aqueous solution.

A concentration cell is, *e. g.*,

$$-\,\mathrm{Ag}\mid \underset{\text{diluted solution.}}{\mathrm{AgNO_3}}\ldots\ldots\ldots\underset{\text{concentrated solution.}}{\mathrm{AgNO_3}}\mid \mathrm{Ag}\,+$$

which may also be arranged with one single piece of Ag as a middle conductor.

$$+\,\underset{\text{diluted sol.}}{\mathrm{AgNO_3}}\mid \mathrm{Ag}\mid \underset{\text{concentr. sol.}}{\mathrm{AgNO_3}}\,-$$

In order to make an electrical connection with the two silver solutions to the poles of a measuring instrument we have to use electrodes which do not introduce any new e. m. f. by themselves, *i. e.*, calomel electrodes.

In some experimental work, carried out by Dr. Jacques Loeb and myself,[2] it was found that certain vegetable and animal skins exhibited a change of potential difference with concentrations of the same kind as metals; but the question was, to what peculiar property or composition of the membrane this effect was due.

I have now found that a number of water-insoluble substances act in the same way. For instance, with *salicylic aldehyde* as a middle conductor we can build up a cell perfectly analogous to the last one above.

$$-\,m/10\ \mathrm{NaCl}\mid \text{salicylic aldehyde}\mid m/1250\ \mathrm{NaCl}\,+\quad \text{e. m. f. } 0.075 \text{ volt.}$$

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[1] See, for example, Patten and Mott, *J. physik. Chem.*, 8, 153 (1904); Abegg, *Handbuch der anorg. Chem.*, Vol. I, p. 116.

Science, **34**, 886; also in *Biochem. Z.*, **41**, 1.