expresses the variation of the activity coefficient of hydrochloric acid at constant total molality, $m = m_1 + m_2$, with a high degree of accuracy. The parameter, α_{21} , computed by equations 3, 4 and 5 varies with both the total molality m, and the molalities of either of the components according to the linear relationship

$$\alpha_{21} = \alpha_{21(0)} + \beta_{21}m_1 = \alpha_{21(m)} - \beta_{21}m_2 \qquad (8)$$

As a result the activity coefficient of potassium chloride is found to vary quadratically with its concentration. Thus

 $\log \gamma_2 = \log \gamma_{2(0)} - \alpha_{21(0)} m_1 - \beta_{21} m_1^2 \tag{9}$

As pointed out by McKay, thermodynamics requires that β_{21} does not vary with the total molality.

In Table III, the quantities necessary for the rapid computation of the activity coefficients in any of these mixtures from 0.5 to 4 total molalities at 25° are compiled. Suitable values at intermediate molalities can be obtained by interpolation. The osmotic coefficients, $\phi(x)$, in any of these mixtures are given by

$$\phi(\mathbf{x}) - \phi(0) = -\alpha_{21(6)}\mathbf{x} + \frac{1}{2}(\alpha_{12} + \alpha_{21(0)})\mathbf{x}^2 - m\beta_{21}\mathbf{x}^2 + \frac{2}{3}m\beta_{21}\mathbf{x}^3 \quad (10)^4$$

where $\phi_{(0)}$ is the osmotic coefficient of a potassium chloride solution at concentration m, and $x = m_1/m$.

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(4) See Ref. 3, p. 616.

NOTES

ELECTROLYSIS OF SODIUM INTO A REACTION VESSEL¹

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In chemical vacuum-line work, it is often necessary to introduce a small, measured amount of sodium metal into a glass reaction vessel. This is usually accomplished by a tedious process culminating in the breaking of a fragile bulb containing a weighed amount of the metal.^{2,3} This note describes a simpler process for accomplishing the same result.

It is well known that hot glass is an electrical conductor, the current being carried by the mobile sodium ions.⁴ Thus, it is a simple matter to electrolyze a molten sodium salt using an evacuated light bulb as a cathode.^{5,6} By a similar procedure it is possible to electrolyze a measured amount of sodium metal into an evacuated reaction vessel. The advantages of the procedure are (1) the sodium introduced is spectroscopically pure,⁵ (2) the amount of sodium introduced is readily determinable with high accuracy, (3) exceedingly small amounts (of the order of micromoles) of sodium may be introduced, and (4) a predetermined amount of sodium may be introduced. The disadvantages are (1) the sodium usually must be introduced before the other reactants, (2) the tungsten filament must be present during the reaction

(1) This research was sponsored in part by the U. S. Atomic Energy Commission.

(2) R. T. Sanderson, "Vacuum Manipulation of Volatile Compounds," John Wiley and Sons, Inc., New York, N. Y., 1948.

(3) G. W. Watt and D. M. Sowards, J. Am. Chem. Soc., 76, 4742 (1954).

(4) G. W. Morey, "The Properties of Glass," 2nd ed., A.C.S. Monograph No. 124, Reinhold Publ. Corp., New York, N. Y., 1954.

(5) R. C. Burt, J. Opt. Soc. Am., 11, 87 (1925).

(6) D. K. Alpern, J. Chem. Educ., 34, 289 (1957).

unless the sodium is first distilled away or dissolved away, and (3) because an ordinary glass reaction vessel is used, the method is not applicable to other alkali metals.

Experimental

Apparatus.—The apparatus is pictured in Fig. 1. The only unusual item is the reaction vessel, which is constructed of Pyrex glass. Two insulated wires are sealed to tungsten rods which project through glass seals from the bottom of the inner glass tube. The filament from a Sylvania 60-watt light bulb is attached by spot-welding the nickel filament leads to the tungsten rods. The filament is about 1 cm. from the bottom of the reaction vessel. The lower part of the reaction vessel is thin-walled.



The iodine coulometer consists of two platinum electrodes immersed in a potassium iodide solution. In order to prevent convection of the triiodide which forms at the anode, the lower half of the coulometer is filled with a more concentrated solution (ca. 1.0 M) than the upper half (ca. 0.1 M). After each electrolysis, the lower half of the solution is drained and titrated with a standard thiosulfate solution.

Procedure and Results.—The apparatus is set up as shown in Fig. 1 and the reaction vessel is evacuated to a pressure of 1 μ . The current is turned on with the rheostat set at ca. 50 ohms. For the first minute or two there is usually no sodium formation, but rather a blue discharge is established in the reaction vessel and the current fluctuates at a low level. It is suspected that, during this "induction period," water that is firmly bound to the glass is being reduced to hydrogen. However, the blue discharge soon stops, sodium metal begins to condense on the walls of the reaction vessel, and the current rises to ca. 5 milliamp.

Several experiments were performed to prove that the iodiene coulometer provides an accurate measure of the amount of sodium formed. The sodium metal was analyzed by allowing it to react with water and then measuring the evolved hydrogen and titrating the resulting sodium hydroxide solution. The results of four runs are presented in Table I. In all four runs, the time of the electrolysis was

TABLE I

CALCULATED MILLIMOLES OF SODIUM

From iodine coulometer	From hydrogen	From NaOH titration
0.231	0.226	0.221
.386	, 383	.374
.558	.554	.547
785	778	766

measured and the average current was estimated from several milliammeter readings. The number of coulombs calculated from these data and that from the iodine coulometer always agreed to within $\pm 5\%$. If a d.c. current regulator were included in the circuit, it probably would be possible to measure satisfactorily the electrolyzed sodium from timecurrent measurements alone.

THERMAL EXPANSION OF SOME TRANSITION METAL CARBIDES

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The linear thermal expansions of titanium carbide and zirconium carbide have been measured by Gangler¹ to 593 and 538° respectively, using a dilatation interferometer. From his tabulated chemical analyses for major metal, combined carbon and free carbon, it can be calculated that the hot-pressed ceramics used were 94.11% TiC_{0.884}, 95.66% ZrC_{0.882} and 95.25% ZrC_{0.854}. No spectrographic analyses were given. For the temperature range 75–1100°F. (24–593° C.), the average linear expansion coefficient of titanium carbide was 4.12×10^{-6} /°F. (7.42 $\times 10^{-6}$ /°C.). For the temperature range 75–1000°F. (24–538°C.), the value for zirconium carbide was 3.74×10^{-6} / °F. (6.73 $\times 10^{-6}$ /°C.).

The thermal expansion of tantalum carbide has been determined by Becker and Ewest² to 2650° using the X-ray powder method. No chemical or spectrographic analyses were given. From room temperature to 2650° the average linear expansion coefficient was $8.2 \pm 0.8 \times 10^{-6}$ /°C.

(1) J. J. Gangler, J. Am. Ceram. Soc., 33, 367 (1950).

(2) Karl Becker and Hans Ewest, Z. Tech. Physik, 11, 216 (1930).

In determining physical and chemical properties of the transition metal carbides, it is particularly important to obtain fairly complete chemical and spectrographic analyses. This is necessitated by the wide range of non-stoichiometric MC_x compounds crystallizing in the MC structure. For transition groups IV and V this MC structure is NaCl-type.

Experimental

The carbide samples were obtained from Donald H. Schell of the powder metallurgy section at the Los Alamos Scientific Laboratory. The finely divided (325 mesh) samples were sealed for high temperature X-ray diffraction in evacuated silica capillary tubes. In cases where reaction occurred between the metal carbide and the SiO_2 at elevated temperatures, the inside of the capillary tube was first covered with a 1-2 mil coating of nickel formed by the thermal decomposition of nickel carbonyl.

The high temperature X-ray diffraction powder camera used (Central Research Laboratories, Inc., Red Wing, Minnesota) had a diameter of 114.6 mm. and provided temperatures to 1000°. The chromel-alumel thermocouple was calibrated against the lattice constant of silver at various temperatures throughout the region between room temperature and 960°.

The lattice constant was determined in all cases by the linear extrapolation method of Nelson and Riley.³

Results and Discussion

The chemical analyses for major metal, total carbon and free carbon are shown in Table I. The metal and the total carbon were determined by combustion; therefore, the metal value must be corrected from the spectrographic results.

TABLE I

CHEMICAL ANALYSIS RESULTS

Material	М, %	Tot. C,	Free C, %	% M. + % comb. C
Titanium carbide	79.8	20.0	1.6	98.2
Zirconium carbide	88.3	11.0	0.5	98.8
Niobium carbide	88.5	10.6	0.5	98.6
Tantalum carbide	93.8	6.15	< 0.05	99.9

The spectrographic analyses, based on the samples as TiO_2 , ZrO_2 , Nb_2O_5 and Ta_2O_5 , are shown in Table II in parts per million by weight.

Table III lists the % major metal (corrected for chief spectrographic impurities), % combined carbon, % M + % comb. C, and the resultant empirical formula if one assumes that only the major metal is combined with carbon.

Table IV shows the measured lattice constants as a function of temperature. Values measured in nickel-lined capillaries are marked with an asterisk. Table V lists the average linear thermal expansion coefficient from room temperature to $t^{\circ}C$, the

$$\overline{\alpha} = \frac{1}{a_0} \frac{a - a}{t - t_0}$$

product of $\bar{\alpha}$ and $T_{\rm m}$ (the melting point in °K.), and the product $\bar{\alpha} \sqrt{T_{\rm m}}$. The melting points of TiC, ZrC, NbC and TaC used were 3443, 3803, 3773 and 4150°K., respectively.

From these data the following conclusions can be drawn: (1) For a given temperature range, the linear thermal expansion of TiC, ZrC, NbC and TaC decreases with increasing molecular weight.

(3) J. B. Nelson and D. P. Riley, Proc. Phys. Soc. (London), 57, 160 (1945).