necessitates the use of the standard potential of the calomel electrode, and the difference between the two values given above apparently is due to the revision of the accepted value of the standard potential of the calomel electrode.

We wish to call attention to a simple unambiguous method by means of which the standard electrode potential of silver may be calculated from the standard potential of the silver–silver chloride electrode, $Ag \mid AgCl(s)$, Cl^- ($a = 1$), and the activity product of silver chloride. The relation between the standard potential of the silver–silver chloride electrode, E^0_{AgCl}, the activity product of silver chloride, K, and the standard potential of the silver electrode E^0_{Ag, Ag^+}, is given by the thermodynamic equation

$$E^0_{AgCl} = E^0_{Ag, Ag^+} - (RT/F) \ln K \qquad (1)$$

The value of E^0_{AgCl} has been determined by several investigators[4] from measurements of the cell $H_2 \mid HCl, AgCl(s) \mid Ag$. A critical examination of the data of these authors has led us to believe that the measurements of Carmody, who used quartz cells and was the only one of these investigators who was able to obtain very concordant results in extremely dilute solutions, are the most reliable. By graphical extrapolation Carmody obtained the value -0.2223 v. for E^0_{AgCl}. We have recalculated the value of E^0_{AgCl} from Carmody's data for the three most dilute solutions (0.0007280, 0.0005518 and 0.0003288 m) by application of the limiting law of Debye and Hückel. This leads to the equation

$$E^0_{AgCl} = -E_{cell} - \frac{RT}{F} \ln m^2 + 2 \times 0.5045 \frac{RT}{F} S^{1/2} \qquad (2)$$

in which S is the total ionic strength of the solution corrected for the solubility of silver chloride. This equation leads to the same value of E^0_{AgCl} for each of the three most dilute solutions, namely, -0.2222 v. at $25°$. We consider this to be the most reliable value of E^0_{AgCl}, and it is in excellent agreement with the value -0.2221 v. estimated by Randall and Young.[5]

The activity product of silver chloride has been determined recently by Brown and MacInnes[6] by a highly precise electrometric titration method. They found a value of K equal to

1.721 $\times$ 10^{-10} at $25°$, and this result is apparently reliable to a few tenths of one per cent.

By substituting these values into equation (1) we obtain for the standard electrode potential of silver at $25°$

$$E^0_{Ag, Ag^+} = -0.2222 + 0.05913 \log (1.721 \times 10^{-10}) = -0.7996 \text{ v.}$$

The close agreement between this result and the value given by Lewis and Randall is remarkable in view of the fact that the value calculated above is based on entirely independent measurements by different investigators. This result therefore constitutes strong evidence in favor of accepting the value -0.7996 v. as the standard potential of the silver electrode, rather than the value -0.7978 v. given in the "International Critical Tables."

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Beta-Octyl Thiocyanate

BY W. GORDON ROSE AND H. L. HALLER

In the course of studies on the relative toxicity to insects of optical isomers of secondary alkyl thiocyanates, the results of which will be reported elsewhere, occasion has been had to prepare the dextro and levo forms of beta-octyl thiocyanate (alpha-methylheptyl thiocyanate). By the action of phosphorus tribromide (138.0 g.) on dextro-beta-octanol (66.0 g.), $[\alpha]^{20}D$ $+9.70°$ homogeneous, $[\alpha]^{20}D$ $+11.88°$ in ethanol ($c = 5.67$), there was obtained 81.3 g. of beta-octyl bromide, $[\alpha]^{20}D$ $-32.15°$ homogeneous, $[\alpha]^{20}D$ $-45.30°$ in ethanol ($c = 5.99$). The latter (81.0 g.), on being refluxed in 100 cc. of methanol with 45.0 g. of potassium thiocyanate, yielded 51.7 g. of beta-octyl thiocyanate, b. p. $98.5–99.0°$ at 4 mm., d^{20} 0.919, $n^{20}D$ 1.4635, MR_D(obsd.) $= 51.30$, MR_D(calcd.) $= 51.09$, $[\alpha]^{20}D$ $+51.7°$ homogeneous, $[\alpha]^{20}D$ $+59.1°$ in ethanol ($c = 5.06$). Anal. Calcd. for $C_9H_{17}NS$: C, 63.08; H, 10.01; N, 8.18. Found: C, 63.14, 63.17; H, 10.02, 10.08; N, 8.44, 8.32.

Beta-octyl thiocyanate has been obtained previously by the interaction of beta-octyl-p-toluenesulfonate and potassium thiocyanate.[1] The beta-octyl sulfonate was obtained on oxidation of the corresponding sulfinate, which in turn

(4) (a) Noyes and Ellis, THIS JOURNAL, **39**, 2532 (1917); (b) Linhart, ibid., **41**, 1175 (1919); (c) Scatchard, ibid., **47**, 708 (1925); (d) Nonhebel, Phil. Mag., [7] **2**, 1085 (1926); (e) Carmody, THIS JOURNAL, **54**, 188 (1932).

(5) Randall and Young, ibid., **50**, 989 (1928).

(6) Brown and MacInnes, ibid., **57**, 459 (1935).

(1) Kenyon, Phillips and Pittman, J. Chem. Soc., 1081 (1935).

was obtained from beta-octanol and p-toluene-sulfinyl chloride. Starting with a dextro-beta-octanol, $[\alpha]^{20}_{5893}$ $+9.48°$ homogeneous, $[\alpha]^{20}_{4359}$ $+22.40°$ in ethanol ($c = 4.992$), Kenyon and his co-workers obtained, through this series of reactions, a levo-beta-octyl thiocyanate, $[\alpha]^{20}_{5893}$ $-71.41°$ homogeneous, $[\alpha]^{20}_{5893}$ $-64.68°$ in ethanol ($c = 5.010$), $n^{17°}$D 1.4651, $d^{20°}_4$ 0.795.

In the series of reactions used by the writers a dextrorotatory octanol yielded a dextrorotatory thiocyanate, while in the procedure used by Kenyon a levo-octyl thiocyanate was obtained from a dextrorotatory octanol. Since an asymmetric carbon atom is involved in both series of reactions, the difference in the results may be explained by the occurrence or absence of the Walden inversion.

The refractive index of the thiocyanate prepared by the writers agrees with that reported by Kenyon and his co-workers, indicating that the compounds are of the same degree of chemical purity. The density of the writers' compound, however, was 0.919, whereas Kenyon reported 0.795.

The molecular refraction of beta-octyl thiocyanate, calculated from the revised values of Eisenlohr for the atomic refractions[2] and employing 13.21 for the thiocyanate radical, is 51.09. The observed molecular refraction for the writers' compound, obtained with the Lorentz–Lorenz formula, is 51.31, whereas with the values for refractive index and density reported by Kenyon 59.31 is obtained.

These results indicate that the value for the density found by the writers is closer to the true value than is that found by Kenyon, et al. Since the specific refraction (homogeneous) is dependent on the density, this value is also subject to revision.

(2) Landolt–Börnstein, "Physikalisch-chemische Tabellen," Aufl. 5, Bd. 2, Julius Springer, Berlin, 1923, p. 985.

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A Stopcock Substitute

By WALTER C. SCHUMB AND H. IRVING CRANE

In the course of a certain investigation in this Laboratory it was found necessary to devise a means of interrupting the flow of a benzene solution. A stopcock could not be used, since the ordinary organic stopcock lubricants are readily attacked by benzene, and the reactivity of the solute toward moisture or reactive hydrogen made the use of certain other types of lubricant, such as phosphoric acid, out of the question. The device shown in the diagram is an adaptation of Stock's stopcock for gases [Ber., 58, 2058 (1925)].

To leveling　　　　　　To leveling
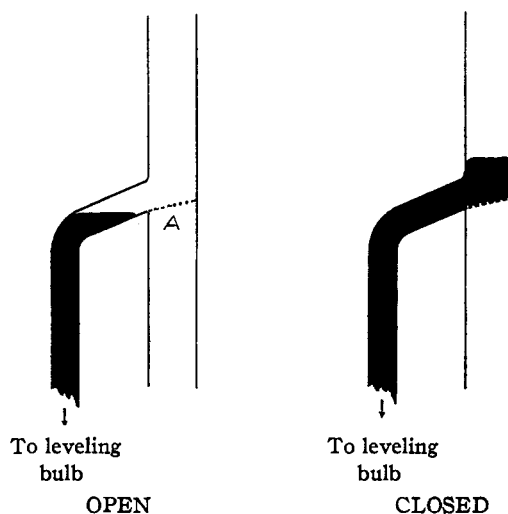bulb　　　　　　　　　　bulb
OPEN　　　　　　　　CLOSED
Fig. 1.

The device, constructed of Pyrex glass, consists essentially of a fritted glass plate (A) (80 mesh), so placed that mercury can be flowed over it at will by means of a suitable leveling bulb.

Obviously the device is applicable to any liquid of not too high viscosity, which does not attack mercury. The high surface tension of mercury prevents any of it passing through the fritted plate.

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The Rearrangement of Alkyl Aryl Thioethers

BY WENDELL H. TAYLOR

In a recent study of the reaction between aromatic mercaptals and formaldehyde, the author[1] postulated a rearrangement of formaldehyde diaryl mercaptals involving the migration of the —CH$_2$ group from sulfur to the benzene nucleus, with regeneration of the —SH groups. Such a change would be essentially similar to the rearrangement of the alkyl aryl thioethers and it was therefore of interest to investigate such thioether rearrangements under conditions comparable to those under which the analogous oxygen com-

(1) W. H. Taylor, THIS JOURNAL, 57, 1065 (1935).