to impurities. No evidence of immiscibility was detected in this system but complete miscibility of some other systems, which have been reported as being azeotropic, has not been confirmed.

TABLE I								
VAPOR	Pressures	of	Acetic	Acid	AND	Benzene	Mix-	
			TURES AT	г 25°				

Mole per cent. benzene	Total pressure, mm.	Partial pressure acetic acid, mm.	Partial pressure benzene, mm.
0	15.43	15.43	0
3.1	28.63		
12.3	47.54		
21.8	59.46		
25.2	62.65		
32.6	68.38	14.2	54.2
52.1	79.17	13.0	66.2
52.6	79.19		
61.4	82.94	11.9	71.0
63.7	83.85		
66.8	85.56	10.9	74.7
69.8	86.88	10.4	76.5
72.2	87.5	9.7	77.8
75.6	88.37	8.7	79.7
77.4	88.45		
80.3	90.0	7.65	82.35
83.0	90.8	6.8	84.0
85.4	91.16	5.2	86.0
88.6	92.07	4.5	87.6
90.5	92.74	4.1	88.6
92.7	93.2	2.8	90.4
100.0	94.91	0	94.91

In the method here outlined the partial pressures (see Table I) of the two components were determined by the method of  $Rosanoff^{14}$  and his

(14) Rosanoff, Bacon and White, THIS JOURNAL, 36, 1803 (1914).

collaborators, except that allowance was made for the weight of vapor in the apparatus.

As suggested by Othmer<sup>7</sup> this method results in the multiplication of quantitative errors. However, the greatest effect is on the first fractions since the calculations are made from the samples themselves and not the original mixture. These first readings are found also to be less reliable due to dissolved gases, and therefore should be given less weight than the last readings.

The fact pointed out in the introduction concerning the impossibility of obtaining concordant results in systems having benzene as one component, when using the air saturation method and condensing the vapor from the air with liquid air, may be emphasized in the light of some observations made recently in this Laboratory by Prof. R. E. Burk. It seems that small particles of solidified benzene will adsorb sufficient air to be carried through the liquid air trap and lost.

At present other binary systems are being studied, chiefly those that are classified as azeotropic.

# Summary

1. A new method for the study of the total and partial vapor pressures of binary liquid mixtures is described. Total pressures can be readily obtained over a moderate temperature range. The difficulties due to dissolved gases and moisture are eliminated.

2. It has been confirmed that the acetic acid and benzene system is not azeotropic.

CLEVELAND, OHIO RECEIVED APRIL 26, 1934

# Studies on Chromium. III. The Occurrence of Chromium in Certain Soils and Plants in the Province of Quebec

### BY ANDREW DINGWALL AND H. T. BEANS

The finding of chromium in human tumors<sup>1</sup> has led us to investigate the occurrence of chromium in solids and plants. Chromium has long been recognized as widely diffuse in the lithosphere, but we have only found three instances where it has been reported in plants in recent times.<sup>2</sup> The spectrographic technique we employed and the origin and treatment of the soil and plant speci-

 A. Dingwall and H. T. Beans, Am. J. Cancer, 16, 1499 (1932).
E. Demarcay, Compt. rend., 130, 91 (1900); W. O. Robinson,
I. A. Steinkoenig and C. F. Miller, U. S. Dept. of Agriculture Bull., 600 (1917); L. Gouldin, Chem. News, 100, 130 (1909). mens examined have been described elsewhere.3

Five soil specimens, surface and subsoil, ten specimens of vetch grown on different farms, two specimens of timothy, red clover, alfalfa and alsike, one specimen of goldenrod, reed canary grass, field corn\_stalks, ragweed and Canada thistle, and the ash from the liver of a rabbit fed on reed canary grass and distilled water were examined. Chromium was found in all cases.

(3) A. Dingwall, R. R. McKibbin and H. T. Beans, Can. J. Research, July (1934).

<sup>[</sup>CONTRIBUTION FROM THE SPECTROGRAPHIC LABORATORIES, DEPARTMENT OF CHEMISTRY, COLUMBIA UNIVERSITY]

Aug., 1934

Acknowledgments.-The spectrographic laboratory was founded by the Royal Baking Powder Company and has received generous aid from Dr. and Mrs. Reginald Auchincloss.

The specimens of soils and plants were obtained

through the courtesy and coöperation of Dean Snell and Professor McKibbin of Macdonald College, McGill University, Montreal, Canada. The rabbit liver was supplied by Professor Crampton of Macdonald College. NEW YORK CITY

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[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY, PRINCETON UNIVERSITY]

# The Effect of Solvent upon the Moment of a Molecule Containing Movable Dipoles

BY A. E. STEARN AND C. P. SMYTH

Previous work has shown that the dipole moment of ethylene chloride in solution in hexane<sup>1</sup> and in heptane<sup>2</sup> and in the vapor state<sup>3</sup> increases with rising temperature because the increasing rotational energy of the two halves of the molecule overcomes more and more the effect of the potential energy between the two -CH<sub>2</sub>Cl's, which tends to orient the chlorines in a trans position of zero moment. It was found, however, that, in benzene, the apparent moment of ethylene chloride was considerably higher and independent of temperature.1 Similar behavior was found in the case of ethylene bromide.4 As these phenomena are intimately connected with the problem of the energy of rotation within a molecule and of the molecular condition in liquids, it has seemed desirable to obtain information as to the behavior of ethylene chloride in a variety of solvents.

#### **Preparation of Materials**

Ethylene Chloride .--- Material from the Eastman Kodak Company was purified as in previous work;<sup>2</sup> b. p. 83.5-83.7°;  $n_{\rm p}^{20}$  1.44476.

Heptane .---- Normal heptane from the Ethyl Gasoline Corporation was fractionated once;  $n_{D}^{20}$  1.38771.

Benzene .--- The material was treated as in earlier work.5

Carbon Tetrachloride .-- Merck reagent was dried over fused calcium chloride and fractionated; b. p. 76.4°;  $n_{\rm D}^{20}$  1.46023.

Carbon Disulfide.—Merck reagent, which did not darken mercury in two hours, was dried over fused calcium chloride and anhydrous copper sulfate and distilled; b. p. 46.0° (754 mm.);  $d_4^{20}$  1.2622.

Ether .--- Anesthesia grade material was treated with acid permanganate solution, with sodium chloride and sodium hydroxide solution, washed with water, dried

over fused calcium chloride, and distilled; b. p. 34.5° (752 mm.);  $d_4^{20}$  0.7134.

Chloroform .- Merck reagent was dried over calcium chloride and fractionated; b. p.  $61.1-61.2^{\circ}$ ;  $d_4^{20}$  1.4892.

## Method of Determination

The dielectric constants,  $\epsilon$ , and densities, d, were measured with the apparatus used in previous work,6 the former being determined at a wave length of approximately 600 meters. The polarization,  $P_2$ , of the ethylene chloride was calculated by means of the equations  $P_{12} = (\epsilon - 1)$  $(c_1M_1 + c_2M_2)/(\epsilon + 2)d$  and  $P_{12} = c_1P_1 + c_2P_2$ , in which  $P_{12}$  is the polarization of the mixture and  $P_1$  that of the pure solvent, and  $c_1$ ,  $c_2$  and  $M_1$ ,  $M_2$ are the mole fractions and molecular weights of the two components. When a third component was used  $c_3M_3$  was added to  $c_1M_1 + c_2M_2$  in the numerator on the right of the first equation and the term  $c_3P_3$  was added on the right of the second equation. The polarization of ethylene chloride at infinite dilution,  $P_{\infty}$ , was obtained in the usual manner by extrapolation to  $c_2 = 0$ . However, in the dilute solutions, the variation of polarization with concentration appeared to be smaller than the experimental error, so that  $P_{\infty}$ was commonly obtained as the average of the  $P_2$ values for the dilute solutions. The dipole moment  $\mu$  was calculated by subtracting from  $P_{\infty}$ the polarization of the solid  $P_{\rm E} + P_{\rm A} = 23.9$  determined by Dr. C. S. Hitchcock<sup>7</sup> and using the equation  $\mu = 0.0127 \times 10^{-18} \sqrt{(P_{\infty} - 23.9)T}$ , in which T is the absolute temperature. The moments thus obtained for ethylene chloride are given in Table I, the solvent used being given at the head of each column of moment values.

In the ethylene chloride-ether solutions as the (6) Smyth, Morgan and Boyce, THIS JOURNAL, 50, 1536 (1928): Smyth and Morgan, ibid., 50, 1547 (1928); Dornte and Smyth, ibid., 52, 3546 (1930).

(7) Cf. Smyth and Hitchcock, ibid., 54, 4631 (1932).

<sup>(1)</sup> Meyer, Z. physik. Chem., [B] 8, 27 (1930).

<sup>(2)</sup> Smyth, Dornte and Wilson, THIS JOURNAL, 53, 4242 (1931).

<sup>(3)</sup> Zahn, Phys. Rev., 38, 521 (1931).

<sup>(4)</sup> Smyth and Kamerling, THIS JOURNAL, 53, 2988 (1931).

<sup>(5)</sup> Smyth and Walls, ibid., 54, 1854 (1932).