the tetrahydrate at room temperature is not surprising, since metastable transition to the anhydrous salt, even at the higher temperatures at which the sesquihydrate exists in contact with saturated solution, occurs with such ease that the sesquihydrate was not detected by the careful work of at least two previous investigators (*4, 7*).

In the system $Na_2Cr_2O_7$–H_2O, transition temperatures were found at 82.6° C. and 87.3° C., although only one transition, at 84.6° C. (*3*), has been reported previously. These temperatures represent transition from the dihydrate to the monohydrate, which is a new crystal form, and thence to the anhydrous salt, while the previously reported temperature very likely represents the metastable transition from the dihydrate to the anhydrous salt. The monohydrate was identified by analysis of the solid phase isolated from slurry at 85° C. in a heated centrifuge ($Na_2Cr_2O_7$ calculated, 93.6%; found, 93.4%); that it was not a mixture of the two known forms was indicated by its x-ray pattern, of which the principal lines are shown in Table VI. Crystals of $Na_2Cr_2O_7 \cdot H_2O$ are intermediate in color between the dihydrated and anhydrous forms.

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Measurement of Ultraviolet Indices of Refraction with a Differential Refractometer

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Modifications of a commercial differential refractometer are described which permit using the instrument in the ultraviolet. Dispersion data and Lorentz corrections from 5461 to 2655A. are given for fourteen solvents.

IN ORDER TO RELATE macroscopic optical phenomena such as absorption and optical rotation to molecular properties, one must obtain an estimate of the internal electric field on the molecule or on a particular group in the molecule. Numerous formulas have been proposed to relate the local field to the applied macroscopic electromagnetic field (*1, 3*) of which the Lorentz correction $[(n^2 + 2)/3]$ is the most widely used, where n is the refractive index at the wavelength of interest. Though the derivation of this factor asserts its applicability only for gases and cubic lattices, it is customarily used by both experimentalists and theoreticians as a first order estimate of internal field effects in solutions.

In our own work we frequently have to compare absorption and optical rotation measurements obtained in media of differing refractive index either because of a variation in wavelength (dispersion studies) or in solvent composition. The spectral region of interest is normally in the ultraviolet. Since refractive dispersion data on many important solvent systems was nonexistent, a commercial refractometer was adapted for measurements in the ultraviolet and dispersion curves were obtained for a number of widely used solvents.

EXPERIMENTAL

The apparatus was a Pheonix Precision Differential Refractometer supplied by the manufacturer with the modifications described below. Figure 1 is a schematic diagram of the optical parts of the instrument as normally supplied by the manufacturer. Light from a tungsten bulb passes through a narrow band-pass filter and then through a lens which focuses an image of the slit on the nearest edge of the prism, where it is split into two beams of equal intensity when the prism is in balance position. During operation the transverse position of the prism is automatically brought to balance by a servo-controlled micrometer drive. In making a measurement a reference liquid of known refractive index is placed in compartment R and

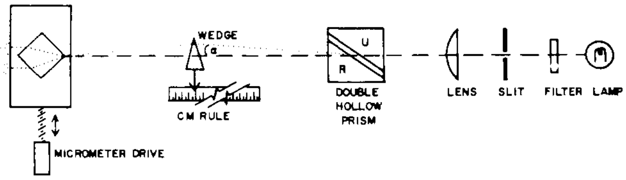

Figure 1. Differential refractometer

Symbols are explained in text. Small deflections are measured by the transverse motion of the micrometer-driven prism. Large deflections are compensated by moving the wedge closer to the double hollow prism.

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the unknown liquid in compartment U of the double hollow prism. The light beam is deflected from its original path by an angle α which depends on the refractive indices of the two liquids and on the angle θ the cell partition makes with the incident beam. For small deflections, α is directly proportional to the difference in refractive index Δn of the two liquids. The theory of the prototype of this instrument has been given by Brice and Halwer (*4*). The angle α and therefore Δn can be measured either by measuring the distance the beam-splitting prism is displaced from its reference position (reference liquid in both compartments) or by the longitudinal distance the wedge must be moved to the right to produce a counter deflection which brings the light beam back to a state of balance with the prism in its reference position. The latter procedure is necessary for all but very small differences in refractive index. In practice the dependence of the transverse displacement of the prism and the longitudinal displacement of the wedge on Δn is established for a given range of refractive index by preparing calibration curves with systems of known refractive index.

The modifications required for the measurements reported below may now be simply explained. On special order the manufacturer substituted throughout optics made of high grade fused silica. The 1P21 photomultiplier of the instrument was replaced by a 1P28 for light detection below 3000A. The lamp and filter were replaced by a Beckman DU monochromator with a low pressure mercury arc as a light source. The range of measurement was extended by replacing the 2° wedge which cane with the instrument by a 7° wedge made by the Karl Lambrecht Optical Co., and by rotating the double liquid prism by 90°, thereby changing the angle θ from its normal value of 20° to 70°. The latter alterations were suggested by the Phoenix Precision Company and increased the range of the instrument by about 25 fold.

Reference Solutions. The liquids investigated have refractive indices which span a considerable range, and it was not possible to find data for substances which covered the range of both refractive index and wavelength required. The standards which proved to be most applicable were water and aqueous soldium bromide solutions whose refractive dispersion has been studied as a function of concentration by M. Bayen (*2*). His results are not recorded for the mercury lines and so a large scale graph (n *vs.* $1/\lambda^2$) of his dispersion curves for various NaBr solutions was made and the values for the mercury lines were obtained by interpolation. Over short spectral regions the Cauchy dependence $n = a + b/\lambda^2$ is a very good approximation so that the interpolations could be made with precision. These interpolated values are given in Table I. The refractive index of the most concentrated NaBr standard falls

Table II. Dispersion Data at 25° and Calculated Lorentz Corrections

λ, mμ	n	$(n^2+2/3)$	λ, mμ	n	$(n^2+2/3)$
Formic Acid			2-Chloroethanol		
265.5	1.4178	1.3367	265.5	1.4940	1.4107
289.4	1.4063	1.3259	289.4	1.4823	1.3991
313.1	1.3982	1.3183	313.1	1.4731	1.3900
365.0	1.3874	1.3083	365.0	1.4608	1.3780
435.8	1.3785	1.3001	435.8	1.4511	1.3686
546.1	1.3709	1.2931	546.1	1.4423	1.3601
8*M*. Urea (Aqueous Solution)			Ethylene Dichloride		
265.5	1.4572	1.3745	265.5	1.5002	1.4169
289.4	1.4433	1.3610	289.4	1.4878	1.4045
313.1	1.4340	1.3521	313.1	1.4778	1.3946
365.0	1.4208	1.3396	365.0	1.4648	1.3819
435.8	1.4105	1.3298	435.8	1.4539	1.3713
546.1	1.4022	1.3221	546.1	1.4447	1.3624
p-Dioxane			Chloroform		
265.5	1.4699	1.3869	265.5	1.5051	1.4218
289.4	1.4583	1.3755	289.4	1.4911	1.4078
313.1	1.4500	1.3675	313.1	1.4806	1.3974
365.1	1.4384	1.3563	365.0	1.4661	1.3832
435.8	1.4293	1.3476	435.8	1.4546	1.3720
546.1	1.4207	1.3395	546.1	1.4454	1.3631
Methylene Chloride			Formamide		
265.5	1.4786	1.3954	265.5	1.5379	1.4551
289.4	1.4661	1.3832	289.4	1.5139	1.4306
313.1	1.4561	1.3734	313.1	1.4980	1.4147
365.0	1.4431	1.3609	365.0	1.4772	1.3940
435.8	1.4323	1.3505	435.8	1.4619	1.3791
546.1	1.4237	1.3423	546.1	1.4495	1.3670
Furan			Carbon Tetrachloride		
265.5			265.5		
289.4			289.4		
313.1	1.4766	1.3935	313.1	1.4985	1.4152
365.0	1.4537	1.3711	365.0	1.4831	1.3999
435.8	1.4369	1.3549	435.8	1.4706	1.3876
546.1	1.4241	1.3427	546.1	1.4603	1.3775
C_6H_{12} (Cyclohexane)			Dichloroacetic Acid		
265.5	1.4741	1.3910	265.5		
289.4	1.4631	1.3802	289.4		
313.1	1.4549	1.3723	313.1	1.5045	1.4212
365.0	1.4432	1.3609	365.0	1.4893	1.4060
435.8	1.4335	1.3516	435.8	1.4776	1.3944
546.1	1.4249	1.3435	546.1	1.4673	1.3843
Dimethyl Formamide			Hydrazine		
265.5			265.5		
289.4	1.4913	1.4080	289.4		
313.1	1.4761	1.3930	313.1		
365.0	1.4564	1.3737	365.0	1.4980	1.4147
435.8	1.4419	1.3597	435.8	1.4837	1.4005
546.1	1.4313	1.3495	546.1	1.4714	1.3883

Table I. Refractive Index of Water (at 17.7°) and Various Sodium Bromide Solutions (at 18°)

The concentrations are expressed in grams of anhydrous salt per 100 grams of solution and the refractive indices as $(n-1)10^4$. Data recalculated from Baven (*2*)

Concn.	Wavelength (Angstroms)										
	5461	4358	4047	3650	3342	3132	3022	2967	2894	2699	2655
Water											
	3347	3404	3429	3472	3517	3558	3583	3598	3618	3684	3701
NaBr Solutions											
5.3718	3420	3483	3511	3557	3607	3652	3679	3694	3717	3791	3811
10.162	3492	3560	3590	3640	3692	3741	3771	3788	3813	3894	3916
17.373	3611	3686	3719	3773	3832	3887	3922	3940	3968	4062	4087
21.678	3684	3763	3798	3856	3918	3978	4014	4034	4065	4166	4194
24.365	3735	3817	3853	3913	3977	4040	4080	4101	4132	4239	4268
28.743	3820	3907	3946	4010	4077	4146	4189	4212	4246	4361	4393
32.265	3891	3981	4022	4089	4163	4234	4279	4303	4338	4462	4496
36.172	3980	4073	4116	4187	4266	4342	4390	4417	4455		

below that of many of the liquids of interest. It was this circumstance which necessitated the alteration of the range of the refractometer described in the preceding paragraph. Even with this range extension it was necessary to use formamide as a secondary reference for measuring the refractive index of carbon tetrachloride, dichloracetic acid and hydrazine.

Bayen's dispersion data for water at 17.7° was corrected to 25° using his temperature dependence of refractive index. These values were then used as standards for measuring the dispersion of formic acid and the 8 molar urea solution. In order to obtain the refractive index of the sodium bromide solutions at 25° the refractometer was first calibrated at 18° using water *vs.* sodium bromide. The sample temperature was then raised to 25° and the calibration (which is independent of temperature) used to determine the difference in refractive index of water and sodium bromide solutions.

Solvents. The solvents used were of the best grade obtainable commercially and were not purified further except for the dioxane and ethylene dichloride which were distilled. The urea was recrystallized once from ethanol. Refractive indices were measured at 25° at the sodium D line with an Abbe refractometer and were: formic acid 1.3692, 8 molar urea 1.3993, *p*-dioxane 1.4191, furan (at 18°) 1.4196, methylene chloride 1.4209, dimethylformamide 1.4273, 2-chlorethanol 1.4392, chloroform 1.4421, ethylene dichloride 1.4423, formamide 1.4431, hydrazine 1.4686, dichloroacetic acid 1.4692.

RESULTS

Table II records the refractive index (at 25°) and Lorentz correction factors of fourteen solvents as a function of wavelength. Blank spaces in the table indicate that absorption of light at the given wavelength was too great to permit measurement. A sharp cutoff in transmitted light as an absorption region is approached is a disadvantage of the hollow prism method.

A short extrapolation of the results of Table II was made for comparison with our measured sodium D line values. Excluding formamide and dichloroacetic acid, the average deviation between the measured and extrapolated values was .0007. But the extrapolated values were .0033 too large for formamide and .0044 too small for dichloroacetic acid. However, even a decrease of .0044 in the refractive index of dichloroacetic acid will only lead to about a 0.3 per cent decrease in the calculated Lorentz correction.

Thus, it would appear that in spite of the many corrections required in obtaining ultraviolet refractive indices with a differential refractometer, the results are quite satisfactory for Lorentz corrections. On the other hand, it would be desirable to have a simpler, absolute method available. For this purpose an ordinary table spectrometer with a fluorescent eyepiece would probably useful as far as the transmission cutoff of glass.

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Estimation of Lennard-Jones Potential Energy Parameters from Liquid Densities

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McKinley has shown that the smoothed-potential cell model for the liquid state is a satisfactory basis for correlating the temperature dependence of the density of nonpolar molecules along the saturated liquid curve from 0° K. to approximately 0.8 of the critical temperature. This paper shows that such a correlation gives estimates of both the energy parameter and the distance parameter in the Lennard-Jones bireciprocal pair-potential energy relationship. The parameters obtained in this way give satisfactory estimates of the second virial coefficients for molecules in the gas phase. Thus, with a single, empirical, potential energy function, the equation of state of the gas phase can be correlated with that of the liquid phase at low pressures.

THIS PAPER investigates the possibilities for correlating by a single pair-potential energy function the volumetric behavior of pure polyatomic molecules in both the gas phase and the liquid phase at low pressures. For this purpose, the Lennard-Jones bireciprocal pair-potential energy function and the smoothed-potential cell model for the liquid state were chosen. These devices lead to empirical relationships that demonstrate such a correlation. In this model (*11*), the pressure P, temperature T, and density x in units of V^* ($x = V^*/V$) are related in the following way:

$$P = \frac{-zE^*m}{6(m/n-1)V}\left[Cx^{n/3} - Dx^{m/3}\right] + kT/V\alpha$$

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