

THE ANALYST.

PROCEEDINGS OF THE SOCIETY OF PUBLIC ANALYSTS AND OTHER ANALYTICAL CHEMISTS.

THE DENSITIES AND REFRACTIVE INDICES OF THE LEAMINGTON SPA WATER.

By C. H. MANLEY, M.A., A.I.C.

IN a pamphlet entitled "The Chemistry of the Leamington Spa Water" (1914) S. Henry Smith remarks that this water is one of peculiar interest as regards its saline constituents. Attention is drawn to the fact that in prehistoric ages the whole of the surrounding district formed the bottom of a large inland sea, which stretched from the Edge Hills to Shuckburgh and Bourton-on-Dunsmore, with an outlet down the Evesham Valley to the Bristol Channel. With the subsequent disappearance of the sea, a huge deposit of saline material covered with silt and earth remained. Surface water gaining access at a later period, a highly saline solution resulted.

The chemical composition of the Leamington Spa water is somewhat complicated. The following figures—the mean of several analyses—are quoted by S. H. Smith (*loc. cit.*):

			Pump Room Supply. Parts per 100,000.	
BaSO ₄	0.1376	
SrSO ₄	1.2088	
CaSO ₄	248.2	
MgSO ₄	125.604	
MgI ₂	0.0032	Traces of manganese and titanium.
MgBr ₂	0.3354	
CaCl ₂	58.36	
MgCl ₂	47.37	
NaCl	1245.127	
KCl	9.9264	
LiCl	0.0665	
NH ₄ Cl	0.0742	
Fe ₂ (CO ₃) ₃	0.286	
CaCO ₃	4.4	
Silicic Acid	0.8	
Total	1741.8991	

Dried residue at 110° = 1739.0000.

Radium is also stated to be present. No details are given as to the actual methods employed for the chemical analysis, and it is therefore impossible for one to form any true estimate of the degree of accuracy attainable.

In this present paper is given an account of certain determinations both of the relative densities and the refractive indices of the Spa water. The water used was drawn from the Engine House supplying the Pump Room on August 30, 1915, a few gallons of water being allowed to flow away before collecting a sample in a large earthenware jar which had first been rinsed with some of the same water; the jar was then corked, sealed and subsequently removed to Oxford, where the necessary measurements were effected in the Laboratory of Magdalen College. Prior to the measurements some of the water was poured into a Winchester quart bottle and allowed to stand until clear, after which portions for the several determinations were carefully decanted off as required; this plan rather than that of filtration was adopted in order to avoid any possible inaccuracy that might be introduced by the adsorptive properties of filter-paper.

Relative Density of the Spa Water.—For determining the relative densities at the several temperatures named below, a modified form of the well-known Sprengel pyknometer was employed; the instrument was narrow of limb and by actual trial it was found that when charged with water the pyknometer and its contents assumed the temperature of the thermostat within ten minutes after immersion; it was also found possible to adjust the liquid content to within approximately $\frac{1}{8}$ mgrm. The weighings of distilled water and spa water at 15°, 18° and 25° C. were carried out with a high degree of accuracy.

The following are the tabulated mean results:

Temperature.	Distilled Water.		Spa Water.	
	Apparent Weight.	Weight [M] in Vacuo.	Apparent Weight.	Weight in Vacuo.
15° C.	9.7286	9.7402	9.8481	9.8597
18° C.	9.7241	9.7357	9.8425	9.8541
25° C.	9.7102	9.7218	9.8272	9.8388

Temperature.	Density [D] of Water (Despretz).	Volume of Pyknometer [V = M/D].	Density [Δ] of Spa Water.
15° C.	0.9991	9.7490	1.01136
18° C.	0.9986	9.7495	1.01073
25° C.	0.9971	9.7501	1.00910

It will therefore be seen that the above values for the Spa water are in terms of pure water at 4° C., and when plotted graphically, lie on three points of a right line

curve. The coefficients of expansion, k_1 and k_2 , of the Spa water between 15° and 18° and 18° and 25° C. respectively were calculated with the aid of the formula

$$k = \frac{d^t/d^\theta - 1}{\theta - t},$$

in which d^t = the density of the Spa water at t° ,
and d^θ = " " " " θ° ,
 θ being $> t^\circ$.

$$\left. \begin{array}{l} \text{Accordingly } k_1 = 0.00021 \\ \quad \quad \quad k_2 = 0.00023 \\ \text{Mean value } k = 0.00022 \end{array} \right\}$$

For pure water, and within the limits of temperature 15° - 25° , k , calculated from the values for Δ by Despretz = 0.00021.

The Refractive Indices.—The refractive indices were measured with the aid of a Troughton and Sims refractometer capable of being read to $15''$ of arc. A hollow glass prism by Hilger was employed, its refracting angle being equal to $50^\circ 59' 15''$. A number of measurements were carried out, every care being taken to regulate the temperature. The refractive index, μ , in each case was calculated from the usual formula. The values given below are for 15° , 18° , and 25° C. Side by side with these are tabulated figures expressing the refractive indices of highly purified water—the result of measurements which were effected with the aid of a refractometer and quartz prism belonging to the Royal Society. If μ_1 and μ_2 denote the refractive indices of the spa water and purified water respectively, the expression μ_1/μ_2 will represent the relative refractivities for the several temperatures. The importance of a measurement of the relative refractivities and of the relative densities has already been pointed out in regard to the examination of samples of sea-water (J. J. Manley, Proc. Roy. Soc., Edinburgh, 1900, pp. 35-43).

Finally, the application of the formulæ $\frac{(\mu - 1)}{d}$ and $\frac{(\mu^2 - 1)}{(\mu^2 + 2)d}$ to the values obtained for the densities and refractive indices of the Leamington Spa water at 15° , 18° , and 25° C. shows that the water conforms to the law of Gladstone and Dale on the one hand and to that of Lorentz and Lorenz on the other, constant values obtaining at each of the three temperatures.

Temperature.	μ_1 (Spa).	μ_2 (purified).	μ_1/μ_2 .	$\frac{(\mu_1 - 1)}{d}$.	$\frac{(\mu_1^2 - 1)}{(\mu_1^2 + 2)d}$.
15°	1.3363	1.3334	1.0017	0.3325	0.2052
18°	1.3360	1.3333	1.0023	0.3324	0.2052
25°	1.3353	1.3330	1.0040	0.3323	0.2051

In conclusion, I desire to express my thanks to Mr. Charles Ravenhill, Manager of the Leamington Spa Pump Room, for facilities allowed me in collecting the water for the above measurements.