VI. *Internal Pressure and Latent Heat of Liquids.* By WM. C. McC. LEWIS, M.A., D.Sc., *Chemical Laboratory, University College, London* *.

IN the Phil. Mag. (xxiii. p. 955, 1912) Mr. Sukhodski has criticised an expression given by the writer for the internal pressure of a liquid. The expression referred to is

$$K - l = T \frac{\partial K}{\partial T}, \quad (1)$$

where K is the internal pressure and l was taken to mean the latent heat of vaporization of 1 c.c. of the liquid (Dupré).

I was aware that the further assumption, viz.

$$\frac{1}{K} \frac{\partial K}{\partial T} = \frac{1}{l} \frac{\partial l}{\partial T}, \quad (2)$$

could not hold over a wide range of temperature, being evidently incorrect at the critical temperature, at which point l is zero while K is still positive (and probably fairly large) as Mr. Sukhodski points out.

It may be mentioned that if l is taken to be the latent heat of expansion of the homogeneous phase (entirely liquid for example), that is, the heat which has to be added to the system while it expands isothermally by 1 c.c., such a quantity will not become zero at the critical temperature, but will have a positive value. By attaching this meaning to l , the physical significance of equation (1) would be of course considerably modified. Equation (2) might, under these circumstances, be fairly correct, but as there is no direct means of testing this, it may be dropped.

Whether we regard l as referring to the latent heat of vaporization of 1 c.c. or to the latent heat of expansion of the liquid itself, equation (1) would still be of little use for experimental purposes, owing to the presence of the term $\frac{\partial K}{\partial T}$. Recently, however, it has become possible to obtain a fairly accurate estimate of this quantity by a new method.*

In the Phil. Mag. (April and September 1912) Mr. H. Davies has put forward several very interesting applications of the Cailletet-Mathias law of the rectilinear diameter. One of these is an expression for the temperature coefficient of the internal pressure of a liquid which is found to be simply identical with the coefficient of expansion, viz.

$$\frac{1}{K} \frac{\partial K}{\partial t} = -\alpha.$$

* Communicated by the Author.

It has also been shown that K itself can be calculated, but as the basis of the method consists in applying an equation of the van der Waals' type, I do not think that it presents much advantage over the method of setting $K = \frac{a}{v^2}$ in van der Waals' equation itself. The temperature coefficient being, however, a much smaller quantity, is no doubt given by Davies' expression with a considerable degree of accuracy, the simplicity of the expression rendering it particularly useful.

Thus starting with equation (1)

$$K - l = T \frac{\partial K}{\partial T},$$

and substituting Davies' expression for $\frac{\partial K}{\partial T}$, one obtains finally

$$K = \frac{l}{1 + T\alpha},$$

this being identical with Davies' equation (24) (*l. c.*).

Davies himself has calculated the value of K in a few cases employing the above expression, in which l is taken as the latent heat of *vaporization* of unit volume of the liquid. The results obtained are given in the second column of the following table, the third column containing the values obtained by Davies' alternative method without introducing equation (1). The last column is the van der Waals' value*.

Substance.	K atmos.	K atmos.	$K = \frac{a}{v^2}$
Benzene	912	1102	1380
Toluene	1042	1188	1180
Aniline	1315	1176	—
Cymene	686	661	—

The agreement between columns 2 and 3 is fairly good.

In the above l is taken to be the latent heat of vaporization of 1 c.c. of the liquid. It seems of interest to see what sort

* Calculated by Traube, *Zeitsch. Phys. Chem.* lxxviii. p. 293 (1909).

of values are obtained if one considers l to be the latent heat of expansion of the liquid itself. A simple expression for l having this signification may be obtained as follows.

For the heterogeneous as well as homogeneous system we have, on purely thermodynamic grounds,

$$l = T \frac{\partial p}{\partial T},$$

and on introducing the further expression

$$\left(\frac{\partial v}{\partial T}\right)_p \left(\frac{\partial T}{\partial p}\right)_v \cdot \left(\frac{\partial p}{\partial v}\right)_T = -1,$$

which holds only for a homogeneous system (say the liquid form), one obtains

$$l = T \frac{\partial p}{\partial T} = \frac{-T \left(\frac{\partial v}{\partial T}\right)_p}{\frac{1}{v} \left(\frac{\partial v}{\partial p}\right)_T} = -T \frac{\alpha}{\beta},$$

where α is the coefficient of thermal expansion and β the compressibility of the liquid.

In the following table are given some values of l thus calculated; the α and β data being taken from Landolt and Börnstein's tables.

Latent Heat of Expansion of non-associated
Liquids at 0° C.

Substance.	l atmos./cm. ² .	l cals./c.c.
Ethyl ether	2730	65
Chloroform	3700	88
Carbon tetrachloride	3332	79
Carbon disulphide	3822	91
Acetone	4336	103
Mercury	13280	316
Cymene	3370	80
Xylene	3547	84
Toluene	3644	86
Benzene	3430	82
Ethyl acetate.....	3305	78

It will be observed that in general the latent heat of expansion of the liquid is of quite the same order of magnitude as its latent heat of vaporization. In the case of associated

liquids, the differences are greater owing to the work involved in breaking down the complexes almost completely on vaporization. The following table allows of a rough comparison.

Substance.	l atmos./cm. ² .	Temperature 0° C.	
		l cal./c.c.	Lvaporization of 1 gram.
Methyl alcohol	4095	97	290
Ethyl alcohol	3453	82	225
<i>n</i> Propyl alcohol	2348	55	165
Isopropyl alcohol.....	3000	71	161

It is rather remarkable that the values of the heat of vaporization and of expansion should be as alike as they are in the case of normal liquids. One would have expected, I think, that the numerical values would have been of a different order of magnitude. In the process of vaporization the molecules are pulled so far apart that they must be nearly independent of one another compared with their relation in the liquid. In expanding a liquid at constant temperature—a process the results of which are realized in experiments in which a completely filled and closed vessel is cooled without corresponding contraction of the liquid—the relative separation of the molecules from one another, even in the expanded state, must be small compared with that of the vapour molecules. The fact that both heat effects are nearly the same suggests that the range of attraction must be extremely small, of the same order as the mean distance apart of the molecules of the liquid in its normal state (about 10^{-8} cm.).

With the values thus obtained for l (latent heat of expansion) we can calculate the values of K by means of the expression

$$K = \frac{l}{1 + \alpha T},$$

the results being as follows :—

Internal Pressure of Liquids at 0° C.

Substance.	K in atmos.
Ether.....	1932
Chloroform	2780
Carbon tetrachloride	2518
Carbon disulphide	2917
Acetone	3188
Mercury.....	12645
Cymene	2718
Xylene	2815
Toluene	2847
Benzene	2639
Ethyl acetate	2466

It will be seen that the values of K obtained by this method are approximately double of those previously given. This in itself is not sufficient to discriminate between the two possible meanings to be attached to *l*. In an associated liquid *l*—in either of its significations—may be no measure of K at all.

It is still an open question, therefore, whether in calculating internal pressures from latent heats, one should employ the latent heat of vaporization of 1 c.c. of the liquid or the latent heat of expansion of the liquid itself.

VII. *The Recombination of Ions produced by Röntgen Rays.*
By S. J. PLIMPTON, *Ph.D., Yale University* *.

WHEN a gas is exposed to the continued action of Röntgen rays the number of ions contained in a unit volume of the gas does not go on increasing indefinitely because of the electrostatic field associated with the ions. A continuous diffusion takes place from the region of maximum ionization, and in addition oppositely charged ions recombine under their attractive forces. The process of diffusion is a relatively slow one, and with properly designed apparatus may be disregarded in measuring the changes in ionization due to recombination.

According to the accepted theory of ionization in gases, the rate of change of the number of ions of either sign per unit volume is proportional to the square of this number; that is,

$$\frac{dn}{dt} = -\alpha n^2, \quad (1)$$

where α is a constant known as the coefficient of recombination and is independent of n .

* Communicated by the Author.