ART. LII.—*Note on the Relation of Volume, Pressure and Temperature in case of Liquids* ;* by CARL BARUS.

MANY experiments made with alcohol, ether, para-toluidine, diphenylamine, paraffine, thymol, and less completely with naphthaline, vanilline, azo-benzol, α -naphtol, monobrom camphor, benzoic acid, caprinic acid, palmitic acid, and monochlor-acetic acid, show that if temperature and pressure vary linearly at a mean rate of about $\cdot 11^{\circ}$ C. per atmosphere there will be no change of volume. My temperatures lie between 30° and 300° , and the pressure between 20 atm. and 500 atm. By judicious extrapolation (enclosure of the experimental data, volume, pressure, temperature, between two mathematical functions, one of which is necessarily above and the other below the observed values; whereas both of the said functions fall within the limits of error, within the interval of observation), the probable contours can be computed to 1000 atm., with results accentuating the above law. The linear relation was predicted from theoretical considerations by Dupré (1869) and by Lévy (1884)—considerations soon proved to be inadequate by Massieu, H. F. Weber, Boltzmann and Clausius. Ramsay and Young (1887) established the relation in question experimentally for vapors, but not, I think, very fully for liquids decidedly below their critical points. Reasoning from these data Fitzgerald (1887) investigated the consequences of the law, viz: (1) specific heat under constant volume is a temperature function only; (2) internal energy and entropy can be expressed as a sum of two terms one of which is a volume function only and the other a temperature function only. Thus Ramsay, Young and Fitzgerald arrive substantially at the same position from which Dupré and Lévy originally started.

* The present communication has the assent of Mr. Clarence King, at whose suggestion and under whose instruction the work was done.

My own results were developed quite independently of the earlier work, and they apply emphatically for liquids. Thymol and toluidine were even under cooled 25° and 15° below their respective melting points. My range of pressures is therefore 6 or 7 times as large as that of Ramsay and Young. Thus my work, supplementing the researches of the English chemists, is not superfluous. Water seems to be a notable exception.

I found furthermore, that the pressure necessary to solidify a substance is, *cæt. par.*, decidedly in excess of the pressure (positive or negative, external) at which it again liquifies. Here therefore is an exceedingly simple, and hence a type lag phenomenon. Making extensive use of it, I am led to results bearing directly on all lag phenomena, and beyond this on the molecular structure of matter in general. Data are in hand for paraffine, naphthaline, palmitic and chloracetic acids.

Operating above 100°C. , I observed that (liquid) water at a pressure of 20 atm. and a temperature of 185° attacks ordinary lead glass so rapidly that in very fine capillary tubes the contents become opaque and solid in about an hour. During this action the compressibility at 185° gradually and regularly increased to a final value (200×10^6), about 3 times the original value (77×10^6). At the same time the isothermal volume of the silicated water decreased fully 13 per cent of its original bulk. So large a contraction will probably not be unaccompanied by rise of temperature.

Finally, in case of mercury, the simultaneous decrements of electrical resistance, r , and volume, v , due to pressure (0 to 400 atm.), were found to be proportional to each other. Approximately $\delta r/r = 10 \delta v/v$. This result initiates a new method of attacking the above thermo-dynamic problems, and it has already led ulteriorly, to results of electrical interest.