

TABLE V.

LIQUID	ΔE_{vis} CAL./MOLE	ΔE_{vap} AT B.P. CAL./MOLE	ΔE_{vap}	
			ΔE_{vis}	n
CCl ₄	2500	6600	2.66	3
C ₆ H ₆	2540	6660	2.62	3
Cyclohexane	2890	6700	2.32	3
CH ₂	719	1820	2.53	3
A	516	1420	2.75	3
N ₂	449	1210	2.70	3
CO	466	1310	2.80	3
O ₂	398	1470	3.69	3½
C ₂ H ₅ Cl ₂	2270	6930	3.05	3½
C ₂ H ₅ Br ₂	2590	7890	3.04	3½
Pentane	1580	5510	3.50	4
Hexane	1715	6220	3.61	4
CHCl ₃	1760	6630	3.76	4
C ₂ H ₅ I	1720	6400	3.72	4
C ₂ H ₅ Br	1585	6080	3.84	4
CS ₂	1280	5920	4.63	4
C ₂ H ₅ CH ₃	2120	7240	3.42	4
Ether	1610	5700	3.54	4
Acetone	1655	6400	3.86	4
C ₂ H ₄	793	3500	4.41	4

calculation was made using $M=440$, and the good agreement is due to this value having been found by trial beforehand. It is, however, within the limit of uncertainty of the experimentally determined molecular weight (of the oil on which the viscosity measurements were made). Considering the fact that the data were from two different Pennsylvania oils, the results appear promising, at least. The pressures of 375 and 1900 kg/cm² were not arbitrarily selected, but were the lowest and highest pressures, respectively, at which $(\partial p/\partial T)_V$ could be evaluated from the PVT data. Experimental data suitable for a test over a wider range of pressures would be desirable, since Eq. (8) appears to hold up to 2000 kg/cm² for pure liquids.

Comparison of the Theory with the Empirical Equation $\eta = Ae^{B/T}$

It is a well-known experimental fact that a plot of $\log \eta$ vs. $1/T$ is a straight line for all normal liquids, or that

$$\eta = Ae^{B/T}$$

$$= Ae^{\Delta E_{vis}/RT} \quad (9)$$

and this relation is now one of the best established empirical rules regarding liquids. All normal liquids, including hydrocarbons and their halogen

derivatives, ketones, ethers, sulfides, esters, acid anhydrides, liquefied gases, covalent inorganic compounds, etc. obey the equation within experimental error, and also most liquid metals and fused salts. In fact, it is so universally obeyed by normal liquids that it can be considered empirically as a necessary condition for a liquid of unchanging molecular state, although it cannot be considered a sufficient condition. Fig. 7 shows a plot of some liquids representing several types of compounds.

This relation has had a long and devious history, having been independently "rediscovered" periodically ever since 1913. Following is a chronological summary of the independent publications, the asterisk indicating those which can be thrown into the identical form of $\eta = Ae^{B/T}$:

1913	de Guzman ¹¹	*
1916	Arrhenius ¹²	$\eta v^{\frac{1}{2}} = Ae^{B/T}$
1917	Kendall and Monroe ¹³	*
1918	Drucker ¹⁴	*
1923	Raman ¹⁵	*
1925	Fulcher ¹⁶	$\eta = Ae^{B/T+C}$
1926	Dunn ¹⁷	*
1929	Busse and Karrer ^{17a}	*
1930	Andrade ¹⁸	*
1930	Sheppard ¹⁹	*
1931	Tonomura ²⁰	$\eta = Ae^{B/T+C}$
1933	Cragoe ²¹	$\eta v = Ae^{B/T}$
1934	Andrade ²²	$\eta v^{\frac{1}{2}} = Ae^{B/vT}$
1937	Souders ²³	$\eta v = Ae^{B/T}$

The symbol V is the specific volume.

The variant forms which contain a volume factor make little or no improvement over the simple equation. In the recent paper by Souders he shows that there is little to choose between his equation and Andrade's 1934 equation, except that the former is easier to use. That $\eta = Ae^{B/T}$ and the variant forms containing the volume work about equally well is due to the slow variation of the volume with temperature.

The several deductions of this relationship have all been based on loose thermodynamic analogies with the vapor pressure, or on vague over-simplified applications of the Boltzmann factor, or on wholly empirical grounds, so that the equation to date must be considered as being purely an empirical one.

From the work of Eyring and the writer^{1, 2} it is obvious that the constant $\Delta E_{vis}(=RB)$ is connected with the energy of vaporization. De

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η (OBS.) POISES	$\frac{\eta_{1900}}{\eta_{375}}$ (OBS.)
0.77	6.95
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