TABLE IV

ESTIMATED LATENT HEATS OF VINYL CHLORIDE

Temp., °C.	Slope of vapor-pressure curve, cm. of Hg/°C.	Latent heat, cal./g. By Clapeyron's equation	Latent heat, cal./g. By corresponding states
−20	25.4	88.4	85.7
−10	35.4	84.1	84.1
0	47.1	81.2	83.0
+10	61.8	79.8	81.7
20	79.7	77.7	80.2
30	100.2	76.2	78.5
40	124	73.2	76.6
50	151	70.1	74.4

Summary

The vapor pressure of vinyl chloride was measured from —28 to 60°. The normal boiling point was found to be —13.9, ±0.1°.

The liquid densities were measured over the temperature range —13 to 60°.

The freezing point was found to be —159.7, ±0.1°.

Estimated values of the vapor densities and latent heats were computed from theoretical relationships.

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NOTE

Calculation of Heats of Combustion.—Kharasch and Sher[1] have applied the electronic conception of valence to the calculation of heats of combustion of organic compounds. They find that the energy change which accompanies the displacement of one valence electron from the position which it occupies in methane, a carbon chain or the benzene nucleus to the position after combustion in carbon dioxide is 26.05 kg. cal. per mole. Thus the heat of combustion of a hydrocarbon is given by the product $26.05 \times N$, where N is the number of electrons displaced.[2] Electrons associated with bonds other than C—C and C—H are accompanied by an additional energy change during combustion. To the term $26.05\ N$, Kharasch and Sher add 26 kg. cal. for each aliphatic ether group, 13 kg. cal. for each ethylenic linkage, primary alcohol, ester or aromatic ether group and 6.5 kg. cal. for each secondary alcohol or ketone group. No correction is added for tertiary alcohol, phenol or acid groups. In most cases this method gives good results, but for aromatic compounds the calculated values are uniformly higher than the experimental values and the

[1] Kharasch and Sher, *J. Phys. Chem.*, **29**, 625 (1925).

[2] Each bond corresponds to two electrons. In oxygen compounds the two oxygen bonds are disregarded. Thus N is 8 for methane, 30 for benzene, 58 for phenyl benzoate, etc.

deviations become greater as the number of benzene nuclei increases. This necessitates a correction for each benzene nucleus. The method proposed for this correction follows.

The electrons associated with three of the bonds of the benzene nucleus (μ electrons) will be assumed to differ in energy relations from those of the other twelve (λ electrons).[3] There is an energy change of 24.85 and 26.05 kg. cal. per mole, respectively, for each μ and λ electron present in the compound being burned. The heat of combustion in kg. cal. per mole at constant pressure of compounds containing C and H, or C, H and O, is given by the equation[4] $Q_p = 26.05\lambda + 24.85\mu + 22.7$ for each ether group + 19.5 for each aldehyde group + 13 for each ethylenic linkage, primary alcohol or ester group + 6.5 for each secondary alcohol group + 3.2 for each phenol or tertiary alcohol group + 0.0 for each acid or ketone group.

Of the 57 aromatic compounds containing C and H, or C, H and O, whose heats of combustion were calculated by Kharasch and Sher, the new method gives results closer to the experimental values in 37 cases and the same in 7 cases. The average per cent. difference between experimental and calculated values is lowered from 0.52 to 0.32%. Table I shows per cent. difference between calculated and experimental values for 171 aromatic compounds of different types.

TABLE I

DIFFERENCE BETWEEN CALCULATED AND EXPERIMENTAL HEATS OF COMBUSTION

Aromatic compounds containing C and H, or C, H and O	No. of calculations	Difference between calculated and experimental values Total %	Average %
Saturated hydrocarbons	26	8.4	0.32
Ethylenic hydrocarbons	11	2.7	0.25
Phenols	24	10.7	0.44
Ethers	22	8.0	0.36
Aldehydes	12	7.3	0.61
Ketones	15	5.5	0.37
Acids	33	13.3	0.40
Esters	28	8.3	0.30
Total	171	64.2	0.37

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[3] See Pauling, THIS JOURNAL, **48**, 1132 (1926).

[4] λ and μ are the numbers of λ and μ electrons present. In aliphatic compounds there are no μ electrons and λ is the same as N in Kharasch and Sher's equation. Each benzene nucleus contains 6 μ electrons. Thus $\lambda = 38$ for hexane; $\lambda = 48$, $\mu = 18$ for anthracene; $\lambda = 46$, $\mu = 12$ for phenyl benzoate, etc.