Surface Tension of Perfluoromethylcyclohexane

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THE SURFACE TENSION of perfluoromethylcyclohexane has been measured at 10° intervals from 0° to 50° C. by the maximum bubble pressure method. The least squares equation, $\gamma = 17.69 - 0.0973t$, where γ is the surface tension in dynes per centimeter, and t is the centigrade temperature, reproduces the experimental results (Table I) with an average deviation of ± 0.04 dyne per cm.

Table I. Surface Tension and Latent Heat of the Surface of Perfluoromethylcyclohexane

Temp., ° C.	Surface Tension, Dynes/Cm.	Latent Heat of Surface, Ergs/Sq. Cm.
0	17.70	26.6
10	16.65	27.6
20	15.70	28.5
30	14.70	29.5
40	13.80	30.5
50	12.90	31.4

EXPERIMENTAL

Purification. Perfluoromethylcyclohexane, Du Pont FCS-326, a sample previously purified for gas solubility work (*1*), was repurified by shaking with concentrated H_2SO_4, washing, drying over Drierite, and distilling. The sample used had a boiling point of 76.0–6.1° C. at 755 mm.; literature (*3*) boiling point 76.14° at 760 mm. The infrared spectrum of the purified sample was identical to that shown by Weiblen (*9*). A gas chromatogram gave only one peak.

Apparatus. The maximum bubble pressure apparatus built and described by Quayle (*6*) was used. The temperature variation was $\pm 0.1°$ between 0° and 10° and $\pm 0.05°$ up to 50° C. Completely independent determinations, which checked within 0.1 dynes per cm., were made by each author. Average results, rounded off to the nearest 0.05 dynes per cm., are given in Table I.

RESULTS AND DISCUSSION

The entropy of surface formation $s = -(\partial\gamma/\partial T)$, latent heat, $Q = -T(\partial\gamma/\partial T)$, and enthalpy, $h = \gamma - T(\partial\gamma/\partial T)$, were calculated (*5*) from the surface tension and the temperature dependence of surface tension for the perfluoromethylcyclohexane and the corresponding hydrocarbon methylcyclohexane (*7*).

The latent heats are given in Table I. The thermodynamics for forming new surface at 30° C. for fluorocarbon and hydrocarbon are compared in Table II. Both entropy and enthalpy appear constant over the 50° temperature range. The entropy (temperature dependence of the surface tension) is only 5% greater for the hydrocarbon, surface free energy is 55% greater, and enthalpy is 22% greater.

Table II. Thermodynamic Properties of Surface Formation of Perfluoromethylcyclohexane and Methylcyclohexane at 30° C.

	C_7F_{14}	C_7H_{14}
Surface free energy, ergs/sq. cm.	14.70	22.62
Enthropy, ergs/deg./sq. cm.	0.0973	0.103
Latent heat, ergs/sq. cm.	29.5	31.2
Enthalpy, ergs/sq. cm.	44.2	53.8

Fluorocarbons have the lowest solubility parameters of any substances liquid at room temperature (*8*). The much lower surface free energy and enthalpy are further indications of lower intermolecular forces between fluorocarbons as compared to the corresponding hydrocarbons. The solubility parameter of the perfluoromethylcyclohexane calculated from the surface tension at 25° C. and the empirical relation $\delta = 4.1(\gamma/V^{1/3})^{0.43}$ (*4*) is 6.2. This compares well with the value 6.1 calculated (*8*) from heat of vaporization data.

The Eötvös constant [slope of a plot of $\gamma(M/d)^{2/3}$ against temperature] of perfluoromethylcyclohexane has the unusually high value of 2.75, and is another indication of the comparatively low intermolecular forces between fluorocarbon molcules.

The atomic parachor of fluorine in perfluoromethylcyclohexane calculated from the surface tension, and assuming values of 9.0 for carbon and 0.8 for a six-membered ring, is 23.2. Quayle (*6*) recommends 26.1 as the parachor of fluorine, but this value is derived from monosubstituted fluorine compounds, not perfluoro compounds. Fowler and others (*2*) report an atomic parachor of 24.6 from measurement at one temperature.

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