

## A Criterion for Normal Liquids

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TABLE I. Calculated distribution of isotopic species of C<sup>13</sup>(16.7 percent)-propane.

Species	Propane synthesized	After intramolecular equilibration	After intra- plus intermolecular equilibration
C <sub>3</sub> <sup>12</sup> H <sub>8</sub>	0.8150	0.8150	0.8237
C <sup>12</sup> H <sub>3</sub> —C <sup>12</sup> H <sub>2</sub> —C <sup>13</sup> H <sub>3</sub>	0.1720	0.1204	0.1100
C <sup>12</sup> H <sub>3</sub> —C <sup>13</sup> H <sub>2</sub> —C <sup>12</sup> H <sub>3</sub>	0.00856	0.0602	0.0550
C <sup>13</sup> H <sub>3</sub> —C <sup>12</sup> H <sub>2</sub> —C <sup>12</sup> H <sub>3</sub>	0.00182	0.00236	0.00734
C <sup>13</sup> H <sub>3</sub> —C <sup>12</sup> H <sub>2</sub> —C <sup>13</sup> H <sub>3</sub>	0.00172	0.00118	0.00367
C <sub>3</sub> <sup>13</sup> H <sub>8</sub>	0.00002	0.00002	0.00025
(46 <sup>+</sup> )/(44 <sup>+</sup> )±0.0003 <sup>a</sup>	0.0037	0.0037	0.0118
(30 <sup>+</sup> )/(29 <sup>+</sup> )±0.0010 <sup>a</sup>	0.1020 <sup>b</sup>	0.1300 <sup>b</sup>	0.1265 <sup>b</sup>

<sup>a</sup> Accuracy of measurement of these quantities.<sup>b</sup> Calculated assuming equal dissociation probability for C<sup>12</sup>—C<sup>12</sup> and C<sup>12</sup>—C<sup>13</sup> bonds.TABLE II. Mass spectral relative intensities in C<sup>13</sup>-propane during isomerization.

Time <sup>a</sup>	(30 <sup>+</sup> )/(29 <sup>+</sup> )	(46 <sup>+</sup> )/(44 <sup>+</sup> )
0 <sup>b</sup>	0.106(3)	0.0038
65	0.119(4)	0.0034
186	0.126(5)	0.0034
261	0.128(3)	0.0036
405	0.130(1)	0.0039
594	0.129(5)	0.0036
1074	0.133(6)	0.0039

<sup>a</sup> Time in hours of contact between vapor at approximately 450-mm pressure with a catalyst prepared by the addition of 0.023-gram H<sub>2</sub>O to anhydrous aluminum bromide (0.40 gram).<sup>b</sup> The propane-1-C<sup>13</sup> as synthesized. The intensities of all of the C<sub>2</sub> and C<sub>3</sub> ions and ionic fragments agreed with the calculated values to within the experimental uncertainty.

of the ions of  $m/q = 44^+$ ,  $43^+$ ,  $42^+$ , and  $41^+$  in the mass spectrum of C<sub>3</sub><sup>12</sup>H<sub>8</sub> are known. Furthermore, the relative concentrations of the isomeric propanes, -1-C<sup>13</sup> and -2-C<sup>13</sup>, can be determined from the relative intensities of the ions of  $m/q = 30^+$  and  $29^+$  since the former species can give rise to but half as many ions C<sup>12</sup>C<sup>13</sup>H<sub>6</sub><sup>+</sup> ( $m/q = 30^+$ ) as can the latter species. This determination of the isotopic isomer distribution presupposes the knowledge of the concentrations of C<sub>3</sub><sup>12</sup>H<sub>8</sub>, C<sub>2</sub><sup>12</sup>C<sup>13</sup>H<sub>3</sub>, C<sup>12</sup>C<sub>2</sub><sup>13</sup>H<sub>3</sub>, and C<sub>3</sub><sup>13</sup>H<sub>8</sub>. Intramolecular equilibration requires the species distribution (statistical) shown in column 3 of Table I, while complete inter and intramolecular equilibration (statistical) requires the distribution shown in column 4. The relative ion intensities (46<sup>+</sup>)/(44<sup>+</sup>) and (30<sup>+</sup>)/(29<sup>+</sup>), which are measures of the relative species concentrations C<sup>12</sup>C<sub>2</sub><sup>13</sup>H<sub>3</sub>/C<sub>3</sub><sup>12</sup>H<sub>8</sub> and C<sup>12</sup>H<sub>3</sub>—C<sup>13</sup>H<sub>2</sub>—C<sup>12</sup>H<sub>3</sub>/C<sup>12</sup>H<sub>3</sub>—C<sup>12</sup>H<sub>2</sub>—C<sup>13</sup>H<sub>3</sub>, respectively, calculated from the mass spectrum of ordinary propane for the three situations, are shown in the last two rows of Table I.

In Table II there are shown the measured values of the relative intensities (46<sup>+</sup>)/(44<sup>+</sup>) and (30<sup>+</sup>)/(29<sup>+</sup>) for the prepared propane-1-C<sup>13</sup> and after 65, 186, 261, 405, 594, and 1074 hours in contact with almost anhydrous aluminum bromide at 25°C. At 65 hours the (30<sup>+</sup>)/(29<sup>+</sup>) ratio had undergone about one-half its maximum change, while even at 1074 hours the (46<sup>+</sup>)/(44<sup>+</sup>) ratio was still unchanged (within the experimental error). The disagreement between the initial and final values in Table II and those given in Table I are believed to be due to a small (~5 percent) difference in the dissociation probabilities of C<sup>12</sup>—C<sup>12</sup>

and C<sup>12</sup>—C<sup>13</sup> bonds. Similar experiments with butane are now in progress.

<sup>1</sup> J. W. Otvos and C. D. Wagner, *Science* **106**, 409 (1947).

\* Recent measurements with a sample containing 54 atom percent C<sup>13</sup> allow a more exact evaluation of the changes in these dissociation probabilities, with the result that the dissociation probability of the C<sup>13</sup>—C<sup>12</sup> bond is decreased by 12 percent±1 percent and that of the C<sup>12</sup>—C<sup>12</sup> bond increased by 7 percent±0.2 percent.

## A Criterion for Normal Liquids

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IN a recent communication Parashad<sup>1</sup> has proposed a formula to distinguish between normal liquids and associated liquids. For liquids which we may regard as normal, he finds

$$\Delta E^v \beta / V \alpha = T, \quad (1)$$

while for abnormal liquids, the left-hand member is greater than  $T$

$$\Delta E^v \beta / V \alpha > T. \quad (2)$$

$\Delta E^v$  is the energy of vaporization,  $\beta$  is the isothermal compressibility,  $V$  is the molal volume,  $\alpha$  is the coefficient of cubical expansion, and  $T$  is the absolute temperature.

In reality, the criterion which Parashad proposed is not novel. Pure thermodynamics yields what has been called the "thermodynamic equation of state"

$$(\partial E / \partial V)_T = T(\partial P / \partial T)_v - P. \quad (3)$$

Since for liquids under normal conditions,  $P$  is negligibly small compared with the other two terms, we may write

$$(\partial E / \partial V)_T = T(\partial P / \partial T)_v. \quad (4)$$

Since  $(\partial P / \partial T)_v = \alpha / \beta$ , we obtain

$$(\partial E / \partial V)_T = T \alpha / \beta.$$

It remains for us to relate  $(\partial E / \partial V)_T$  and  $\Delta E^v / V$ . Over a small range of volumes, we may represent  $E$  and  $(\partial E / \partial V)_T$  in the functional forms:

$$E = a / V^n, \quad (5)$$

$$\partial E / \partial V = -na / V^{n+1} = -nE / V. \quad (6)$$

For most practical purposes the cohesive energy per mole  $E$  may be replaced by  $-\Delta E^v$ , and Eq. 5 may be rewritten

$$T \alpha / \beta = n \Delta E^v / V. \quad (7)$$

For a van der Waals liquid  $n$  is unity, and this last Eq. 8 reduces to the first. Although the van der Waals equation is certainly a poor approximation for liquids, Hildebrand and co-workers have measured  $(\partial P / \partial T)_v$  directly for a number of normal liquids and on comparison with  $\Delta E^v / V$ , it was found that  $n$  is, in fact, not far from unity.<sup>2</sup> For methyl alcohol and mercury, although for different reasons, the calculated  $n$  falls far short of unity, in agreement with Eq. (2).

<sup>1</sup> R. Parashad, *J. Chem. Phys.* **15**, 761 (1947).

<sup>2</sup> J. H. Hildebrand, *Phys. Rev.* **34**, 984 (1929); see also J. H. Hildebrand, *Solubility of Non-Electrolytes* (Reinhold Publishing Corporation, New York, 1936), second edition, pp. 93–101, and *J. Chem. Phys.* **15**, 727 (1947), particularly Table VII.