Table VI gives a comparison of values of t_{25}, the time for 25% pressure increase, in both cases taken from smoothed curves, and referred to that for ethyl ether as 1.00, to eliminate temperature differences.

<div align="center">TABLE VI</div>

Pressure, cm.	t_{25}, methyl / t_{25}, ethyl		t_{25}, mixture / t_{25}, ethyl	
	Steacie	Kassel	Steacie	Kassel
30	1.23	1.27	1.54	1.35
10	1.27	1.34	1.42	1.37

That is, in the present work methyl ether has been found to decompose slightly more slowly, and the 1:1 mixture rather faster than in that of Steacie, the rate for ethyl ether being assumed to be the same. No reason is evident why this should be so. In both investigations the experiments were performed in random order, and hence almost every systematic error was eliminated.

Summary

It has been found that mixtures of methyl and ethyl ether decompose significantly faster than the rate calculated from the partial pressures of the separate ethers. This result, which is in disagreement with a report made by Steacie, means that the transfer of internal energy between unlike ether molecules at collisions takes place about as readily as between like ether molecules; the exact value found is 66%, on which, however, not much confidence should be placed. A similar result is found for mixtures of acetone and ethyl ether.

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NOTE

The Standard Electrode Potentials of Silver–Silver Chloride and Calomel Electrodes and the Single Potentials of Calomel Electrodes

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Carmody's[1] accurate data on the potentials of the cells H_2, HCl (xM), AgCl(s), Ag in quartz apparatus, when transformed into the form

$$\log \gamma + \text{const.} = \frac{E^\circ}{0.11831} + \log \gamma = -\frac{E}{0.11831} - \log m^\pm$$

superimpose beautifully on the curve of $\log \gamma$ vs. $m^{1/2}$, calculated by Randall and Young.[2] The constant obtained in this way is -1.8782, corresponding to

$$Ag(s) + Cl^- = AgCl(s) + E^-; \quad E^\circ_{298\cdot 1} = -0.2222_1 \text{ v.}$$
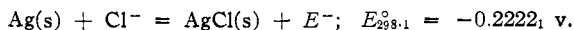
whereas Carmody's extrapolation of E' yielded -0.2223 v.

[1] W. R. Carmody, THIS JOURNAL, 54, 188 (1932).

[2] M. Randall and L. F. Young, ibid., 50, 989 (1928).

Since comparable measurements of the hydrogen–calomel cell do not exist, the best value for the standard potential of the calomel electrode is to be had from measurements of the cell

$$\text{Ag (elect. crystals)} + \text{HgCl(s)} = \text{Hg(l)} + \text{AgCl(s)}$$

Randall and Young confirmed Gerke's[3] value, $E_{298.1} = 0.0455$ v., and found the same value when the silver–silver chloride electrodes were of the spiral type, also used by Carmody. This held for potassium chloride solutions and for hydrochloric acid solutions so long as the latter were free of oxygen. We may thus write

$$\text{Hg(l)} + \text{Cl}^- = \text{HgCl(s)} + E^-; \quad E^0_{298.1} = -0.2677 \text{ v.}$$

From the "International Critical Tables," 1 Vol. M KCl at 18° has a density 1.04491 and is thus 7.135% KCl and 1.030_5 M. Also 0.1 Vol. M KCl at 18° has a density 1.0034 and is thus 0.743% KCl and 0.1004_1 M. These two solutions as well as 0.1 M KCl are used in reference calomel electrodes.

With the values of activity coefficients determined from freezing point measurements and corrected for the heats of dilution[4] the potentials listed in Table I result.

TABLE I

ELECTRODE POTENTIALS OF VARIOUS CALOMEL ELECTRODES

m	0.1	0.1004	1.0305
γ	0.7707	0.7704	0.6610
E	-0.3335_4	-0.333_{45}	-0.279_{56}

Since the potential of the "normal calomel electrode" by convention includes that of the liquid junction, KCl (1 Vol. M), KCl (0.1 M), which is -0.0004 v., its value is -0.2800 v. Attention is directed to the fact that the single potential of the 0.1 M KCl or 0.1 Vol. M KCl calomel electrode plus that of the cell

$$\text{Hg, HgCl(s)KCl(1 Vol. } M\text{), KCl(0.1 Vol. } M\text{)HgCl(s) Hg}$$
$$E_{298.1} = 0.0529 \text{ v.}$$
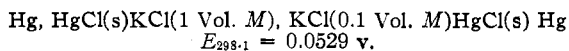
or -0.2806 v. does not agree with the value -0.2800 v.

[3] R. H. Gerke, THIS JOURNAL, 44, 1684 (1922).
[4] H. M. Spencer, ibid., 54 (1932).