[CONTRIBUTION FROM THE KENT CHEMICAL LABORATORY OF THE UNIVERSITY OF CHICAGO]

VAPORIZATION IN STEPS AS RELATED TO SURFACE FORMATION

Seventh Paper on the Orientation of Molecules in Surfaces[1]

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Introduction

That the process of vaporization may occur in steps is evident. Thus, mechanical forces may cause a liquid to spread out in a thin layer, or may throw it out into sheets, or atomize it into minute drops. Any of these processes increases the proportion of the liquid in the surface, and since the molecules in the surface are more nearly in the vapor state, both in the sense of contiguity and of the energy relations involved, than those inside the liquid, surface formation may be considered as one of the steps in the process of vaporization. It is therefore evident that a part of the energy necessary for vaporization may be supplied directly in the mechanical form.

It is the purpose of the present paper to consider to what extent the different steps in the vaporization of a liquid may be evaluated in terms of energy. At all temperatures below the critical point all molecules which pass from the interior of a liquid into the vapor must pass through the surface, so the principal stages in the process of vaporization are, first, surface formation, and second, the jumping out of the molecules from the surface into the vapor. The energy of surface formation is supplied partly

[1] Presented in a seminar at the University of Illinois in the year 1918-19.

as heat, specified as the latent heat of surface formation, and partly in the mechanical form which gives rise to the free surface energy.

It would be very simple to determine the energy values for the steps listed above if a definite amount of liquid, as that corresponding to 1 mol of vapor, could first be drawn from the interior into the surface, and then vaporized. However, while it is very easy to do this for the total change from the interior of the liquid to the vapor, it is not so simple in the steps in which the surface is involved, since the number of molecules in the surface is not known. However the work of Langmuir,[2] and of Harkins and his coworkers Clark, King and Grafton,[3] has given extensive data on the number of molecules in surface films of organic sub *tances on water which should enable us to make an estimate of the number of molecules in the surface of a pure liquid, which, presumably, will not be very far from the actual number. When this is done it becomes possible to calculate the molar latent heat of surface formation and the molar free surface energy, and to compare these with the molar heat of vaporization. In the present paper these molar values will be divided by 6.062×10^{23}, thus converting them into the mean molecular values.

Calculation of the Energy Values for the Vaporization Steps

In estimating the number of molecules per square centimeter of surface of a liquid, the corresponding number determined in surface films on water may first be considered. These are listed for a few substances taken as examples, in Table I.

TABLE I

NUMBER OF MOLECULES IN THE "MONOMOLECULAR FILM" ON A WATER SURFACE[2,3]

Substance	No. atoms carbon	No. molecules per sq. cm. $\times 10^{-14}$
1. Formic acid	1	(1.7)
2. Acetic acid	2	(2.0)
3. Propionic acid	3	2.6
4. Butyric acid	4	2.8
5. Valeric acid	5	(3.1)
6. Caproic acid	6	(3.2)
7. Heptylic acid	7	2.9
8. Nonylic acid	9	3.1
9. Decylic acid	10	3.3
10. Palmitic acid	16	4.8
11. Stearic acid	18	4.6
12. Cerotic acid	25	4.0
13. Octyl alcohol	8	2.9
14. Myricyl alcohol	30	3.7
15. Propyl formate	4	3.7

[2] The results listed for Compounds 10 to 15 in Table I, were obtained by Langmuir, THIS JOURNAL, **39**, 1848–1906 (1917).

[3] The results for Compounds 1 to 9 were obtained by Harkins, Clark and King in the years 1916 to 1919, but have not previously been published.

The most complete data which have been collected for a single series of compounds are those for the acids listed in the table. The results which are inclosed in parentheses are less accurate than the others. One remarkable feature of the values is that the larger the molecule, until the number of carbon atoms reaches close to 16, the smaller the area covered. This is evidently because the attraction between the molecules in the surface film increases with their length. Since this attraction is small in the case of the shorter molecules, they spread out more over the surface of the water; but as the attraction becomes greater they are held together more closely and the orientation is more exact. However, if it were not for this effect, the larger molecules would be expected to occupy the greater surface, even when they are oriented, since, on account of their heat motion, some molecules would be doubled and turned out of their regular positions, which would increase the surface occupied. These two effects result in the appearance of a maximum number of molecules (minimum area per molecule) somewhere near 16 carbon atoms, where the number of molecules per square centimeter is 4.8×10^{14}. While short or small molecules may thus occupy a greater area on water by spreading out somewhat over the surface, this is not possible in the case of a pure liquid, since, if the outermost molecules spread out, the openings thus produced are filled by like molecules, so that in a pure acid or alcohol, the number of molecules per square centimeter for short molecules may be expected to be as high as or even higher than the maximum listed above.

While the molecules in the surface of a liquid may be supposed to have a random arrangement in the plane of the surface (with an orientation with respect to the perpendicular to the plane), a simplifying assumption will be introduced for purposes of calculation. This is that the number of molecules in unit area of the surface is equal to the two-thirds power of the number in unit volume. While the orientation of the molecules in the surface would cause a very lack of *space* symmetry in the case of such molecules as those of palmitic, stearic and cerotic acids, it seems evident that there are many cases in which orientation need not result in any considerable lack of symmetry of this sort. This may be illustrated most easily by the use of an analogy. Suppose a sphere to consist of one heavy and one light hemisphere, and that it rests upon a frictionless plane. It is evident that it would orient with the light hemisphere up, but that the space symmetry would be complete. Most of the molecules listed in the tables of this paper are not of the type which would be expected to depart widely in the sense of space symmetry with respect to general form, though it need not be assumed that they actually take on a spherical form; nor need it be assumed that all of the molecules in the surface lie in a plane. Some molecules undoubtedly lie higher in the surface than others, and the former will in general possess more surface energy of the potential form. The energy

TABLE II A
ENERGY VALUES FOR THE VAPORIZATION IN STEPS OF NON-ASSOCIATED LIQUIDS

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
T	$\mathfrak{C}$	Γ $\frac{ergs}{cm^2.}$	E $\frac{ergs}{cm^2.}$	$\frac{d\Gamma}{dT}$	Λ_i cal g.	$\frac{10^4 E}{T\Lambda_i}$	d	$n \times 10^{21}$	λ $\times 10^{14}$ ergs	l $\times 10^{14}$ ergs	e $\times 10^{14}$ ergs	j $\times 10^{14}$ ergs	λ_i $\times 10^{14}$ ergs	$\frac{e}{\lambda}$	$\frac{e\,d^{2/3}}{\lambda_i \mathfrak{C}}$	s $\times 10^{16}$ ergs	s' $\times 10^{16}$ ergs
Carbon Tetrachloride $T_c = 556$																	
293	0.527	25.68	....	....	....	...	1.594	6.28	7.85	10.6	18.5	29.3	47.8	0.315	....	....	....
313	0.563	24.41	60.87	0.117	....	...	1.554	6.12	7.29	10.9	18.2	...	37.4	0.322	....	3.48	2.88
413	0.743	12.22	54.80	0.103	35.27	37.6	1.345	5.30	4.02	14.0	18.0	...	37.4	0.481	0.789	3.39	2.93
463	0.833	7.28	51.26	0.095	29.52	37.5	1.219	4.80	2.56	15.5	18.0	13.3	31.3	0.574	0.785	3.34	2.96
503	0.905	3.56	47.30	0.087	23.73	39.6	1.086	4.28	1.35	16.6	17.9	7.3	25.2	0.712	0.832	3.30	2.95
523	0.941	1.93	41.68	0.076	19.85	40.2	0.998	3.93	0.77	16.0	16.7	4.4	21.1	0.794	0.827	3.05	2.83
533	0.959	1.20	36.91	0.067	17.15	40.4	0.941	3.71	0.50	14.9	15.4	2.8	18.2	0.846	0.832	2.79	....
Diethyl Ether $T_c = 467.5$																	
313	0.670	14.05	49.1	0.112	75.02	20.9	0.6894	5.64	4.43	9.6	13.4	25.0	30.4	0.350	0.407	3.05	....
323	0.691	12.94	48.9	0.111	72.66	20.8	0.6764	5.54	4.14	11.5	15.6	21.5	37.2	0.421	0.469	3.56	3.11
373	0.798	7.63	45.5	0.102	60.4	20.2	0.6105	4.95	2.67	12.9	15.6	15.3	30.9	0.504	0.455	3.47	2.98
423	0.905	2.88	39.3	0.086	44.3	21.0	0.5180	4.24	1.10	13.9	15.0	7.6	22.7	0.662	0.472	3.28	2.29
443	0.948	1.33	32.8	0.071	34.3	21.6	0.4658	3.81	0.55	12.9	13.4	4.1	17.5	0.766	0.486	2.91	2.70
458	0.980	0.38	23.0	0.049	23.0	21.8	0.4018	3.29	0.17	10.2	10.4	1.4	11.8	0.885	0.492	2.24	....
Benzene $T_c = 561.5$																	
363	0.647	19.16	61.3	0.116	84.69	19.9	0.8041	6.25	5.65	12.4	18.1	27.5	45.6	0.396	0.530	3.42	2.83
413	0.763	13.45	59.1	0.111	73.45	19.5	0.7440	5.78	4.18	14.2	18.4	21.2	39.6	0.464	0.518	3.43	2.95
463	0.825	8.16	54.5	0.100	62.51	18.8	0.6758	5.25	2.70	15.3	18.0	15.6	33.7	0.536	0.500	3.31	2.88
513	0.914	3.41	48.1	0.087	46.53	20.1	0.5851	4.54	1.21	15.9	17.5	7.5	25.1	0.699	0.535	3.17	2.89
533	0.949	1.75	43.6	0.079	37.55	21.8	0.5328	4.14	0.68	16.2	16.9	3.3	20.2	0.836	0.579	3.05	2.79
Chlorobenzene $T_c = 63.3$																	
433	0.684	16.62	59.7	0.100	64.14	21.5	0.9480	5.11	5.73	14.9	20.6	29.2	49.8	0.414	0.584	3.43	2.89
473	0.747	12.72	58.6	0.097	58.50	21.2	0.8955	4.83	4.45	16.2	20.5	24.9	45.4	0.452	0.562	3.40	2.92
503	0.795	9.88	56.7	0.093	53.90	20.9	0.8518	4.59	3.58	16.9	20.5	21.3	41.9	0.491	0.555	3.37	2.93
533	0.842	7.14	53.8	0.088	48.17	21.0	0.8016	4.32	2.69	17.6	20.3	18.0	38.3	0.530	0.543	3.30	2.93
Ethyl Acetate $T_c = 524$																	
363	0.693	15.14	57.6	0.117	76.40	20.8	0.8112	5.58	4.81	13.5	18.3	28.1	46.4	0.394	0.495	3.72	3.18
413	0.788	9.57	53.8	0.107	64.42	20.2	0.7378	5.08	3.24	15.0	18.2	21.0	39.2	0.465	0.482	3.62	3.15
463	0.884	4.54	47.6	0.093	49.48	20.8	0.6441	4.43	1.68	15.9	17.6	12.5	30.1	0.587	0.495	3.45	3.08
483	0.922	2.80	43.1	0.084	42.08	21.2	0.5944	4.09	1.09	15.8	16.8	8.8	25.6	0.659	0.505	3.26	2.95
503	0.960	1.18	35.9	0.069	31.32	22.8	0.5281	3.64	0.50	14.7	15.2	3.8	19.0	0.798	0.542	3.92	2.86

Methyl Formate $T_c=487$

313	0.643	21.56	68.8	0.151	101.1	21.7	0.9447	9.54	4.79	10.5	15.3	26.8	42.1	0.363	0.544	3.36	2.87
363	0.745	14.29	65.5	0.141	85.25	21.2	0.8634	8.72	3.37	12.1	15.5	19.8	35.3	0.438	0.533	3.33	2.85
413	0.848	7.54	60.4	0.128	68.10	21.5	0.7638	7.71	1.93	13.5	15.5	12.7	28.2	0.548	0.540	3.28	2.90
443	0.910	3.90	53.7	0.113	54.41	22.3	0.6844	6.91	1.08	13.7	14.8	7.7	22.5	0.657	0.561	3.10	2.78
436	0.951	1.78	46.2	0.096	41.93	23.8	0.6148	6.21	0.53	13.2	13.7	3.7	17.4	0.787	0.599	2.84	2.64

Nitrogen $T_c=127$

70	0.551	10.53	26.63	0.230	44.85	84.8	0.8446	18.27	1.51	2.32	3.84	4.83	8.67	0.442	0.717	3.32	2.75
80	0.630	8.27	25.87	0.220	41.72	77.5	0.7988	17.28	1.24	2.63	3.87	4.20	8.07	0.480	0.656	3.29	2.85
88	0.693	6.57	24.61	0.205	39.00	71.7	0.7622	16.49	1.01	2.79	3.80	3.74	7.54	0.504	0.608	3.16	2.74

Oxygen $T_c=154.2$

70	0.454	18.35	36.90	0.265	48.95	107.6	1.2393	23.47	2.24	2.26	4.50	6.31	10.81	0.416	1.058	3.23	....
78	0.506	16.25	36.53	0.260	48.10	97.4	1.2008	22.75	2.13	2.53	4.55	6.07	10.62	0.428	0.956	3.24	2.70
84	0.545	14.72	35.64	0.255	47.56	89.2	1.1719	22.20	1.86	2.72	4.56	5.94	10.50	0.434	0.884	3.18	2.70

TABLE II B

ENERGY VALUES FOR THE VAPORIZATION IN STEPS OF MERCURY AND OF ASSOCIATED LIQUIDS

Methyl Alcohol $T_c=513$

363	0.708	15.72	49.5	0.093	232.1	5.9	0.7250	13.72	2.74	5.9	8.6	42.7	51.3	0.168	0.192	1.62	1.39
413	0.805	10.79	54.4	0.106	195.4	6.7	0.6640	12.57	2.00	8.1	10.1	33.1	43.2	0.233	0.220	1.95	1.64
463	0.903	5.23	59.4	0.117	147.5	8.7	0.5770	10.82	1.06	11.0	12.1	20.5	32.6	0.370	0.284	2.38	2.13
483	0.942	2.93	58.0	0.114	119.5	10.1	0.5255	9.95	0.63	11.9	12.5	13.9	26.4	0.475	0.329	2.47	2.19
503	0.981	0.77	47.5	0.093	74.6	12.7	0.4410	8.35	0.19	11.4	11.6	4.9	16.5	0.700	0.414	2.26	....

Ethyl Alcohol $T_c=516.1$

333	0.645	18.43	48.7	0.091	199.2	7.3	0.7572	9.97	3.98	6.54	10.5	52.8	63.3	0.166	0.209	1.97	1.61
383	0.742	13.69	51.8	0.100	174.9	7.7	0.7057	9.29	3.10	8.62	11.7	43.8	55.6	0.211	0.225	2.25	1.88
433	0.839	8.45	55.4	0.109	141.7	9.0	0.6329	8.34	2.06	11.42	13.5	31.6	45.0	0.299	0.263	2.64	2.30
473	0.917	3.99	56.3	0.111	104.0	11.5	0.5568	7.33	1.06	13.85	14.9	18.2	33.0	0.449	0.332	2.93	2.64

Water $T_c=647$

283	0.437	71.94	109.0	0.131	559.3	6.9	0.9997	33.63	6.90	3.56	10.5	59.1	69.6	0.150	0.344	1.26	1.22
333	0.515	64.27	120.2	0.168	525.4	6.9	0.9834	33.09	6.24	5.43	11.7	53.7	65.3	0.179	0.343	1.63	1.40
383	0.592	55.25	128.8	0.192	489.2	6.9	0.9512	32.00	5.48	7.20	12.8	48.1	60.8	0.210	0.343	1.91	1.70

Acetic Acid

423	0.711	14.46	51.0	0.087	82.37	14.6	0.8963	9.05	3.33	8.42	11.8	22.3	34.1	0.344	0.449	1.99	1.66
463	0.779	10.93	53.1	0.091	77.97	14.7	0.8413	8.49	2.63	10.13	12.8	19.5	32.3	0.395	0.452	2.19	1.86
503	0.846	7.28	54.1	0.093	71.44	15.0	0.7764	7.84	1.85	11.87	13.7	15.9	29.6	0.463	0.462	2.36	2.06
543	0.913	3.59	51.6	0.089	60.37	15.8	0.6900	6.97	0.98	13.16	14.2	10.8	25.0	0.565	0.483	2.48	2.15
563	0.947	1.92	46.1	0.079	50.32	16.3	0.6334	6.39	0.56	12.82	13.4	7.5	20.9	0.642	0.500	2.28	2.06

Mercury ($T_c=1500?$)

313	(0.208)	479.7	552.6	0.233	69.58	253.7	13.497	40.79	40.48	6.16	46.6	49.7	96.3	0.484	13.2	1.97	1.45
363	(0.242)	468.0	552.6	0.233	68.77	221.3	13.376	40.42	39.73	7.18	46.9	48.3	95.2	0.493	11.4	1.98	1.50
413	(0.275)	456.4	552.6	0.233	67.97	196.8	13.257	40.06	38.97	8.22	47.2	46.9	94.1	0.501	10.2	1.99	1.50
443	(0.295)	449.4	552.6	0.233	67.48	184.8	13.186	39.85	38.54	8.85	47.4	46.0	93.4	0.506	9.6	2.00	1.55

values in the tables are intended to be as nearly the arithmetical mean values as it is now possible to determine them.   That the assumption used as the basis for the calculation is of value will be seen from the remarkable relations which emerge.

At $20°$ the calculations indicate the presence of 4.2×10^{14} molecules of ethyl alcohol per sq. cm., while the results on films of alcohol on water show that when the film is closely packed the number of molecules is very close to 4.0×10^{14}, or the same number as that found for the pure alcohol.

Notation

The symbols used in Table II have the following significance.

T = absolute temperature.

τ = T/T_c, where T_c is the critical temperature.

Γ = surface tension in ergs per cm., or free surface energy in ergs per sq. cm.

γ = free surface energy in ergs per area occupied by one molecule.

S = entropy of surface in ergs per degree per sq. cm.

s = entropy of surface in ergs per degree per constant area equal to the area occupied by one molecule at the definite temperature specified.

s' = the same as s but calculated for a changing area equal to that occupied by one molecule at the different temperatures. internal latent heat of vaporization in calories per gram.

$\dfrac{10^4 E}{T}$ Whittaker's constant.

$\dfrac{cd^{2/3}}{x\ \tau}$ molecular capillary constant.

d = density of liquid.

n = number of molecules per cc. of liquid.

n_s = number of molecules per sq. cm. of surface.

l = latent heat of the area of surface occupied by one molecule in 10^{-14} ergs.

e = total surface energy of same area or the surface energy per molecule in 10^{-14} ergs.

j = energy changed from kinetic to potential when one molecule jumps from the *surface* into the vapor (in 10^{-14} ergs). or the molecular *energy of thermal emission.*

L = latent heat of the surface per sq. cm.

E = total energy of the surface per sq. cm.

Λ_i = internal latent heat of vaporization per mol.

λ_i = mean internal latent heat of vaporization per molecule.

Defining Equations

$$e = \gamma + l$$
$$\lambda = e + j = \gamma + l + j$$
$$\gamma = \frac{\Gamma}{n_s}$$
$$l = \frac{L}{n_s}$$

TABLE II C

ENERGY VALUES FOR THE VAPORIZATION IN STEPS OF NON-ASSOCIATED LIQUIDS AT
ORDINARY TEMPERATURES (ENERGY VALUES IN MICRI-ERGS 10^{-14} ERGS)

T	T/T_c	d	$n_s \times 10^{-14}$	e	j	λ	e/λ
	$= \tau$		Carbon Tetrachloride $T_c = 556$				
255	0.459	1.659	3.496	18.5	37.2	55.66	0.333
273.1	0.491	1.632	3.458	18.0	35.6	53.58	0.337
298	0.526	1.585	3.392	17.1	33.6	50.72	0.338
308	0.554	1.560	3.356	16.4	33.2	49.57	0.331
328	0.590	1.525	3.305	16.6	29.5	46.12	0.361
			Ethyl Ether $T_c = 467$				
198	0.424	0.818	3.552	15.2	36.4	51.59	0.295
252	0.541	0.758	3.376	15.0	30.3	45.32	0.332
273.2	0.585	0.735	3.307	15.4	37.5	42.94	0.358
283.9	0.607	0.723	3.271	12.7	29.0	41.71	0.304
298.3	0.639	0.707	3.223	12.8	27.3	40.05	0.293
302.5	0.647	0.703	3.210	11.8	27.8	39.57	0.298
			Benzene $T_c = 561.5$				
278.4	0.496	0.895	3.64	21.6	33.3	54.9	0.393
282.5	0.503	0.889	3.63	20.8	33.5	54.3	0.382
298.1	0.531	0.873	3.58	19.5	33.3	52.8	0.369
308.1	0.549	0.862	3.55	18.2	33.5	51.7	0.353
328	0.585	0.841	3.49	17.3	32.2	49.5	0.350
347.6	0.619	0.817	3.43	17.6	29.7	47.3	0.373
			Chlorobenzene $T_c = 363$				
257	0.406	1.144	3.362	20.9	48.8	69.7	0.299
273	0.431	1.128	3.33	21.0	46.9	67.9	0.310
298	0.471	1.101	3.28	21.9	43.2	65.1	0.336
308	0.486	1.090	3.26	22.3	41.6	63.9	0.349
323	0.510	1.073	3.22	22.4	39.8	62.2	0.360
343.5	0.543	1.051	3.18	22.6	37.3	59.9	0.378
363	0.574	1.029	3.13	22.9	35.9	58.8	0.390
375	0.592	1.016	3.11	23.0	33.3	56.3	0.409
387.5	0.612	1.003	3.08	23.2	31.7	54.9	0.423
395	0.624	0.995	3.07	23.3	30.7	54.0	0.431
			Ethyl Acetate $T_c = 524$				
213	0.406	0.999	3.61	18.4	44.6	63.0	0.292
243	0.464	0.961	3.52	18.7	40.9	59.7	0.314
273	0.521	0.924	3.43	17.7	38.6	56.4	0.314
303	0.578	0.887	3.34	16.0	37.1	53.1	0.302
333	0.636	0.847	3.24	14.7	35.1	49.8	0.295

Note to Table II. The surface tension values for nitrogen and oxygen are those of Baly and Donnan [*J. Chem. Soc.*, **81**, 919 (1902)]. The values for nitrogen were calculated by Planck [*Physik. Z.*, **11**, 642 (1910)] from results by Bestelmayer and Valentin [*Ann. Physik*, **15**, 61 (1901)]; Baly and Donnan, and Alt. [*Sitz. Bayer. Akad. Wiss.*, **22**, 529 (1903) and *Physik. Z.*, **6**, 346 (1903)].

The values for the internal latent heat of vaporization of oxygen were calculated by the writers from the vapor-pressure data of Estreicher [*Phil. Mag.*, [5] **40**, 454 (1895)].

The constants of the Hertz equation were determined graphically. The equation for nitrogen is

$$\text{Log } p = k_1 - k_2 \log T - \frac{k_3}{T}$$

where k_1 is 8.455, k_2 is 0.64847, and k_3 is 392.84.

The values of dp/dt for mercury were obtained from the equation given by Menzies:

$$\log p = 9.9073 - 0.65199 \log T - \frac{3276.6}{T}$$

and the values of p and T were taken from Smith and Menzies [THIS JOURNAL, **32**, 1412 (1910)].

In the case of carbon tetrachloride and similar other liquids, use was made of the values of the latent heat of vaporization calculated by Mills [THIS JOURNAL, **32**, 164 (1910)]. However, all of the values of the latent heat of vaporization used in Table II C, were calculated by the writers.

Table II as given above is a condensed outline of a much more elaborate table calculated by the writers, and contains enough data to illustrate the characteristic features of the relations. The surface tension data used in Parts A and B are those of Ramsay and Shields,[4] in Part C those of Jaeger, and the vapor-pressure data from which the internal heats of vaporization were obtained, are those of Young,[5] except when otherwise specified. *Practically all* of the experimental data cited in the literature, which give the variation of the surface tension of liquids with the temperature, *were plotted and carefully compared.* These were largely results obtained by Ramsay and Shields, Morgan, Jaeger, Renard and Guye, Walden, and those obtained in this laboratory. The data on organic liquids as obtained by Ramsay and Shields covered on the whole the largest temperature range, and were mostly in moderately good agreement with our own data, as well as those of Morgan, though they are in general about 3% too low at 20°, as is shown by the experimental results obtained both by Richards and his coworkers, and by the workers in the Chicago laboratory. If the results are consistently too low by this percentage, the latent surface heat would not be all in error on this account, and this percentage difference in the free surface energy would make little difference to the results of the calculations as presented in Table II.

In comparing the surface tension data of Jaeger, as given in Table II C, with those of Ramsey and Shields, it is found that the distinguishing feature of the latter is that the surface tension for unassociated liquids is nearly always found to be a linear function of the temperature, while the surface-tension data obtained by Jaeger are nearly always such as to show considerable curvature. A comparison with other data indicates that probably the latter are too highly curved. On the other hand those of Ramsay and Shields seem to be considerably more linear than is probable, but nevertheless they seem to be in better agreement with the other data than those of

[4] Ramsey and Shields. *Z. physik. Chem.*, **12**, 433 (1893).
[5] Young. *Sci. Proc. Roy. Dublin Soc.*, **12**, 374 (1910).

Jaeger, which seem to show considerable irregularity. Seemingly Jaeger's method is better designed for the determination of surface tension at high and low temperatures, than it is for the finding of temperature coefficients.

Ratio of the Total Surface Energy to the Latent Heat of Vaporization

It has been commonly accepted by those who have considered at all, the connection between the energy of surface formation and the heat of vaporization, that the relation developed by Stefan[6] in 1886 is approxi-
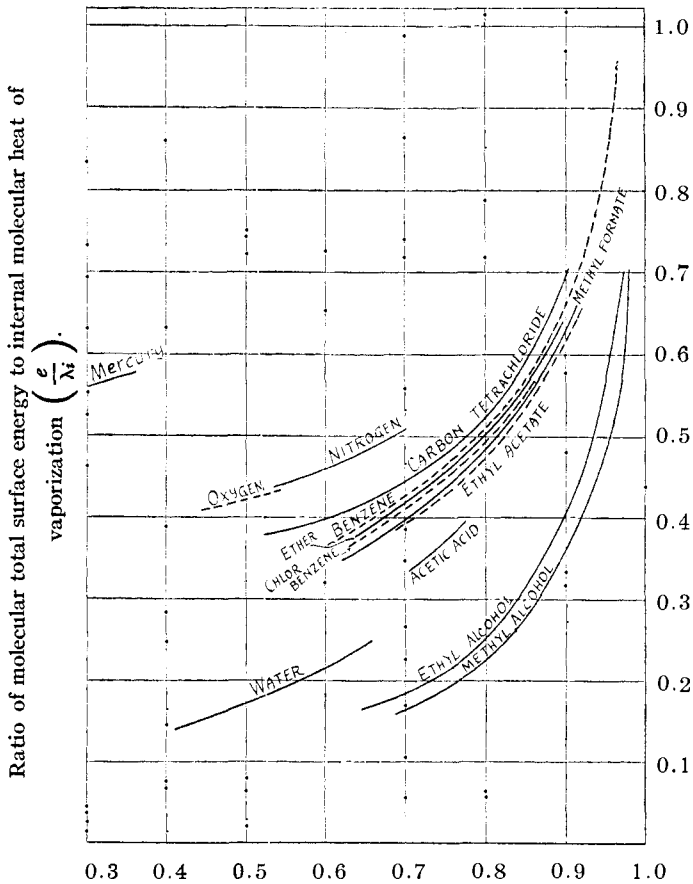

Fig. 1.--Corresponding temperature.

mately correct. Stefan considers that the work of carrying a molecule into a surface is one-half of the energy of vaporization (λ). It seems evident that what is meant by Stefan is not the "work" or free energy (γ), but rather the mean total energy required to carry the molecule

6 Stefan, *Wied. Ann.*, **29,** 655–65 (1896).

from the interior of the liquid to the surface (e).   However, the calculations presented in Table II are not at all in agreement with the relation of Stefan, since they indicate that *the ratio of the molecular total surface energy to the molecular heat of vaporization* (e/λ) *is an increasing function with increasing corresponding temperature, since the molecular surface energy remains nearly constant until the critical temperature is approached, that is until the corresponding temperature rises nearly to 1.00, while the molecular heat of vaporization decreases very rapidly with increasing temperature*. (See Fig. 1.) Thus in the sense of the relative amounts of energy involved a molecule which is in the surface of a liquid at a high temperature has passed much more nearly into the vapor than when the temperature is low.   While this is true in general, the details involved necessitate considerable discussion, and this will be presented in a somewhat elementary form in the following paragraphs.

   In considering the surface energy relations involved, the surface energy per square centimeter (E), instead of the molecular value (e) will be considered first.   It has been shown by Jaeger[7] that there are three types of curves which represent the relation between the free surface energy (Γ, plotted on the Y axis) and the temperature (plotted on the X axis). These are (1), concave, (3) convex to the temperture axis, and (2) which is a straight line.   Harkins, Davies and Clark[8] showed that corresponding to these there are three curves representing the total surface energy, (1) rising to a maximum near the critical temperature, (2) remaining constant till the critical temperature is approached, and (3) constantly decreasing. All of these decrease rapidly near the critical temperature and come to zero at the critical temperature; and this is also the case with the curve which would represent the latent heat of vaporization.   Only when the total energy curve has the form (3) would it be possible that the Stefan relation should hold, and even in this case it would probably never happen that the curve would have the precise form essential for this purpose.   While it is true that for the data now available Type 3 is the most common, it may nevertheless be seen from the table that the total surface energy does not decrease so rapidly as the latent heat of vaporization, so the ratio E/λ increases with the temperature.

The Molecular Total Surface Energy

   The molecular total surface energy (e) is very nearly constant at low temperatures (curve of Type 2) in the case of the nonassociated liquids listed in Table II A, B (see Fig. 2) though there is little doubt that in some instances it rises to a maximum, and then falls, as the temperature increases. Quite a number of substances which show this characteristic, have been

[7] Jaeger, *Verslag. Akad. Wetenschappen Amsterdam*. **23**, 416–30 (1914).
[8] Harkins, Davies and Clark, THIS JOURNAL. **39**, 551–86 (1917).

investigated by Jaeger, and acetic acid is shown by Table II B to belong
to this class.   The data for the alcohols indicate that the molecular surface
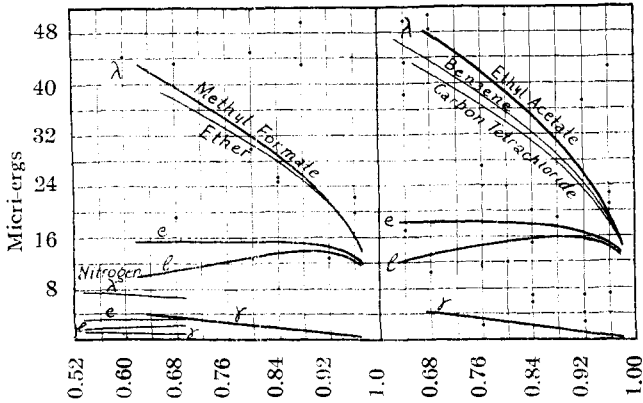energy rises rapidly as the critical temperature is approached, reaching
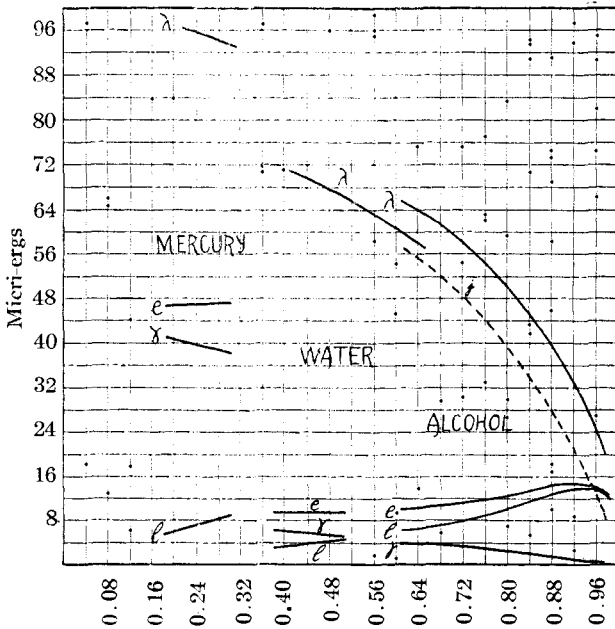

Fig. 2.—Corresponding temperature.

Fig. 3.—Corresponding temperature.

maximum close to 0.9, and then falls still more rapidly (Fig. 3).   If this is
true it may be explained as the result of the heat motion of the molecules,
which, as the temperature increases, more and more overcomes the orienta-

tion in the surface of these unsymmetrical molecules, thus throwing the polar end of the molecules into the surface, thereby increasing the surface energy. However, as the critical temperature is approached still more closely, the vapor begins to increase rapidly in density, and the drop in the intensity of the electromagnetic stray field which occurs at the surface is thus lessened, so the surface energy again decreases.

The vertical position of the curves in Figs. 2 and 3 is based upon the assumption that the surface film is monomolecular. There is much evidence, both that presented by Langmuir and that secured in this laboratory, that this is true at a corresponding temperature of 0.5. At the critical temperature, however, the film has thickened so greatly that it has swallowed up both the liquid and the vapor phases. The form of the curve for the total surface energy depends upon how rapidly the film thickens as the corresponding temperature approaches unity, but it seems likely that the greatest part of the thickening occurs very close to the critical temperature, especially as the linear character of the curve representing free surface energy commonly persists to corresponding temperatures somewhat above 0.9. However, the vertical position of the e curves at temperatures above 0.8 should be considered doubtful, and in Figs. 2 and 3 it seems practically certain that the extreme right hand end of these curves should all be lowered somewhat from the positions which they occupy. The position and shape of the right end of these curves in the diagram are also indications that possibly they should turn downward a little to the left of the actual point of inflection, since the e curves can never rise above those for λ_i, and must come to zero when τ rises to unity. However, this change would not alter the *general features* of the relationships involved, and it is believed by the writers that these are well represented by the figures. It would have been possible, of course, to have made an allowance for this factor in drawing the curves, and this possibility was carefully considered; but on account of the uncertainty in regard to the temperature at which the thickening of the film becomes of importance, it was decided to draw the figures so that they would give a more direct representation of the experimental results, and to point out the direction in which they will undoubtedly be modified by later work.

Molecular Symmetry, and the Orientation of the Molecules in Surfaces as Related to the Ratio of the Surface Energy to the Heat of Vaporization (e/λ_i)

The earlier papers of this series have shown that when a molecule consists of a polar group, such as OH, NH_2, COOH, $CONH_2$, CN, etc., at one end of the chain, and a slightly polar group, such as a hydrocarbon chain, its action with respect to the energy changes on passing into the surface may be predicted by the use of a model which consists of a heavy weight

at one end while the other end is made from some light material. This model may be represented by the symbol ——○, in which ○ represents weight. When a molecule of this class is raised into the surface it is only the "light" end which is lifted, so the surface energy (e) is relatively small, while when the molecule jumps out of the surface the "heavy" end must be lifted out, so the "jumping-out energy" or the energy of thermal emission (j) is relatively large. As an example of this latter type of molecule we may choose that of ethyl alcohol. In the case of a symmetrical molecule, such as that of carbon tetrachloride, it is to be expected that the energy of surface formation and that of thermal emission from the surface will be very much more nearly the same. It will be shown later that it is essential that different liquids shall be compared at the same corresponding temperatures.

For convenience the energy unit for use in the present paper will be taken as 10^{-14} erg. In order to prevent the frequent use of the negative exponent this unit will be specified as a micri-erg. A micro-erg is a millionth of an erg, and the new unit is one hundred million times smaller than this. The term micri-erg has no philological justification, but the Greek terms which would be justified in this sense are considerably more awkward for common use.[9]

At a corresponding temperature equal to 0.743 the mean amount of energy required to carry a molecule of carbon tetrachloride from the interior of the liquid into the surface is 18.0 micri-ergs, while the energy of thermal emission or that used up in causing it to jump out of the surface into the vapor is almost the same, or 19.4 micri-ergs. If instead of this very symmetrical molecule we consider the molecule of ethyl alcohol, which is very unsymmetrical with reference to the electrical forces around it, it is found that the energy (e) required to carry the molecule into the surface is only about one-half as great, or 11.7 micri-ergs, while the jumping-out energy or energy of thermal emission is more than doubled, and has the remarkably high value 43.8 micri-ergs. *The energy of thermal emission for the alcohol is thus four times the energy of surface formation, while in the symmetrical carbon tetrachloride, the two are almost equal.*

The corresponding values for the methyl alcohol molecule are almost exactly the same as those for ethyl alcohol, while those for benzene are nearly the same as those for carbon tetrachloride. If we assume that the ratio e/j may be used as an index of the symmetry of the molecules in the surface, then the values are such as to indicate that in this sense the benzene molecule is slightly less symmetrical than that of carbon tetrachloride, which is exactly what would be expected from the formulas. The values of the ratio e/j for a number of different types of molecules are given in Table III.

[9] The distinction between micro and micri may be easily preserved if the final i in the latter is pronounced as a long i.

Instead of plotting the values of e/j, which would be somewhat more striking with respect to the relations disclosed, it seemed better from other standpoints to plot e/λ, as has been done in Fig. 3. This ratio has already been discussed to some extent. Since e/λ is equal to $\dfrac{e}{e+j}$ it is evident that if the value of e/j increases with increasing symmetry of the molecule, then that for e/λ will also increase, though not so markedly. Table III gives 13 liquids arranged in the increasing order of e/λ, which according to the preceding discussion should on the whole be that of increasing symmetry of the molecules in the surface.

TABLE III

LIQUIDS ARRANGED IN THE ORDER OF THE RATIO OF THE ENERGY NECESSARY TO CARRY A MOLECULE INTO THE SURFACE TO THAT REQUIRED FOR COMPLETE VAPORIZATION, AND PRESUMABLY IN ORDER OF INCREASING SYMMETRY IN THE SURFACE

(CORRESPONDING TEMPERATURE = 0.7)

Molecule	e/λ	e/j
Class 1		
1. Methyl alcohol..................	0.164	0.191
2. Ethyl alcohol...................	0.186	0.228
Class 2		
3. Water.......................	0.282	0.372
4. Acetic acid....................	0.336	0.474
Class 3		
5. Ethyl acetate...................	0.397	0.606
6. Methyl formate	0.402	0.618
7. Chlorobenzene.................	0.417	0.714
9. Ethyl ether....................	0.423	0.667
10. Benzene.......................	0.441	0.711
11. Carbon tetrachloride............	0.452	0.742
Class 4		
12. Oxygen.......................	0.497	0.872
13. Nitrogen......................	0.514	0.927
Class 5		
14. Mercury......................	0.636	1.41

The important feature of this table is that the arrangement is not only such as to group chemically similar substances together, but also that it actually gives the expected order of increasing symmetry of the molecules with reference to the forces around them. This is shown both by the arrangement of the classes of substances, and by the arrangement of the substances in the classes. Thus in Class 3, the order ethyl acetate, methyl formate, chlorobenzene, ethyl ether, benzene, and carbon tetrachloride, is very plainly that of increasing symmetry of the forces around the molecule. Minor variations might easily be caused by small errors in the data, or by errors in the determination of the number of molecules in the surface. However, Table III proves that these errors are not sufficient to obscure the general relationships.

As has already been stated, Stefan's "law" states that the energy of surface formation is equal to half the energy of vaporization, but it was shown that instead of being constant, the ratio is an increasing function with increasing temperature. Table III and Fig. 1 indicate that this ratio is also an increasing function with increasing symmetry of the molecules. It may be seen in Table II that at a corresponding temperature of 0.7, the different liquids are from 0.16 to 0.64 vaporized, in terms of energy. At lower temperatures all of these values decrease, while at higher temperatures they increase, this increase being very rapid as the critical temperature is approached. The curves in Fig. 1 seem to have a form such as to indicate that the ratio e/λ approaches its maximum 1.00 at the critical temperature, which would mean that at temperatures very slightly below this nearly all of the energy is utilized in carrying the molecules from the body of the liquid into the surface, and that the energy of thermal emission from the surface is very small. Thus these curves seem to have the same general form in approaching the critical temperature, which is the limit for the existence of the liquid, as is found for the specific heat curves when they approach the absolute zero of temperature, which is the limit for the existence of heat. The experimental determination of either curve near its limit is in either case a matter of extreme difficulty.

The Energy of Thermal Emission of a Molecule from the Surface of a Liquid

The energy of thermal emission (j) of a molecule from the surface of a liquid into the vapor, has values ranging from about 4 to 50 micri-ergs at corresponding temperatures between 0.4 and 0.98, in the case of the liquids listed in Table II. In all cases the value decreases very rapidly as the temperature increases. The variation with the temperature is very much the same as that of the molecular free surface energy, except that as the critical temperature is approached closely the free surface energy decreases more slowly while the energy of emission decreases more rapidly. In the case of chlorobenzene the value for the latter decreases by 11.2 micri-ergs between 0.68 and 0.84 as the corresponding temperatures, but this decrease is nearly linear, while the increase of the free surface energy is almost exactly linear, and the value of the molecular surface energy is nearly constant at 20.5 micri-ergs. In general the curve for j is slightly concave toward the τ axis, but usually not so much so as the curve for λ, as may be seen in Fig. 3.

As has already been pointed out, the energy of thermal emission is particularly high in the case of molecules of the polar-nonpolar type, such as the alcohols, which are highly polar at one end and "non-polar" at the other. This should be true also of the amines, nitriles, etc. Its value is larger for the alcohols than for water. While the total energy

necessary to carry a molecule of mercury into a surface is about four times as high as that required for an ethyl alcohol molecule at the same corresponding temperature, the energy of thermal emission is only slightly higher for the former. The value for acetic acid is very much lower, which is partially accounted for by the fact that the vapor of this substance is somewhat associated. The total surface energy is increased very little, and the energy of thermal emission, considerably, when one atom of chlorine is substituted for hydrogen in benzene, as would be expected from the orientation theory.

The Surface Energy Constant

If the ratio e/λ_i, which increases rapidly with a rise of the corresponding temperature, is multiplied by the ratio $d^{2/3}/\tau$, the product $\dfrac{e\,d^{2/3}}{\lambda_i\tau}$ is found to be nearly constant for nonassociated liquids and seems to be very nearly constant over a moderate range in the case of water. It rises rapidly with the temperature in the case of the unsymmetrical molecules of the alcohols. The value for mercury is very high. Whittaker's constant, given in Col. 7 of Table II applies to the large scale properties of the substances, and varies in about the same way.

Summary

1. This paper gives the amount of energy involved in the various steps in the process of vaporization, based upon the assumption that the surface through which the vaporization occurs is not highly curved. The unit of energy used is the *micri-erg*, defined as 10^{-14} erg. The relations found at a corresponding temperature equal to 0.7 are summarized in brief in Table IV.

TABLE IV

MOLECULAR ENERGY VALUES (IN MICRI-ERGS) FOR THE VAPORIZATION OF LIQUIDS AT A CORRESPONDING TEMPERATURE EQUAL TO 0.7

LIQUID	T_c	γ	l	e	j	λ_t
1. Non-associated Molecular $= \tau$						
Nitrogen................	127	1.51	2.33	3.84	4.8	8.7
Oxygen................	154.2	2.24	2.26	4.50	6.1	10.8
Ethyl ether	467.5	4.0	11.7	15.6	20.9	36.5
(Ethyl acetate)	(524)	(4.6)	(13.7)	(18.3)	(27.7)	(46.0)
Carbon tetrachloride	556	4.7	13.5	18.2	22.0	40.2
Benzene...............	561.5	4.8	13.7	18.4	23.3	41.7
Chlorobenzene.........	633	5.3	15.0	20.3	28.5	48.8
2. Associated						
Methyl alcohol	513	2.8	5.7	8.5	43.1	51.6
Ethyl alcohol	516.1	3.5	7.7	11.2	48.1	59.3
		(4.4)	(12.5)	(16.9)	(20.4)	(37.3)

The data indicate that *at a definite corresponding temperature, in the case of non-associated liquids whose molecules are symmetrical, the molecular*

values for the latent heat of surface formation (*l*), *the total surface energy* (*e*), *the energy of thermal emission* (*j*), *and the internal latent heat of vaporization* (λ*ᵢ*) *are nearly proportional to the critical temperatures of the liquids.* The same relation seems to hold for the free surface energy (γ) provided the temperature range is not too great. Thus the free surface energy of ethyl ether at a corresponding temperature of 0.7 is 4.0 as calculated from the value for carbon tetrachloride, and 3.9, as calculated from the value for chlorobenzene, while the experimental value is 4.0. This statement as applied to the latent heat of vaporization alone, is somewhat similar to Trouton's law, which is known to be not entirely exact. Since the principle expressed above is much more general in its application, it is to be expected that it will prove to be somewhat less exact. That the energy values for ether in Table IV are lower than those for carbon tetrachloride is related to the lower critical temperature of the ether.

2. *The effect of a lack of symmetry in the molecule, especially when marked, is to lower the molecular free surface energy, latent heat of surface formation, and total surface energy, and to increase the energy of thermal emission.* The values given in parentheses under those for ethyl alcohol, are those calculated from the critical temperature under the assumption of a symmetrical molecule, using the values for carbon tetrachloride as a basis. It is evident that the molecular free surface energy, and total surface energy, and more markedly the latent heat of surface formation, are considerably lowered by the dissymmetry of the molecule. The most striking effect is, however, the very great increase in the energy of thermal emission. The symmetry referred to in this discussion is that of the electromagnetic forces around the molecule, rather than a symmetry with respect to mass. The substitution of the slightly polar chlorine atom for hydrogen in benzene gives almost exactly the calculated value for a symmetrical molecule except in the case of the thermal emission (*j*), which is considerably increased, since it is the most sensitive of all of the quantities to changes of molecular symmetry. Since *e* is decreased, and *j* increased by increasing dissymmetry of the molecule, the ratio *e*/*j* serves as a remarkably sensitive index of molecular symmetry. This is illustrated in Table III. The related ratio *e*/λ, which is equal to $\dfrac{e}{e + j}$, varies in the same way, but not so greatly.

3. According to "Stefan's law" the ratio of the total energy necessary to carry a molecule from the interior of a liquid into the surface to its total heat or energy of vaporization (*e*/λ) is equal to 1/2. That this is not the case is easily seen by a reference to Tables II and III, and Fig. 1. Not only is this an increasing function with increasing symmetry of the molecule, but also with increasing corresponding temperature. Its value seems to approach unity as the corresponding temperature approaches unity.

Thus a molecule in the surface at a high corresponding temperature is, in terms of relative energy, very much more nearly in the vapor phase than when the corresponding temperature is low.

4. The relations discussed in Paragraphs 1 and 2 of the summary are just those indicated by the theory that molecules in the surface are oriented, the orientation increasing with increasing dissymmetry, and decreasing with increasing thermal agitation of the molecules. The effect of thermal agitation is illustrated in the case of the alcohols; compounds of the polar-nonpolar type. Fig. 3 indicates that for these compounds the molecular surface energy increases with the temperature. The effect of increased agitation is to overcome the orientation partly, and to throw the more polar groups into the outer surface, thus increasing the surface energy.

CHICAGO, ILLINOIS

IONIC EQUILIBRIA OF STRONG ELECTROLYTES

BY ALLEN E. STEARN
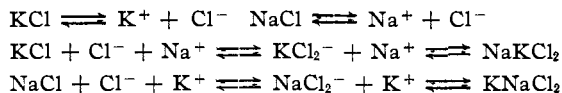
I

The ionic relationships in relatively concentrated solutions of mixed strong electrolytes have been studied especially by Smith[1] and his students, who have shown that, as the total concentration of a salt mixture of equivalent amounts of two salts increases, the ion fraction of one of the metallic constituents gains on the ion fraction of the other. Recently Kendall[2] has attacked the problem of "complex formation" between solute and solvent.

II. Conductivity of Concentrated Solutions

When such salts as sodium and potassium chlorides are mixed in solution such equilibria as the following may be set up.

$$KCl \rightleftharpoons K^+ + Cl^- \quad NaCl \rightleftharpoons Na^+ + Cl^-$$
$$KCl + Cl^- + Na^+ \rightleftharpoons KCl_2^- + Na^+ \rightleftharpoons NaKCl_2$$
$$NaCl + Cl^- + K^+ \rightleftharpoons NaCl_2^- + K^+ \rightleftharpoons KNaCl_2$$

The formation of such molecular or ion complexes in solution, causing the gain of one ion fraction on another[3] in a salt mixture, should decrease the conductivity of such a solution of mixed salts. Thus the conductivity of an equimolar solution of sodium and potassium chlorides of a

[1] G. McP. Smith, *Am. Chem. J.*, **37**, 506 (1907). Smith and Ball, THIS JOURNAL, **39**, 179 (1917). Smith and Braley, *ibid.*, **40**, 1802 (1918). Wells and Smith, *ibid.*, **42**, 185 (1920).

[2] Kendall, *ibid.*, **39**, 2328 (1917); **43**, 1416 (1921); **43**, 1426 (1921).

[3] Noyes and Falk have suggested the existence of SrCl₄, etc., in solution from the results of transference experiments. *Ibid.*, **33**, 1455 (1911).