for the interval 0–12.5° to 20,750 cal. for 25–37.5°, corresponding to a mean heat capacity of activation of 63 cal./deg.

5. The form of the curve E *versus* T for this reaction is similar to that for the depolymerization of diacetone alcohol by hydroxyl ion.

6. The action constant B—which is equal to the entropy of activation plus a frequency term—varies from 13.2 at 6.33° to 14.45 at 31.3°. The magnitude and temperature dependence of B furnish additional evidence of the inadequacy of the collision theory, and of the existence of an appreciable entropy of activation.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, COLUMBIA UNIVERSITY]

Orthobaric Densities of Substances as a Function of Reduced Temperatures

BY HAROLD A. FALES AND CLARA S. SHAPIRO

In the present investigation it is our purpose to make a comparative study of the equilibrium between the liquid and vapor phases of different elements and chemical compounds over the entire range of coexistence of the two phases from the melting point to the critical temperature with particular reference to the relationship between the orthobaric densities and the "reduced" temperatures.

Cailletet and Mathias studied the densities of the liquid and gaseous phases and discovered in 1886[1] that the arithmetical mean of their sum is a function of centigrade temperature. Likewise, they found that the "reduced" mean density can be expressed as a function of "reduced" temperature; this relationship is discussed in detail by Van Laar.[2] Recently two interesting papers have appeared along the lines of our subject. One is by C. H. Meyers[3] in which orthobaric volumes are connected with "reduced" pressures and absolute temperatures. This author shows for twenty-three substances that provided the vapor pressure–temperature relation for the saturated fluid, the critical pressure, and approximate values for liquid densities are known, the specific volume of the saturated vapor can be calculated, except near the critical temperature, with the determination of one empirical constant in the equation

$$\log_{10}\left(1 - \frac{pv}{RT}\right)\left(1 - \frac{pv'}{RT}\right) = A \log_{10} \frac{p}{2.718p_c} \quad (1)$$

where p = saturation pressure, p_c = critical pressure, v and v' = specific volumes of liquid and vapor respectively, R = gas constant, T = absolute temperature and A = empirical constant which varies slightly from 0.72 for noble gases to 0.61 for methanol, with an average value of 0.69 for twenty-three substances. The above relationship is very accurate up to one-fourth to one-half the critical pressure, which corresponds to 0.8 to 0.9 the absolute critical temperature.

The second paper is by J. Horiuchi[4] and deals with the expression $\ln v_g/v_l$. Assuming that Maxwell's distribution law and van der Waals' equation apply to the equilibrium liquid $\rightleftarrows$ saturated vapor, and introducing a certain correction Horiuchi develops an equation which expresses $\ln v_g/v_l$ in terms of two variables: the volumes themselves and the absolute temperatures, namely

$$\ln v_g/v_l = \frac{A}{RT}\left(\frac{1}{v_l - E} - \frac{1}{v_g - E}\right) \quad (2)$$

where A and E are constants characteristic for each substance. This equation holds well for a large number (60) of organic and inorganic liquids up to 0.8–0.9 of the critical temperature. It deviates considerably in the case of methyl alcohol and does not hold at all for water; according to Horiuchi this discrepancy is due to the strong association of these liquids. As to constants A and E they differ in numerical value for different substances. For normal organic liquids $A = 32.3\ T^2_{cr}/P_{cr}$ and $E = 0.17\ V_{cr}$, so that a "reduced" equation is obtained for these liquids[4]

$$\ln \frac{\phi_g}{\phi_l} = \frac{1.47}{R\tau}\left(\frac{1}{\phi_l - 0.17} - \frac{1}{\phi_g - 0.17}\right) \quad (3)$$

where τ, ϕ_g, ϕ_l are the reduced temperatures and reduced volumes, respectively.

The expression $\ln v_g/v_l$ has previously received considerable attention in the literature, mostly in

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(1) Cailletet and Mathias, *Compt. rend.*, **102**, 1202 (1886); **104**, 1563 (1887); Mathias, *ibid.*, **200**, 1643 (1935); **200**, 1902 (1935).

(2) Van Laar, "Zustandgleichung," ed. 1924, pp. 74, 342–350.

(3) C. H. Meyers, *Bur. Standards J. Research*, **11**, 691 (1933).

(4) J. Horiuchi, *Bull. Chem. Soc. Japan*, **1**, 189 (1926); and **2**, 213 (1927). *Sci. Papers, Inst. Phys. Chem. Research, Tokyo*, **15**, 89 (1931).

the effort to connect it with the latent heat of evaporation. Of the numerous though only partially successful attempts in this direction the most interesting is perhaps the equation of Crompton[5]

$$\ln \frac{v_g}{v_l} = \frac{Ml_{ev}}{2RT} \tag{4}$$

where M is the molecular weight, l_{ev} the latent heat of evaporation, R the gas constant, and T the absolute temperature.

This equation is approximately true for many organic liquids, giving particularly good agreement in the neighborhood of the critical point, but it shows considerable deviation for alcohols, acetic acid, ammonia, water and other liquids commonly called "associated" although the deviations become small as the critical point is approached.

Considering the relationships which Horiuchi and Crompton have sought to develop one might infer that liquids fall into two types, commonly known as associated and non-associated, since equations (2) and (4) give agreement with observed values in a certain number of cases but not in others. On the other hand, no such division into classes follows from the equation of Meyers because it applies equally well to twenty-three diverse substances including alcohols, ammonia and water.

The question may now be asked: is there some inherent peculiarity in the function $\ln v_g/v_l$ which necessitates that liquids be divided into two classes? We will attempt to show in this paper that it is possible to use the function $\ln v_g/v_l$ in conjunction with "reduced" temperature and obtain a relationship which is equally applicable to substances of the utmost chemical diversity and that on the basis of this there is no support to the contention that liquids are divisible into two classes.

We have selected thirty substances which represent every type of element, inorganic substance and organic compound for which measurements of orthobaric densities are available.

These substances arranged in the ascending order of the volume ratio are:

1 Helium
2 Hydrogen
3 Neon
4 Argon
5 Oxygen
6 Carbon monoxide
7 Nitrogen
8 Ethylene
9 Ethane
10 Hydrogen chloride
11 Nitrous oxide
12 Acetylene
13 Methyl ether
14 Carbon tetrachloride
15 Benzene
16 *i*-Pentane
17 *n*-Pentane
18 Monofluorobenzene
19 Sulfur dioxide
20 Ammonia
21 Methyl formate
22 Ethyl ether
23 *n*-Hexane
24 Acetic acid
25 Ethyl propionate
26 Sulfur trioxide
27 Water
28 Methyl alcohol
29 Ethyl alcohol
30 Nitrogen tetroxide

In studying the ratio of the volumes we have employed the natural log of the ratio v_g/v_l instead of the ratio itself, since the variation of the latter with temperature is far too fast. We have also employed the reduced temperature instead of the absolute temperature in order to have a common scale of comparison. It is obvious that at the critical point the ratio becomes unity and its natural log becomes zero for all substances; therefore in plotting the $\ln v_g/v_l$ against the reduced temperature $\tau = T/T_{cr}$ for different substances we obtain a series of curves all having a common origin at the point $\tau = 1.000$. Comparing these curves we find that they all belong to one and the same family as illustrated by the eight representative curves a,. . .h, in Fig. 1.

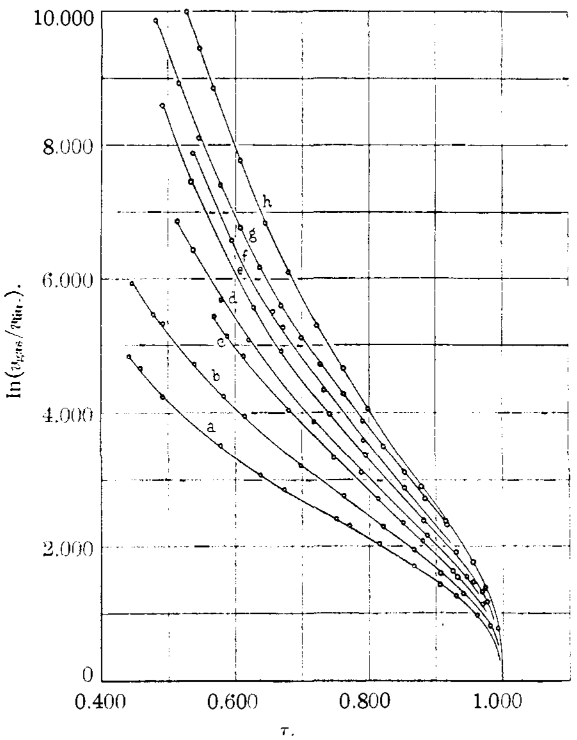

Fig. 1.—$\ln(v_{\text{gas}}/v_{\text{liq.}}) = k[(1-\tau^2)^m/\tau^n]$: a, helium; b, hydrogen; c, neon; d, nitrogen; e, carbon tetrachloride; f, *n*-hexane; g, water; h, ethyl alcohol.

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(5) Crompton, *Proc. Chem. Soc. London*, **17**, 61 (1901).

The domain bounded by the curves a and h includes all the curves for the thirty typical substances, while the more restricted domain bounded by c and g includes a majority of the curves. The eight representative curves a, . . .h portray the behavior of the following substances:

a—Helium
b—Hydrogen
c—Neon
d—Nitrogen
e—Carbon tetrachloride
f—n-Hexane
g—Water
h—Ethyl alcohol

Analytical Expression of the Curves.—We find that all these curves can be represented by the equation

$$\ln \frac{v_g}{v_l} = k \frac{(1 - \tau^2)^m}{\tau^n} \qquad (5)$$

where v_g and v_l are the orthobaric volumes; $\tau = T/T_{cr}$ is the reduced temperature and k, m and n are constants characteristic for a given liquid.

If we use "reduced" volumes instead of orthobaric volumes we get the same functional relationship, namely

$$\ln \frac{\phi_g}{\phi_l} = \ln \frac{\frac{v_{gas}}{v_{cr}}}{\frac{v_{liq.}}{v_{cr}}} = k \frac{(1 - \tau^2)^m}{\tau^n} \qquad (6)$$

where ϕ_g and ϕ_l are the "reduced" volumes.

Equation (5), as well as (6), is applicable to all substances tried and in most cases represents the data within the experimental accuracy as will be seen from the ensuing Tables I to III. It embraces substances of utmost diversity in physical and chemical properties. Thus the critical temperature ranges from 5.19°K. for helium to 674.2°K. for water; the number of atoms from 1 for helium to 20 for hexane; and the molecular weight from 2 for hydrogen to 153 for carbon tetrachloride.

This equation holds equally well for associated and non-associated liquids. It will be seen from the tables that the typical associated substances—acetic acid, water, ethyl alcohol, ammonia—show just as good an agreement between calculated and experimental curves, as do the representatives of normal liquids—benzene, carbon tetrachloride or hexane.

In Table I we give an example of our calculations in detail for water represented in Fig. 1 by curve g. In this table the three reference points used for calculating k, m and n are marked with an asterisk; at these points the deviation is, of course, always zero. Also in this table are given the de-

TABLE I

Water, Curve (g) Fig. 1. $k = 4.122$, $m = 0.3770$, $n = 1.338$

Gas volumes in parentheses have been extrapolated by the Bureau of Standards. The corresponding observed ln values are also in parentheses.

t, °C.	τ	v_{gas} obsd., cc./g.	$v_{liq.}$ obsd., cc./g.	$\ln \frac{v_g}{v_l}$ obsd.	$\ln \frac{v_g}{v_l}$ calcd.	Differences Actual[a]	Percentage[b]
0	0.4220	(206430)	1.000	(12.24)	12.15	−0.09	−0.7%
+ 20	.4529	(57872)	1.002	(10.97)	10.92	− .05	− .4
+ 40	.4838	(19550)	1.008	(9.873)	9.871	− .002	− .0
+ 60	.5147*	7678.8	1.017	8.930*	8.930*	.000	−0*
+ 80	.5456	3409.4	1.029	8.106	8.118	+ .012	+0.1
+100	.5765	1673.3	1.0434	7.380	7.399	+ .019	+ .3
+120	.6074	891.79	1.0603	6.735	6.755	+ .020	+ .3
+140	.6383	508.61	1.0798	6.155	6.172	+ .017	+ .3
+160	.6692	306.78	1.1021	5.629	5.641	+ .012	+ .2
+180	.7001	193.80	1.1275	5.147	5.153	+ .006	+ .1
+200	.7310*	127.16	1.1565	4.700*	4.700*	.000	0*
+220	.7619	86.060	1.1900	4.281	4.276	− .005	−0.1
+240	.7928	59.674	1.2291	3.883	3.872	− .011	− .3
+260	.8237	42.145	1.2755	3.498	3.484	− .014	− .4
+280	.8546	30.124	1.3321	3.119	3.104	− .015	− .5
+300	.8855	21.634	1.4036	2.736	2.722	− .014	− .5
+320	.9164	15.454	1.4992	2.333	2.323	− .010	− .4
+340	.9473	10.776	1.6409	1.882	1.879	− .003	− .2
+350	.9628*	8.798	1.7468	1.617*	1.617*	.000	0*
+360	.9782	6.941	1.9070	1.292	1.298	+ .006	+0.5
+374.11	1.0000	3.1975	3.1975	0	0		...

[a] Values are the differences, $\ln_{obsd.} - \ln_{calcd.}$. [b] Values are the percentage differences, $\frac{\Delta \ln v_g/v_l}{\ln v_g/v_l} \times 100$.

* Asterisks signify the reference points used for calculating k, m and n.

viations between calculated and observed values of $\ln v_g/v_l$. They are expressed as actual differences in the natural log, and also as percentage differences. By percentage difference we mean the proportional error in the logarithm of the ratio of the volumes × 100, namely, $\Delta \ln v_g/v_l / \ln v_g/v_l \times 100$.

If it is desired to find the percentage difference in the ratio of the volumes themselves, multiply the differences $\ln_{\text{obsd.}} - \ln_{\text{calcd.}}$ in column 7 of Table I by 100. This follows from the property of natural logarithms that for two nearly equal numbers the difference between their natural logarithms is sensibly equal to the proportional difference of the numbers themselves, thus

$$\ln (x + \Delta x) - \ln x = \ln x + \ln \left(1 + \frac{\Delta x}{x}\right) - \ln x = \ln \left(1 + \frac{\Delta x}{x}\right) = \frac{\Delta x}{x} - \frac{1}{2}\left(\frac{\Delta x}{x}\right)^2 + \ldots \doteq \frac{\Delta x}{x}$$

In Table II we give the differences between observed and calculated values of $\ln v_g/v_l$ for the remaining seven substances of Fig. 1 represented by curves (a) helium, (b) hydrogen, (c) neon, (d) nitrogen, (e) carbon tetrachloride, (f) *n*-hexane, (h) ethyl alcohol, and one additional substance, acetic acid, the curve for which is closely adjacent to that for water (g). The differences $\ln_{\text{obsd.}} - \ln_{\text{calcd.}}$ were obtained from an enlarged graph giving the differences as ordinates against τ as abscissa and then selecting for each substance the values of the differences corresponding to $\tau = 0.400$, $\tau = 0.450$, *et cetera*. The average difference in each case was obtained by integrating the area under a curve and dividing this area by the appropriate length of the abscissa.

TABLE II

ACTUAL DIFFERENCES: $\ln v_g/v_l$ obsd. − $\ln v_g/v_l$ calcd.

Substance:	(a) Helium	(b) Hydrogen	(c) Neon	(d) Nitrogen	(e) Carbon tetrachloride	(f) *n*-Hexane	(g) Acetic acid[a]	(h) Ethyl alcohol
Constants: k	2.659	3.166	3.134	3.203	3.724	3.837	3.960	4.266
m	0.4003	0.430	0.3735	0.351	0.3896	0.386	0.388	0.388
n	.8215	.900	1.247	1.315	1.290	1.376	1.396	1.558
τ = 0.400	...	+0.003	...	...	...	...	...	...
.450	−0.066	.000	...	...	...	...	...	...
.500	.000	+ .002	...	+0.045	...	...	+0.016	...
.550	+ .016	+ .008	...	− .005	...	...	+ .003	0.000
.600	+ .035	+ .018	+0.012	− .011	...	...	− .004	− .026
.650	+ .051	+ .035	− .008	− .004	0.001	0.000	− .015	− .013
.700	+ .020	+ .035	− .020	− .023	+ .008	+ .006	− .002	− .008
.750	.000	+ .005	− .030	− .030	+ .010	+ .003	− .001	− .004
.800	− .005	+ .010	− .004	+ .001	+ .001	+ .002	+ .006	+ .002
.850	− .002	+ .012	+ .014	+ .004	+ .006	+ .012	+ .006	− .003
.900	+ .005	+ .040	+ .029	.000	+ .002	+ .010	+ .005	− .002
.950	− .002	+ .010	+ .015	− .020	+ .001	+ .003	+ .002	+ .013
1.000	.000	.000	.000	.000	.000	.000	.000	.000
Av. diff.	,023	.014	.019	.012	.005	.006	.006	.010

[a] The curve for acetic acid is closely adjacent to that for water.

If it is desired to find the percentage difference in the ratio of the volumes themselves, multiply the differences $\ln_{\text{obsd.}} - \ln_{\text{calcd.}}$ by 100.

Table III gives a summary of the results obtained for all 30 substances. For each substance its calculated curve was constructed from only three known density data, and the differences between observed and calculated values were obtained for the whole experimental range exactly as illustrated in Table I, but for lack of space the results are given only in very condensed form.

The liquids are arranged in the ascending order of the curves in the coördinate system. In each case are given: the critical temperature, the molecular weight, the number of atoms, the value of $\ln v_g/v_l$ at $\tau = 0.600$, the values of the constants k, m, n, the average difference $\ln_{\text{obsd.}} - \ln_{\text{calcd.}}$, and the average percentage difference. These two sets of values were obtained by the use of graphs in a manner entirely analogous to that described in the preceding paragraph for Table II. For the sake of comparison estimated deviations are also given in the last column. These estimates are based upon the assumption that the effects of errors in v_g and T_{cr} upon $\ln v_g/v_l$ are additive as explained subsequently in the text.

Evaluation of the Constants *k*, *m* and *n*.—In evaluating the constants k, m and n it has been our purpose to find a method applicable to any known substance for which only three density measurements have been made (at three different temperatures). With this view in mind, we have used only three known data for densities and corresponding temperatures in calculating the constants k, m and n of each substance given in Table III.

In selecting the three reference points we have been guided by the following considerations: (1) to use a uniform procedure for all substances, so as to obtain comparable results; (2) to use only those density values as reference data which have been actually observed, or calculated from a trustworthy equation of state; (3) to have the first reference point always between the melting and the boiling point, *i. e.*, at $\tau = 0.5$ to 0.65; to have the third point always in the abrupt region of the curve, namely, the third point should always lie between $\tau = 0.96$ and 0.97 but not any closer to unity. This is an important precaution to observe, since in the region between $\tau = 0.97$ to 1.000 the expression $1 - \tau^2$ becomes so small as to be very much influenced by the errors in measurements of the critical temperature. Hence, in this small region the equation is not expected to hold with the same accuracy as in the other parts of the curve. The second point is always to be chosen as close as possible to midway between the two extreme points. This was found by experience to be the best procedure. (4) To choose the intervals between the points 1 and 2 and the points 2 and 3 as large as possible, which is in accordance with the mathematical theory of equations. In a few cases one or more of these conditions could not be observed, for lack of corresponding density data. In such cases the calculated constants were considered slightly inaccurate and in Table III they are enclosed in parentheses.

Accuracy of the Proposed Equation.—In the two columns preceding the last of Table III we have given the averages of the actual and the percentage differences of the function $\ln v_g/v_l$. We see upon examining the differences that they vary from substance to substance. This variation is to be expected since the equation

$$\ln v_g/v_l = k\,\frac{(1-\tau^2)^m}{\tau^n} \qquad (5)$$

TABLE III

SUMMARY OF RESULTS

A = number of atoms. The substances in this table are arranged in the ascending order of the curves.

	Substance	[a]	T_{cr}, °K.	Mol. wt.	A	$\ln v_g/v_l$ obsd. for $\tau = 0.600$
1	Helium	(1)	5.19	4.00	1	3.35
2	Hydrogen	(2)	33.18	2.0156	1	4.100
3	Neon	(3)	44.38	20.18	1	5.03
4	Argon	(2)	150.65	39.94	1	5.10
5	Oxygen	(2)	154.19	32.00	2	5.25
6	Carbon monoxide	(4)	132.89	28.00	2	5.40
7	Nitrogen	(2)	125.99	28.02	2	5.43
8	Ethylene	(5)	282.6	28.03	6	5.56
9	Ethane	(6, 12)	405.3	30.05	8	5.67
10	Hydrogen chloride	(6)	324.6	36.46	2	5.85
11	Nitrous oxide	(6)	309.6	44.02	3	5.87
12	Acetylene	(6)	309.1	26.02	4	Below triple point
13	Methyl ether	(6)	400.0	46.05	9	6.00 (extrap.)
14	Carbon tetrachloride	(7)	556.2	153.83	5	6.05
15	Benzene	(7)	561.6	78.05	12	6.17
16	*i*-Pentane	(7)	460.6	72.09	17	6.20
17	*n*-Pentane	(7)	470.3	72.09	17	6.30
18	Monofluorobenzene	(7)	559.6	96.04	12	6.37
19	Sulfur dioxide	(8)	430.3	64.06	3	6.38
20	Ammonia	(9)	406.1	17.03	4	6.43
21	Methyl formate	(7)	487.1	60.03	8	6.45
22	Ethyl ether	(7)	466.9	74.08	15	6.49
23	*n*-Hexane	(7)	507.9	86.11	20	6.53
24	Acetic acid	(7)	594.7	60.03	8	6.78
25	Ethyl propionate	(7)	546.0	102.08	17	7.03
26	Sulfur trioxide	(6)	491.4	80.06	4	7.50 (extrap.)
27	Water	(10)	647.2	18.02	3	6.83
28	Methyl alcohol	(7)	513.2	32.03	6	7.75
29	Ethyl alcohol	(7)	516.2	46.05	9	7.95
30	Nitrogen tetroxide	(11)	431.3	92.02	6	8.00 (extrap.)

[a] The numbers in column 3 indicate the corresponding references on orthobaric densities and critical data, given in Table V.

TABLE III (*Concluded*)

$$\ln \frac{v_g}{v_l} = k\,\frac{(1-\tau^2)^m}{\tau^n}$$

		Constants[b]			Average differences actual[c]	Average percentage differences actual[d]	Average percentage deviations estimated[e]
		k	m	n			
1	Helium	2.659	0.4003	0.8215	0.023	0.56	4.0
2	Hydrogen	3.166	.4300	.9000	.014	.54	0.9
3	Neon	3.134	.3735	1.247	.019	.61	1.0
4	Argon	3.297	.3767	1.198	.027	1.5	1.1
5	Oxygen	(3.084)	(.3407)	(1.345)	(.010)	(0.54)	1.0
6	Carbon monoxide	3.251	.3790	1.320	.016	.58	1.0
7	Nitrogen	3.203	.3510	1.315	.012	.37	1.0
8	Ethylene	(3.421)	(.3881)	(1.298)	.020	.52	0.7
9	Ethane	3.345	.3492	1.331	.018	.64	.5
10	Hydrogen chloride	3.623	.3855	1.264	.010	.32	.7
11	Nitrous oxide	3.691	.4068	1.262	.010	.40	.7
12	Acetylene	3.677	.3946	1.331	.012	.40	.7
13	Methyl ether	3.641	.3856	1.353	.017	.50	.5
14	Carbon tetrachloride	3.724	.3896	1.290	.005	.14	.5
15	Benzene	3.798	.3932	1.300	.008	.18	.5
16	*i*-Pentane	3.707	.3863	1.343	.002	.06	.5
17	*n*-Pentane	3.755	.3867	1.352	.004	.18	.5
18	Monofluorobenzene	3.687	.3763	1.397	.004	.10	.5
19	Sulfur dioxide	3.977	.4111	1.257	.027	.80	.5
20	Ammonia	(3.881)	(.3858)	(1.331)	.004	.05	.25
21	Methyl formate	3.807	.3853	1.367	.005	.18	.5
22	Ethyl ether	3.757	.3833	1.403	.010	.24	.5
23	*n*-Hexane	3.837	.3861	1.376	.006	.07	.5
24	Acetic acid	3.960	.3879	1.396	.006	.11	.5
25	Ethyl propionate	3.967	.3842	1.443	.004	.05	.5
26	Sulfur trioxide	(4.297)	(.4012)	(1.102)	.017	.73	.5[f]
27	Water	4.122	.3770	1.338	.017	.26	.25
28	Methyl alcohol	4.329	.3780	1.460	.004	.08	.5
29	Ethyl alcohol	4.266	.3883	1.558	.010	.20	.5
30	Nitrogen tetroxide	(4.910)	(.4197)	(1.240)	.010	.20	.5[f]

[b] Values of the constants k, m, n in parentheses are not quite reliable, since the corresponding substances have only a very short range of observed densities. Consequently the intervals between the three reference points are too small. Also, in the case of ethylene, ammonia and nitrogen tetroxide, the third reference point lies below $\tau = 0.96$, *i. e.*, above the characteristic abrupt portion of the curve, because the corresponding vapor densities are not accurately known near T_{cr}. [c] Values are the average of the differences $\ln_{obsd.} - \ln_{calcd.}$. [d] Values are the average of the percentage differences $(\Delta \ln v_g/v_l)/(\ln v_g/v_l) \times 100$. [e] Values are estimated deviations based on the assumptions that the effects of errors in v_g and T_{cr} upon $\ln v_g/v_l$ are additive as explained subsequently in the text. [f] The figures given for sulfur trioxide and nitrogen tetroxide in the last 3 columns are for the range of temperatures: 100–218.3° and 0–60°, respectively.

is influenced largely by errors in the measurements of critical temperature and to some extent by errors in the measurements of vapor density; and these errors are not the same in all cases.

The effect of an error in τ can be obtained by differentiation of equation (5) whence

$$\frac{\Delta \ln v_g/v_l}{\ln v_g/v_l} = -\frac{\Delta\tau}{\tau}\left(\frac{2m\tau^2}{1-\tau^2} + n\right) \tag{7}$$

One finds that for a given absolute error in τ, the corresponding proportional error in $\ln v_g/v_l$ is large either for $\tau = 0$ or 1 and is a minimum between these values, while for a given proportional error in τ, the corresponding proportional error in $\ln v_g/v_l$ is n times as large when $\tau = 0$ and infinite when $\tau = 1$.

In this connection we should like to point out the following: although in general the temperature can be measured very accurately, yet at the critical point the procedure is a very difficult one. It follows from the survey of critical data by Pickering[6] that even the most careful observers do not always check each other, since for some substances the critical temperature values differ by one or more degrees. Therefore, we believe it is fair to assume that the critical temperature is known accurately to within ±0.1–0.5° only. The effect of an error in T_{cr} upon τ is obviously

$$\Delta\tau/\tau = \Delta T_{cr}/T_{cr} \tag{8}$$

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(6) Pickering, *Bur. Standards Sci. Papers*, No. 541, p. 598 (1926).

or the proportional error in τ is equal to the proportional error in T_{cr}.

On the basis of equations (7) and (8) we can figure out the effect of an error in the measurement of the critical temperature upon the calculation of $\ln v_g/v_1$. Taking ten representative substances we get the results tabulated in Table IV.

TABLE IV

Substance	Crit. temp., T_{cr}, °K.	Error in crit. temp., ΔT_{cr}, °K.	Effect upon $\ln v_g/v_1$ $\frac{\Delta \ln v_g/v_1}{\ln v_g/v_1} \times 100$, %			
			τ = 0.5	0.75	0.9	1.0
Helium	5.19	0.1	2.0	3.6	9.6	∞
Hydrogen	33.18	.1	1.2	2.0	4.5	∞
Neon	44.38	.2	0.5	0.6	1.5	∞
Nitrogen	125.99	.5	.5	.6	1.5	∞
Ethylene	282.6	.5	.25	.35	0.70	∞
Ammonia	406.1	.2	.08	.12	.23	∞
Sulfur dioxide	430.3	.5	.16	.23	.46	∞
n-Hexane	507.8	.5	.13	.18	.37	∞
Acetic acid	594.7	.5	.12	.17	.35	∞
Water	647.2	.3	.08	.12	.23	∞

The effect of separate errors in the measurements of v_g and v_1 upon the $\ln v_g/v_1$ can be shown to be

$$\frac{\Delta \ln v_g/v_1}{\ln v_g/v_1} = \frac{\Delta v_g/v_g + \Delta v_1/v_1}{\ln v_g/v_1} \tag{9}$$

The liquid density can be measured very easily to 1 part in 2000 or better, so that the term $\Delta v_1/v_1$ is usually negligible and (9) reduces to

$$\frac{\Delta \ln v_g/v_1}{\ln v_g/v_1} = \frac{\Delta v_g/v_g}{\ln v_g/v_1} \tag{10}$$

which involves only the error in the vapor volume.

For large values of $\ln v_g/v_1$ and a given proportional error in v_g the corresponding proportional error in $\ln v_g/v_1$ is small, while at the critical temperature where $\ln v_g/v_1 = 0$, the corresponding proportional error in $\ln v_g/v_1$ is infinite.

In applying equation (10) we must have knowledge of the proportional error $\Delta v_g/v_g$ for each individual case. The most accurate work is probably that of the Bureau of Standards for ammonia and water where the errors in v_g do not exceed a few tenths of one per cent.[7] In Young's work on organic liquids the vapor density is known to 0.0001 which amounts to about 2% in the neighborhood of the normal boiling point and to only about a few tenths of one per cent. as we approach the critical point.[8]

The Leiden laboratory gives only two significant figures for the vapor densities of hydrogen, nitrogen and oxygen in the region below the boiling point.[9] We assume, therefore, that the accuracy of their data is of the same order as Young's density measurements for the range normal boiling point to critical point.

We see that for most substances the proportional error in v_g for $\tau = 0.6$ is of the order 2 to 3% and decreases with increasing τ until at $\tau = 0.95$ it is about 0.3–0.5%. From Fig. 1 it is evident that the least value of $\ln v_g/v_1$ for $\tau = 0.6$ is 3.25 for helium, and the greatest value is 7.95 for ethyl alcohol, while for $\tau = 0.95$ the values range from 1.0 for helium to 1.7 for ethyl alcohol; therefore from equation (10) the proportional error in $\ln v_g/v_1$ will be between 0.25–0.50% for $\tau = 0.6$ and between 0.2–0.5% for $\tau = 0.95$. For water and ammonia because of the high accuracy of the v_g data the proportional error in $\ln v_g/v_1$ will not exceed 0.1% for the same range of τ. The above shows that the proportional error in $\ln v_g/v_1$ is practically constant for $\tau = 0.6$–0.95, and can be taken as equal to 0.1% for water and ammonia, and equal to 0.3% for the remaining substances.

We can now estimate the total effect of errors in the measurement of critical temperature and of vapor volumes upon the calculated values of $\ln v_g/v_1$. It is obvious that the total proportional error in $\ln v_g/v_1$ will not exceed the sum of the two effects: effect *a* due to error in the critical temperature as shown in Table IV and effect *b* due to errors in the vapor volumes as discussed above.

For each substance we estimated effect *a* as a percentage difference for intervals of τ equal to 0.05 and obtained the average. Effect *b* was considered constant and equal to 0.1% for water and ammonia and 0.3% for the remaining substances; these values were added to the average of effect *a* in the respective cases. The sums thus obtained, we believe, represent fair estimates of the upper limits of the proportional errors in $\ln v_g/v_1$ arising from errors of experimentation. They give a view of the reliability of the proposed equation (5) for the range melting point to 0.95 critical point and therefore are included in Table III (last column)

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(7) The Bureau of Standards data for v_g are calculated from the measured latent heat of evaporation. For details, see Bur. Standards Circ. No. 142, 1923; and Osborn, Stimson and Ginnings, *Mech. Eng.*, **57**, 162 (1935).

(8) Correspondingly, we find only two significant figures at the normal boiling point in Young's vapor densities as given by "Int. Crit. Tables," Vol. III, 1928, p. 244. Other observers usually give less accurate measurements. For the estimate of error in density measurements of Young and others, see J. Timmermans, *ibid.*, p. 244.

(9) The density tables and the discussion of experimental errors are given in the papers by Mathias and co-workers: *Ann. phys.*, **17**, 416–474 (1922).

for comparison with the percentage differences actually found.

Both the actual and estimated deviations refer to temperature ranges for which the vapor densities are accurately known, namely, measured or calculated from a reliable equation of state. Some of the substances investigated by Young, such as benzene, carbon tetrachloride, etc., have vapor densities roughly extrapolated (by Young) in the region below the boiling point. The corresponding values of ln v_g/v_l are unreliable and were not taken into account in making the computations.

We see upon examination of the table that twenty-seven substances show smaller actual deviations than the estimated, while three, argon, sulfur dioxide and sulfur trioxide, show greater.

A few words should be said regarding sulfur trioxide and nitrogen tetroxide. Each of these substances gives a curve which in part follows the typical shaped curves shown in Fig. 1 and in part deviates more or less as shown by the dotted lines in Fig. 2.

In the case of sulfur trioxide the explanation of this behavior seems to be that part of the data (100–218.3°) was observed[10] while the rest of the data (44–100°) was apparently calculated by means of an equation involving mean density.[11] In plotting the ln values against τ we find that the observed values (100–218.3°) give the typical shape while the calculated values (44–100°) depart from it. The constants k, m and n in Table III were evaluated from the observed data; accordingly we find upon applying the proposed equation (5) that it holds fairly well only for the range (100–218.3°) and not at all for the range (44–100°).

As to nitrogen tetroxide, its densities have been observed all along the saturation line by Mittasch and co-workers (0 to 55°),[12] and by Bennewitz and Windish (30 to $t°$ crit.).[12] In constructing the corresponding curve we find that the portion (0 to 60°) falls right along that of ethyl alcohol, but the portion (60 to 158.2°) is very unusually shaped (Fig. 2 dotted line). We expected our equation to fit in the range (0–60°) and this was found to be the case with very good agreement, but above 60° the deviation from observed values of ln is very large. It is possible that this discrepancy is caused by partial dissociation of $N_2O_4 \longrightarrow 2NO_2$ under saturation pressure[13] which is probably small below 60° and hence does not affect the corresponding value of ln v_{gas}/v_{liq}.

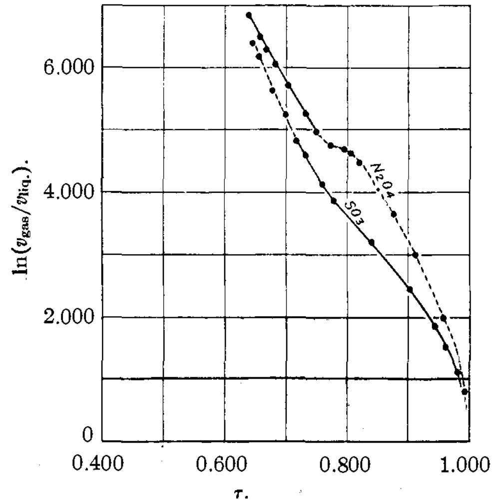

Fig. 2.— ——— Part of experimental curve which follows equation; ------ part of experimental curve which deviates from equation.

Comparison of the Constants k, m and n.—When we compare the values of the three constants for different substances given in Table III, we see that each of them varies but little in comparison with the wide variation in physical and chemical properties.

Thus k increases from about 3.2 to 4.3 with the two exceptions helium, $k = 2.66$; nitrogen tetroxide, $k = 4.9$.

m ranges from 0.347 to 0.420 and for many organic substances it is equal to about one-tenth of k.

n ranges from 0.821 to 1.558.

The curves are described accurately by the proposed equation and consequently the order of arrangement should bear close relationship to the corresponding values of the constants k, m and n. We find that m and n do not show any striking regularity, but k is quite characteristic. It increases regularly in about the same order in which the curves succeed each other with a few exceptions. Further, we observe that in general closely adjacent curves such as those for nitrogen and carbon monoxide, or normal and i-pentane, have almost identical values of k.

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[10] Berthoud, *Helv. Chim. Acta*, **5**, 513 (1922); *J. chim. phys.*, **20**, 77 (1923).

[11] "Int. Crit. Tables," Vol. III, 1928, p. 228; see bottom line of the sulfur trioxide table.

[12] Mittasch, Kuss and Schleuter, *Z. anorg. Chem.* **159**, 29 (1927); Bennewitz and Windish, *Z. physik. Chem.*, **A166**, 401 (1933).

[13] Nitrogen tetroxide dissociates partially under saturation pressure as is indicated in the corresponding pressure–temperature table (bottom line). See "Int. Crit. Tables," Vol. III, 1928, p. 229.

The close parallelism between the values of k and the location of the curve $\ln v_g/v_l$ suggests at once that the constant k itself is a function of the physical and chemical properties of substances.

This supposition proves to be correct. We find that both the position of the curve and the value of the constant k depend very closely on the properties of substances in the critical state, namely, on their critical constants.

Relation between the Constant k and the Critical Coefficient.—Upon examining the values for k we find that they are almost identical with the critical coefficient for gases K_{cr} defined by the equation

$$K_{cr} = RT_{cr}d_{cr}/Mp_{cr} \qquad (11)$$

In Table V we give the results of this comparison. The thirty substances studied are the same as before. They are arranged in the ascending order of the curves. In columns 3–5 we give the number of atoms in the molecule and the values of k and K_{cr}. The ratio K_{cr}/k is calculated for each substance and is given in column 6.

TABLE V

A = number of atoms. $k = [\ln d_l/d_g]/[(1 - \tau^2)^m/\tau^n]$. $K_{cr} = RT_{cr}d_{cr}/Mp_{cr}$.
The substances in this table are arranged in the order of ascending position of curves

	Substance[a]	A	k	K_{cr}	Ratio K_{cr}/k	Literature
1	Helium	1	2.659	3.270	1.230[b]	(1)
2	Hydrogen	1	3.166	3.276	1.035	(2)
3	Neon	1	3.134	3.249	1.037	(3)
4	Argon	1	3.297	3.425	1.039	(2)
5	Oxygen	2	(3.084)	3.346	1.085	(2)
6	Carbon monoxide	2	3.251	3.395	1.044	(4)
7	Nitrogen	2	3.203	3.420	1.068	(2)
8	Ethylene	6	(3.421)	3.524	(1.030)	(5)
9	Ethane	8	3.345	3.587	1.072	(12)
10	Hydrogen chloride	2	3.623	3.801	1.049	(6)
11	Nitrous oxide	3	3.691	3.630	0.9835	(6)
12	Acetylene	4	3.677	3.635	.9886	(6)
13	Methyl ether	9	3.641	3.719	1.022	(6)
14	Carbon tetrachloride	5	3.724	3.680	0.9882	(7)
15	Benzene	12	3.798	3.755	.9887	(7)
16	*i*-Pentane	17	3.707	3.735	1.007	(7)
17	*n*-Pentane	17	3.755	3.766	1.003	(7)
18	Monofluorobenzene	12	3.687	3.796	1.030	(7)
19	Sulfur dioxide	3	(3.977)	3.600	(1.140)[b]	(8)
20	Ammonia	4	(3.881)	4.125	(1.067)	(9)
21	Methyl formate	8	3.807	3.922	1.030	(7)
22	Ethyl ether	15	3.757	3.798	1.011	(7)
23	*n*-Hexane	20	3.837	3.830	0.9982	(7)
24	Acetic acid	8	3.960	4.991	1.260[b]	(7)
25	Ethyl propionate	17	3.967	3.923	0.9889	(7)
26	Sulfur trioxide	4	(4.297)	3.805	(0.8855)[b]	(6)
27	Water	3	4.122	4.234	1.027	(10)
28	Methyl alcohol	6	4.329	4.559	1.053	(7)
29	Ethyl alcohol	9	4.266	4.026	0.9437	(7)
30	Nitrogen tetroxide	6	(4.910)	4.385	(0.8727)[b]	(11)

[a] The value for $K_{cr} = RT_{cr}d_{cr}/Mp_{cr}$ is calculated from the corresponding critical data. The bibliography is given below. [b] Values show disagreement between k and K_{cr}.

BIBLIOGRAPHY ON EXPERIMENTAL DATA

Orthobaric Densities and Critical Data; References

(1) Helium: Leiden Lab. Comm. No. 172b (1925); 179c (1926).
(2) H_2, A, O_2, N_2: *Ann. phys.*, [9] 17, 416 (1922).
(3) Neon: *ibid.*, [9] 19, 231 (1923).
(4) Carbon monoxide: Leiden Lab. Comm. No. 221b (1932).
(5) Ethylene: *Ann. phys.*, [9] 11, 343 (1929).
(6) Acetylene, hydrogen chloride, methyl ether, nitrous oxide, sulfur trioxide, ethane: Tables and references, see "Int. Crit. Tables," Vol. III, 1928, pp. 228–236.

(7) Carbon tetrachloride, benzene, monofluorobenzene, *i*- and *n*-pentanes, *n*-hexane, methyl formate, ethyl propionate, methyl and ethyl alcohols, and acetic acid: see original tables of Young, *Proc. Roy. Dublin Soc.*, **12**, 374 (1910).

(8) Sulfur dioxide: observed volumes—(0°C. to $t°$ Crit.) also critical data tables and references, see "Int. Crit. Tables," Vol. III, 1928, p. 236. Liquid volumes and vapor volumes (calcd. by means of equation of state between −40 and 0°). See the SO_2 table, "Refrigerating Data Book," 1934. Also original paper by Fiske, *Refrigerating Eng.*, December, (1924).

(9) Ammonia: observed volumes (−59 to +53°), tables and references; also critical data, see Bur. Standards, *Circ.*, No. 142, 1923.

(10) Water: observed liquid volumes: (0 to 30°) see Keenan Steam Tables, ed. 1930. Observ. liquid volumes (+30 to +360°); also crit. vol. and $t°$ crit., Smith and Keyes, *Proc. Am. Acad. Arts Sci.*, **69**, 285 (1934). Vapor volumes (0 to +360°) calcd. from observed latent heat and pressure with the aid of liquid volume data of Keyes and Smith. See prelim. report of the Bur. Standards (Osborn, Stimson and Ginnings), *Mech. Eng.*, **57**, 162 (1935). Critical pressure for water, see Keyes, Smith and Gerry, *Proc. Am. Acad. Arts Sci.*, **69**, 139 (1934).

(11) Nitrogen tetroxide: observed densities (+3 to +55°) see Mittasch, *et al.*, *Z. anorg. Chem.*, **159**, 29 (1927). Observed densities (+60°C. to $t°$ crit.). Also critical data, see Bennewitz and Windish, *Z. physik. Chem.*, **A166**, 401 (1933).

(12) Critical data for ethane by Cardozo, see Pickering's table, "Int. Crit. Tables," Vol. III, 1928, p. 248.

The agreement between k and K_{cr} is as follows:

% Difference	0.5–6	6–10	10–15	23–26
Number of substances	21	4	3	2

The deviations from unity can in part be accounted for by errors in the critical coefficients, these errors being mostly due to errors in the determination of the critical density. Beattie and co-workers[14] discuss this question and assign an estimate of error of about 1–2% for the best values of critical volumes; however, it must be said that in some of the earlier work the critical volumes are probably in error by as much as 5–10%. It appears, therefore, that for the large majority of cases the ratio of K_{cr} to k is very nearly equal to unity.[15] This fact leads to an important conclusion.

The theory of corresponding states requires that the critical coefficient be a constant for all substances and all known equations of state lead to a constant value of K_{cr}, independent of the nature of the substance.[16] (Thus van der Waals' equation gives $K_{cr} = 2.67$; Dieterici's and Wohl's equations lead to the values $K_{cr} = 3.69$ and 3.75, respectively.)

Actually, however, the critical coefficient is far from being a constant. Table V shows that it changes from about 3.0 for monoatomic to about 4.0 for polyatomic substances and in some cases it is greater than 4.0. In general organic substances have an almost constant value of K_{cr} averaging 3.7. These substances are considered normal.[16]

As to the values of K_{cr} departing from the constant value 3.7, the corresponding substances are classed as abnormal. It is customary to explain these departures as being due to the association of the given liquid.[16] As far as we know, a rational treatment of this question has not yet been attempted.

The investigation of the ratio of orthobaric densities here presented leads to another view of this matter.

Comparing the values of k and K_{cr} we see that they change quite parallel to each other as we go from substance to substance. Since the ratio K_{cr}/k is close to unity and both factors in the ratio are established by independent methods, it follows that K_{cr} cannot be a constant. Its gradual rise follows the order of the curves ($\ln v_g/v_l$) in the coördinate system. Therefore, it appears to be a normal phenomenon not at all indicative of the molecular association of the given liquid. It further appears that a correct equation of state should take account of the variation of K_{cr} from substance to substance.

We should like to express our appreciation to Mr. David L. Fiske, Editor of the Refrigerating Data Book, New York, for many valuable suggestions and for his interest in this work. We should also like to thank Dr. Henry Fleishmann and the Educational Alliance, New York, for the financial assistance given to one of us (C. S.) during this work.

Conclusions

1. The ratio of orthobaric densities is a function of reduced temperature and consequently

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(14) Beattie, Poffenberger and Hadlock, *J. Chem. Phys.*, **3**, 96 (1936).

(15) With respect to the five discrepant cases, where k and K_{cr} differ by more than 10%, namely helium, sulfur dioxide, acetic acid, sulfur trioxide and nitrogen tetroxide, we can offer no explanation at present.

(16) A collection of the best known equations of state and a discussion of the critical coefficient are given in the "Handbuch der Experimental-Physik," Vol. VIII (2), 1929, pp. 224–234.

the vapor volume can be expressed as a function of reduced temperature and liquid volume along the saturation line, namely

$$\ln v_g/v_l = k\frac{(1-\tau^2)^m}{\tau^n} \qquad (5)$$

$$v_g = v_l \exp.\, k\frac{(1-\tau^2)^m}{\tau^n} \qquad (12)$$

2. The constant k of the suggested equation is almost identical with the critical coefficient K_{cr}, their ratio being nearly equal to unity for most substances investigated.

The critical coefficient is not a constant but varies from substance to substance, increasing with the order of curves ($\ln v_g/v_l$) in the coördinate system.

3. There seems to be a definite similarity in the mechanism of evaporation of substances as shown by the fact that the respective expansion curves can be expressed by one and the same equation and that the constants of this equation have values very close to each other for substances of the most diverse chemical and physical properties.

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[CONTRIBUTION FROM THE MALLINCKRODT CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

The Kinetics of Thermal *Cis-Trans* Isomerization. VI

BY G. B. KISTIAKOWSKY AND WALTER R. SMITH

In one of the earlier papers[1] of the present series, evidence was presented indicating that the first order rate of isomerization of methyl cinnamate began to fall off at a pressure of 6 mm. Unfortunately, due to the analytical method employed, it was not feasible to study the reaction at still lower pressures. This compound and dimethyl maleate[2] have been the only two in a series of geometric isomers in which this phenomenon, characteristic of unimolecular reactions, has been observed.

In β-cyanostyrene the number of contributing degrees of freedom could be expected to be appreciably less than in methyl cinnamate, because of substitution of a CN group for the $COOCH_3$ group. Hence, with β-cyanostyrene the rate might begin to fall off at a higher pressure and an extensive study of the rate-pressure dependence could be made.

The present paper describes a number of experiments on the rate of isomerization of β-cyanostyrene performed at various temperatures and over an extensive range of pressures.

Experimental Details

Preparation of β-Cyanostyrene.—The nitrile was prepared according to the method of Ghosez[3] by the condensation of benzaldehyde and cyanoacetic acid in the presence of pyridine. Sixty per cent. of the theoretical yield was obtained.[4]

The resulting mixture of the geometric isomers was distilled in an all glass still 3 m. tall and 18 mm. in diameter, packed with Pyrex glass spirals.[5] A 20–1 reflux ratio was used. Two fractions were obtained, one boiling at 139.1° at 30 mm. and the other at 152° at 30 mm. The high boiling fraction was further purified by freezing and allowing it to melt at 20°. The solid portion remaining was distilled at 122° at 2 mm. in a Claisen flask. The weight ratio of high to low boiling isomers was 62:38. Ghosez[3] obtained 63% high boiling compound.

The high boiling isomer melted at 22° and had $n^{20.2}D$ 1.6031. For the low boiling isomer the melting point was −4.4° and $n^{20.2}D$ 1.5843. According to Ghosez and in conformity with other evidence[6] the low boiling isomer must be assigned the *cis* configuration. This is also in agreement with equilibrium data presented below.

Analytical Method.—The appreciable difference in the refractive indices of the two isomers provided a rapid and convenient method of analyzing the reaction mixtures. An Abbé refractometer, thermostated to 20.2° and employing a sodium vapor lamp, was calibrated with a series of known mixtures of the isomers. A strictly linear relationship between composition and refractive index was found. It was possible to detect 0.5% of either isomer.

The melting points of these mixtures were also determined by means of a single junction copper–constantan thermocouple. The couple was used sometimes to check the values obtained from the refractometer, as described below.

The apparatus was of the usual static type. Both it and the experimental procedure have already been described elsewhere.[2]

Some of the earlier runs were analyzed both by the refractive index method and the freezing point. In all cases the two methods gave analyses agreeing to 1%, which is to be regarded as indicating the absence of side reactions.

The reaction was further established by connecting the nitrile to cinnamic acid. The product from a run on the

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[1] Kistiakowsky and Smith, THIS JOURNAL, **57**, 269 (1935).

[2] Kistiakowsky and Nelles, *Z. physik. Chem.*, Bodenstein Festband, 369 (1931), and THIS JOURNAL, **54**, 2208 (1932).

[3] Ghosez, *Bull. soc. chim. Belg.*, **41**, 477 (1932).

[4] We are greatly indebted to Dr. George F. Wright for preparing the compound for us.

[5] Kistiakowsky, *et al.*, THIS JOURNAL, **57**, 877 (1935).

[6] Wright, *ibid.*, **57**, 1993 (1935).