712. *Correlation of Critical Temperature, Boiling Point, and Critical Pressure.*

By Leo H. Thomas.

A reliable method of evaluating critical temperatures and pressures from b. p. data is presented. By means of additive functions, the b. p. of a given liquid at a given pressure less than atmospheric may be estimated with satisfactory accuracy from the b. p. under atmospheric pressure.

The importance of a reliable method of estimating critical temperatures and pressures has often been pointed out (Meissner and Redding, *Ind. Eng. Chem.*, 1942, **34**, 521); a critical survey of existing methods has been supplied by Hertzog (*ibid.*, p. 1072).

Critical Temperatures.—The most recent and apparently the most reliable method is that due to Hertzog (*loc. cit.*) who relates critical temperature (T_C) with the b. p. (T_B) on the absolute scale under a pressure of 760 mm. of mercury, by means of the equation

$$T_C/T_B = a - b(P) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where (P) is the parachor and a and b are constants.

The relation between (T_C/T_B) and the parachor for a homologous series is sensibly linear, and tolerably so for a set of compounds closely related chemically. By a division into six groups, the critical temperatures of a selected number (140) of compounds were satisfactorily calculated. The division must of necessity be arbitrary, and it will be appreciated that for a given polyfunctional compound, a choice must be made as to which of the six a and b values should be employed. For such compounds then, the calculated critical temperatures cannot be accepted with any confidence.

The correlation proposed of critical pressure (p_c) with parachor is of a similar nature, *viz.*,

$$\log p_c = a - b \log(P) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

Further work by the author has brought to light a surprisingly simple correlation of T_C and T_B, and it has been found that the ratio T_B/T_C (defined as θ) is an additive function of the atoms and bonds in the molecule.

The fundamental interval for CH_2 was found for the paraffin series by application of Campbell's " zero-sum " method (*Phil. Mag.*, 1920, **39**, 177; 1924, **47**, 816) to the equations of type

$$\theta_{methane} = \theta_{2H} + \theta_{CH_2}$$

for the hydrocarbons from methane to octane.

This procedure gave $\theta_{CH_2} = 0{\cdot}016$. Similarly, esters gave a value 0·014, ethers 0·015, sulphides 0·019, thiols 0·016, aromatic hydrocarbons 0·015, cyanides 0·013, etc. The value ultimately selected was 0·0165 and was chosen by weighting the various series according to the number of CH_2 intervals and the estimated reliability of the critical data.

By proceeding in the usual way, the following list of atomic and structural constants was drawn up (for the figures in parentheses see p. 3413).

C = −0·557 (−0·393)
Si = −0·542 (−0·390)
Sn = −0·536 (−0·386)
N (tertiary) = −0·272 (−0·190)
N (primary and secondary) = −0·260 (−0·168)
O (ethers) = 0·018 (0·020)
O (alcohols) = 0·063 (0·082)
P = −0·273 (−0·198)
As = −0·250 (−0·177)
B = −0·239
O (phenols) = 0·028 (0·042)

S = 0·012 (0·017)	F = 0·293 (0·208)
Cl, Br, I = 0·297 (0·216)	H = 0·286 (0·203)
CO (aldehydes and ketones) = 0·045 (0·047)	CN = 0·339 (0·252)
NO_2 (nitrites and nitro-compounds) = 0·319	COO (esters) = 0·038 (0·043)
	COO (acids) = 0·070 (0·081)
Double bond = 0·566 (0·400)	Treble bond = 1·143 (0·830)
Six-membered ring (aromatic) = 0·577 (0·397)	Five-membered ring = 0·544 (0·386)
,, ,, (aliphatic) = 0·543 (0·380)	Three-membered ring = 0·559

It has not been necessary to assign a finite value to a co-ordinate covalency, and the value of NO_2 was based on nitro-compounds and the isomeric nitrites.

Critical data for the latter types are lacking; instead, the values of T_0 have been evaluated from the viscosity–temperature relationships developed by the author (*J.*, 1946, 573; equation 3 and Table II). A value thus calculated for any one member of these series is not reliable, but over the whole series, the derived average values of θ_{NO_2} is quite consistent. Thus its value in various compounds was as follows:

Nitromethane	0·325	Propyl nitrite	0·342
Nitroethane	0·314	Butyl nitrite	0·340
Nitropropane	0·315	Amyl nitrite	0·304
Nitrobutane	0·311	*iso*Amyl nitrite	0·297
Nitropentane	0·319	Mean value	0·321
Mean value	0·317		

Critical temperatures and pressures have been taken from the International Critical Tables, and additional or more recent data from Stull's compilation (*Ind. Eng. Chem.*, 1947, **39**, 517).

The measure of agreement between calculated critical temperatures and the experimental values for a representative selection of substances is shown in Table I.

TABLE I.

Compound.	T_0, calc.	T_0, found.	Error.	p_0 (atm.), calc.	p_0 (atm.), found.	Error, %.	T_{10}, calc.	T_{10}, found.	Error.
Methane	189°	190°	1°	52·8	52·5	0·6	79°	78°	1°
Silicomethane	267	273	6	51	48	6·2	113	110	3
Ethylene	282	283	1	50·9	50·7	0·4	120	120	0
Propylene	365	365	0	45·2	45·4	0·4	161	161	0
Propane	367	369	2	42·8	42·0	1·9	164	165	1
Allene	394	394	0	51·8	51·8	0·0	171	172	1
Methylamine	433	430	3	65·3	73·6	11·3	196	199	3
Ethyl chloride	463	460	3	48·4	53·3	9·2	206	207	1
Ethyl ether	472	467	5	33·7	35·5	5·1	225	225	0
Methyl formate	487	487	0	56·6	59·1	4·2	225	224	0
$CCl_2F{\cdot}CClF_2$	487	490	3	37·5	33·7	11·3	237	233	4
Ethanethiol	502	498	4	—	—	—	225	223	2
Ethylidene chloride	528	528	0	48	52	7·7	261	259	2
Chloroform	538	536	2	57	55	3·6	247	243	4
Dipropylamine	551	550	1	30	31	3·2	—	—	—
Ethyl sulphide	563	557	6	41·2	39·1	5·4	267	265	2
n-Butyl alcohol	556	560	4	45·0	48·4	7·0	300	303	3
*iso*Butyl acetate	561	561	0	30	31	3·2	288	286	2
Octane	565	569	4	22·3	24·6	9·4	289	292	3
Propionic acid	612	612	0	50·5	53·0	4·7	313	313	0
Ethyl benzene	618	620	2	36·6	38·1	3·9	299	299	0
Amyl cyanide	617	622	5	30·8	32·2	4·3	320	320	0
Phenetole	653	647	6	34·3	33·8	1·5	329	329	0
Bromobenzene	669	670	1	47·2	44·6	5·8	315	313	2
Dimethylaniline	692	688	4	37·1	35·8	3·6	343	343	0
cis-Decahydronaphthalene	687	690	3	—	—	—	333	337	4
p-Cresol	699	704	5	49·3	50·8	2·9	361	362	4
Benzyl cyanide	723	723	0	—	—	—	375	376	1
Naphthalene	743	752	9	41	40	2·5	359	359	0
Mean	—	—	3	—	—	4·4	—	—	2

Of the 174 substances taken into consideration, 104 show calculated values of T_0 differing from the experimental figures by $<5°$, and 149 by $<12°$. The remaining 25 show errors of 12—27°.

It is difficult to arrive at a figure which may be reasonably assigned to experimental error. Accurate determination of critical temperatures is difficult and great discrepancies are to be found in the literature, especially in the earlier measurements. Thus those of Pawlewski

(*Ber.*, 1882, **15**, 2460) carried out on eight lower fatty esters are consistently higher by 6—8° than the presumably more reliable determinations by Young and Thomas (*J.*, 1893, **63**, 1242).

Pawlewski's values for the higher esters and for a number of other substances are consistently higher than the calculated values, *viz.*, *iso*butyl propionate (14°), propyl butyrate (15°), ethyl allyl ether (11°), *iso*amyl alcohol (18°), and methylal (19°). It seems reasonable then to ascribe ~8° at least of these errors to experimental error.

The same remarks may also well apply to Brown's results (*J.*, 1906, **89**, 311), of which eight higher esters and *tert.*-amyl alcohol have been included in this correlation. These again are all higher by 14—26° than the calculated values. In support of this supposition, it may be pointed out that his figures for *iso*propyl and *iso*butyl alcohols—the only data for which comparative figures by other workers are available—are 9° and 14° higher respectively than those of Nadejdine (*J. Russ. Phys. Chem. Soc.*, 1883, **15**, 25). Work conducted on seven lower esters by the latter resulted in critical-temperature measurements virtually identical with those of Young and Thomas (*loc. cit.*).

It seems probable then that, of the 25 substances mentioned above showing errors >12°, the relatively large errors of 15 may, at least in part, be ascribed to experimental error on the part of two earlier workers. The remaining substances are of a simple nature and mostly of a polyhalide type, *viz.*, boron and silicon fluorides, chlorotrifluoro-methane and -silane, bromine, hydrogen iodide and cyanide, and carbonyl chloride.

Estimation of Vapour Pressures.—The fact that the b. p. of a substance is merely that temperature when its vapour pressure is equal to the arbitrary atmospheric pressure suggests that the ratio of the b. p. under any other chosen pressure to the critical temperature should also be an additive function. Although the author has not been able to show that this must of necessity follow from some general temperature–pressure relationship, it may be empirically demonstrated by applying the above method to the b. p. under a selected pressure of say 10 mm. Thus the values (θ_{10}) in parentheses in the table on p. 3411 have been calculated from the b. p.s under 10 mm. pressure as tabulated by Stull (*loc. cit.*). We have then $T_{760}/T_C = \theta_{760}$ and $T_{10}/T_C = \theta_{10}$. Eliminating T_C, we get

$$T_{10} = (\theta_{10}/\theta_{760}) \times T_{760} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

which provides us with a method of evaluating the b. p. of a substance under 10 mm. pressure from its b. p. under 760 mm. pressure or *vice versa*.

Clearly, to determine the b. p. at, say, 100 mm., we may either (*a*) construct a list of θ values at the new pressure, or (*b*) calculate it directly from T_{10} and T_{760} by the use of one of the well-known two-constant vapour-pressure equations.

Values of T_{10}, some of which are included in Table I, have been calculated from T_{760} for most of the substances previously considered, and the measure of agreement is very satisfactory. Thus of 157 substances, 139 show errors of <4°, and the remaining 18 errors of 4—8°. The average error was 2°.

TABLE II.

Compound.	T_{10}, calc.	found.	Error.	Compound.	T_{10}, calc.	found.	Error.
Carbon tetrafluoride	104°	104°	0°	Di-(2-chloroethyl) ether ...	332°	335°	3°
Hydrogen chloride	136	137	1	Benzylamine	343	340	3
Methylsilane	152	153	1	Ethyl carbamate	348	351	3
Hydrogen iodide	171	171	0	Nitrobenzene	362	358	4
Chlorine	174	171	3	Dodecane	357	363	6
Formaldehyde	185	185	0	Trichloroacetic acid	367	361	6
Carbonyl chloride	211	204	7	*p*-Dibromobenzene	365	361	4
Cyanogen chloride	211	219	8	Nonan-1-ol	374	373	1
Hydrogen cyanide	218	225	7	Quinoline	377	377	0
Trichloromethylsilane	247	242	5	Acetamide	375	378	3
Tetramethylstannane	250	252	2	*s*-Tetrabromobenzene ...	388	383	5
Piperidine	282	277	5	Diphenyl	391	390	1
Ethylenediamine	298	294	4	Benzoic acid.....	402	405	3
Methyldichloroarsine	297	297	0	Glutaric anhydride	426	423	3
Bromoform	315	307	8	Hexaethylbenzene	423	423	0
*cyclo*Hexanone	316	312	4	Succinimide	437	430	7
Ethyl orthoformate	316	313	3	Benzophenone	438	431	7
Ethyl dichloroacetate	324	319	5	Butyl phthalate	473	471	2
Thiophenol	326	329	3	Palmitic acid	481	479	2
Methyl oxalate	332	329	3	Stearic acid	493	498	5

Mean error = 4°.

It is noteworthy that the above-mentioned 25 substances whose calculated critical temperatures are markedly different from the measured values gave calculated values of T_{10} which differ from the actual values also by a mean error of 2°, a fact which again may indicate that the discrepancies arise in no small part from inaccuracy of the critical data.

The most satisfactory test for the validity of (3) is to predict T_{10} from T_{760} for a selection of substances whose critical temperatures are not known and which therefore could not have been taken into consideration in evaluating the above atomic and structural constants. Such a test is provided by the data of Table II.

When such a test is applied to substituted alcohols and phenols, the calculated b. p.s under 10 mm. pressure are consistently ~15° too high. A possible reason is that such hydroxy-compounds have a lower degree of association, or at least become more associated with fall in temperature at a lower rate than unsubstituted compounds. This possibility is being examined by the author's viscometric method of determining degrees of association (*J.*, 1948, 1345, 1349).

Large discrepancies are also apparent for polyhydric alcohols.

Critical Pressures.—In previous papers (*J.*, 1946, 573; 1947, 822) the author has shown (1) that at corresponding temperatures for any homologous series, there is an approximately constant percentage increase in $\eta\sqrt{v}$ from one member to the next, where η is the viscosity and v the specific volume, and (2) that non-associated liquids in equilibrium with their vapours at the same reduced pressure have approximately the same value of $\eta\sqrt{v}$. It may easily be shown that these observations can be correlated by assuming that in the equation

$$\log p_c/p = A\,[(T_C/T - 1]$$

the constant A is additive.

Such an equation was shown to be closely obeyed for vapour pressures and temperatures between the b. p. and the critical point. Hence

$$A = (\log p_c/p_B)/(T_C/T_B - 1) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

The fundamental interval for CH_2 was evaluated as above for the paraffin series from methane to octane, which procedure gave $A_{CH_2} = 0{\cdot}12$. Esters similarly gave a value 0·10, and cyanides 0·11, the value ultimately selected being 0·107.

Critical-pressure data are not so extensive as critical-temperature data, and, apart from the series just mentioned, critical pressures are not known beyond the second or third member. Accordingly, in order to get atomic and structural constants consistent with the corresponding θ constants, *calculated* values of T_B/T_C have been employed in (4) to evaluate all those tabulated below with the exception of those based on paraffins, esters, and cyanides.

C = −2·247	O (ethers) = 0·19
Si = −2·13	O (alcohols) = 1·112
N (tertiary) = −0·950	O (phenols) = 0·53
N (primary and secondary) = −0·720	S = 0·20
Cl = 1·313	CO = 0·64
Br = 1·31	CN = 1·775
I = 1·27	COO (esters) = 0·472
F = 1·183	COO (acids) = 0·985
H = 1·177	
Double bond = 2·333	6-Membered ring (aromatic) = 2·271
Treble bond = 4·83	,, ,, (aliphatic) = 2·13
	5-Membered ring = 1·97

The extent of agreement between the measured values of critical pressure and those calculated by means of the tabulated A increments and θ_{760} is shown in Table I. Of the 103 substances taken into consideration in compiling the additive constants, 60 show errors of <5%, and 97 of <10%. The remaining six liquids show errors of 10—50% and include dichlorodifluoromethane (16%), trichlorofluoromethane (19%), ethyl fluoride (14%), silicon tetrafluoride (49%), dimethylaniline (19%), and carbon tetrachloride (27%). The large error exhibited by the last is quite unexpected in view of the normal errors shown by other polyhalides such as chloroform (4), methylene chloride (4), ethylene chloride (10), and ethylidene chloride (8%).

In addition, large errors are shown by such simply constituted substances as chlorine (22), hydrogen chloride (35), hydrogen bromide (28), hydrogen iodide (31), and hydrogen sulphide (39%).

As stated above, experimental errors in all but the most accurate and recent determinations

of critical temperature may well be of the order of 2—7°, and even higher errors seem very likely in many cases. From consideration of the vapour pressure–temperature variations for temperatures approaching the critical, a 2—7° error in critical temperature is equivalent to an error in critical pressure of 3—10%, which agrees well with the actual error distribution.

GLAMORGAN TECHNICAL COLLEGE, TREFOREST. [*Received, September 19th,* 1949.]