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Parameters in the Simon Equation Relating Pressure and Melting Temperature*

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PROBLEM AND PROGRAM

THE first observation of the effects of pressure upon the melting point of a substance was made by Perkins,[1] (see pages 412 to 413 for all references in this article) who stated: "The most remarkable result I obtained was with concentrated acetic acid; which, after compression with a force of 1100 atmospheres, was found to be beautifully crystallized, with the exception of about 1/10 part of fluid, which, when poured out was only slightly acid."

This observation was made at pressures truly phenomenal for 1826, but was apparently completely ignored. The significance of the result was unappreciated, for Clapyeron[2] did not derive his equation until 1834 and then applied it only to boiling. The first theoretical discussion confined to melting came in 1849, by J. Thomson,[3] with experimental confirmation by his brother W. Thomson[4] (Lord Kelvin), who hailed this as the prediction of a hitherto unobserved effect, in the same year. Clausius[5] then put the Clausius–Clapyeron equation on a sound theoretical basis in 1850.

These theoretical discussions led to a rash of experimental efforts to determine the effects of pressure upon the melting points of pure substances, and this has been a fairly popular field of research since. To date, the melting curves of over 200 substances have been traced over varying ranges of pressure and temperature. A considerable body of discussion has also been published on the eventual course of the melting curve as the pressure is increased indefinitely, with the result that this has become an almost classic problem in physics.

Numerous investigators have represented their data in equation form, the most successful of which was proposed by Simon and Glatzel.[6] This equation may be written in the following form:

$$(P - P_0)/a = (T/T_0)^c - 1 , \tag{1}$$

where T_0 and P_0 are the coordinates of the triple point of the phase in question, and a and c are constants that are substance dependent. For most substances discussed here, P is on the order of thousands of bars and P_0 is on the order of millimeters of mercury, and hence, will be neglected.

Unfortunately, when one starts to evaluate a and c for a given substance for some given experimental data, he is faced with a formidable task, for the equations are transcendental and a nuisance to solve. The additional requirement that the numbers a and c represent a best fit only complicates the arithmetic. Accordingly, until quite recently, few investigators represented their data in this form.

Anticipating a need for fitting a number of sets of experimental data to the Simon equation, the problem was programmed for an IBM 650 computer. Once the program was working, it was decided to re-examine the literature concerning melting curves and fit the Simon equation to those substances for which sufficient experimental data were available.

The object is to minimize the quantity

$$S = \sum [P - P_0 - ax_i]^2 , \quad x_i = (T_i/T_0)^c - 1 \tag{2}$$

by variation of a and c, where the sum extends over all experimental points. For any given c, the value of a which will minimize S is given by

$$a = \sum (P_i - P_0)x_i/\sum x_i^2 . \tag{3}$$

This suggested that c could be artificially varied, a computed, and then S computed. The next step was to guess again at c, and repeat the process until c is known to enough places. After being within 1 of the correct value, the successive changes in c were halved every time. By an examination of three previous values of S which had been computed, it was possible to find the direction of change needed in c, and thus, cut the number of steps to a reasonable figure. When this problem was programmed, the range of accuracy for the values of a and c was unknown, so c was calculated to six places; then the values were rounded to the number of significant figures.

Since this program was to be applied to a large number of substances run by different investigators,

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it was decided not to weight the measurements. Thus, all measurements have equal weight. A computation of the errors in a and c, is given in Appendix I. For most of these substances, the error in the determination of the pressure far outweighs the errors in the temperature determination, so the temperatures were assumed to be free from error. This assumption is not satisfied in some of the modern experiments, and is discussed below.

The values of the parameter T_0 were taken in most cases from the original investigator, and thus, no attempt was made to evaluate them by least-squares analysis, primarily due to the remarkable insensitivity of S to the values of T_0. The exceptions are those substances which were reasonably impure. There are few of these which have not been rerun. For these substances values of T_0 were taken from the International Critical Tables[7].

In quite a few cases it was not possible to determine the Simon equation constants from the published data. This occurs when this data falls too close to a perfectly straight line. Substances for which this occurred were run through a secondary program which computed the linear least-squares fit and the uncertainty of the slope. It is often possible to fit a second-degree equation to data which will not suffice to determine the Simon constants. Since c appears as an exponent, data for its determination must be either more accurate or more extensive than that which is sufficient to determine both constants in a second-degree expression. When the uncertainty in c approaches its value, the linear fit is used for simplicity.

The melting data are collected in three tables. The normal substances are given in Table I, the abnormal substances in Table Ia, and those substances for which only occasional bits of information are known are listed in Table II, which is incomplete by its very nature.

The columns in the tables are mostly self-explanatory. In Tables I and Ia occasional parentheses are placed about the standard deviations. This signifies that these numbers were given by the original authors, and thus might be on a somewhat different basis than the others. The places where no Simon constants are given and instead "$A =$," are those substances for which the Simon constants cannot be evaluated from the given data, and A represents the slope of the melting curve, measured in bars/°K. The column labeled "fit" is the value of $[S_0/(N-1)]^{1/2}$, where S_0 is the minimum value of S.

Quite a number of substances have been determined by several investigators. For this situation, one must either include all of the data, or exercise some criteria to eliminate some data. The latter course has been followed. The numbers therefore represent the "best" values of these parameters.

Any operation of this nature depends to a certain extent upon personal judgment of the person doing the operation, and thus is, to an extent, open to question. Several criteria are used. Higher purity samples are to be preferred, accuracy of temperature and pressure measurement, etc. All other things being equal, the larger the pressure range, the better the values, but all other things are rarely equal.

The work of Tammann, for instance, is open to several objections, chief of which are the facts that his pressure guages were calibrated at the factories where they were constructed, the samples were usually somewhat impure, and the method was not the best. The work of Deffet, on the other hand, is characterized by very pure samples and very careful measurements of pressure and temperature, but an insufficient pressure range. Other investigators vary somewhat in their characteristics. Some attempts were made to combine the data from various authors, but this resulted in no over-all improvement of the constants, and so was abandoned.

This selection of material leads to several oddities in the table. Occasionally the work which appeared best was not to the highest pressure. In this case there appears in the $P_{\max}$ column two numbers, one of which is in parenthesis. This latter is the highest pressure to which the substance has been studied. In case a range is shown, P_0 is the lowest number of this range.

In the references, there are two divisions. The first is that from which the data were taken, the second is to other investigations. The aim has been to keep this second column rather complete. No great effort has been expended to find all references for work under 1000 bars or for work earlier than 1900. Any other omissions are pure oversight. The body of references to Tables I and Ia, are alphabetically arranged from number 8 to 121, and to Table II, from 122 to 131. No attempt has been made to include discussion papers where the various data are discussed by various authors. Hamann's listing[132] is largely superceded by this paper. One could well consult Bridgman's review article,[7] as well as a very recent review by Bundy and Strong[133] in which several errors appearing in former publications are rectified.

Somewhat beyond the scope of this paper are the numerous investigations of the melting curves of He^4 and He^3 in the immediate vicinity of 0°K. Here

TABLE I. Normal melting curves

Substance	T_0 (°K)	a (bars)	$\sigma(a)$ (bars)	c (A bars/°C)	$\sigma(c)$	Fit (bars)	$P_{\max}$ (kbars)	Reference	Other references
Aluminum^{a,b}	933.3			A = 156			18 (50)	57	
Argon	83.812	2114	(4)	1.593	(0.0015)	0.1	1.5 (18)	82	14, 25, 26, 41, 76a 98
Bismuth VI^{a,c}	558	6600	1500	11.1	1.7	412	42.6–50(70)	72	32, 89a
Bismuth VII^{a,c}	462	6600	2200	6.2	1.3	1700	27.2–42.6	72	32, 89a
Cadmium^{a}	594.1	45 000	11 000	2.4	0.4	2800	50	72	37, 68
Cesium	302.9	2674	82	4.49	0.09	13	4 (50)	24	73
Copper^{a,b}	1356.2			A = 213			18	57	
Gallium II	276			A = 437			11.7–30	67	
Gallium III	318	50 000	2000	2.4	0.1	750	30–70	67	
Helium, He^3 II	3.252	117.60	0.12	1.5178	0.00047	0	0.14346–3	85	
Helium, He^4	2.046	50.96	0.11	1.5602	0.00087	1	0.03923–3	85	63
Hydrogen, H_2	14.155	274.22	...	1.744070	...	5.86	3.6 (10)	86	38, 60, 69, 70, 71 85, 98
Hydrogen, D_2	18.811	429.67	...	1.787213	...	4.11	3.5	86	38, 40, 85
Hydrogen, T_2	20.681	529.94	...	1.764179	...	2.84	3	86	
Hydrogen, HD	16.6	259.6	34.2	2.23	0.26	0	0.09	16	
Indium^{d}	429.76	35 800	400	2.30	0.23	51	10 (50)	12	54, 67
Iron^{a,e}	1805	1 070 000	(170 000)?	1.76	(0.2)?	...	80	34	
Krypton	115.745	2376	(4)	1.6169	(0.0015)	0	1.5 (12)	82	41, 76a, 99
Lead^{a}	600.2	32 300	810	2.405	0.046	85	33 (50)	35	12, 68
Lithium^{a}	453.7	9000	760	14.8	0.6	6600	50	89	23, 91
Magnesium^{a}	923	6400	2000	5.8	1.0	5500	50	72	
Mercury	234.29	38 215	817	1.177	0.023	6	10 (20)	120	17, 84, 104, 121
Neon	24.617	1037.53	...	1.599916	...	4.82	3.4	85	98
Nickel^{a,e}	1726	1 020 000	(31 000)?	2.2	...	...	80	34	
Nitrogen	63.1604	1606.56	(1.5)	1.79100	(0.0011)	1.75	3 (10)	85	14, 25, 26, 42, 98, 117
Oxygen	54.383	2732.95	...	1.742594	...	5.00	3	85	78
Phosphorus (White)	317.4	5525	56	1.92	0.02	5	6	19	64, 80, 102, 106
Platinum^{a,e}	2046	1 020 000	(400 000)	2.0	...	...	80	34	
Potassium	335.7	4270	74	4.44	0.04	18	12 (50)	19	88, 90
Rhodium^{a,e}	2253	500 000	...	1.30	...	...	80	34	
Rubidium	311.9	3951	20	3.74	0.02	6	6 (90)	24	33, 89
Silver^{a}	1234	9000	3000	7.6	1.1	1400	50	72	
Sodium	370.78	11 971	123	3.533	0.028	13	12 (50)	19	89, 91, 104
Selenium	495.5	11 700	700	2.04	0.1	44	10	11	
Sulfur, *L*-mono	387.2	2795	114	4.18	0.16	2	1.6	104	
Sulfur, *L*-Rhom	393.17	2914	194	4.31	0.22	21	0.202–3	104	
Tellurium II	716			A = 336 ± 7			30–50	72	
Thallium^{a}	576.8	64 000	...	1.38	...	...	30	37	12, 67
Tin I^{a}	505.05	57 000	16 000	3.4	0.8	1800	33.5	72	11, 12, 35, 54, 68
Tin II^{a}	591	14 700	2900	5.2	0.5	1700	33.5–80	54	72
Xenon^{f}	161.364	2610	(4)	1.5892	(0.0015)	0	(0.2)–1.5 (6)	82	41, 76a, 99
Zinc^{a}	692.7	60 000	11 000	2.4	0.4	1700	50	72	37, 108
				COMPOUNDS					
Acetamide I	354.7	3330	260	7.5	0.4	31	5	22	74
II	400.2	843	≈10	4.62	≈0.05	13	5.39–11	22	
unstable	342.6	100	5	13.9	0.4	0	3	74	
Acetic Acid I	289.84	2400	77	4.89	0.12	4	2	22	45, 47, 103, 107
II^{g}	327.3	5740	110	3.45	0.04	19	1.96–12	22	
Acetonitrile	229.3	5250	270	2.06	0.08	20	10	115	

Acetophenone	292.9	3160	140	3.7	0.1	10	3	114	46
Aminocrotonate, ethyl									
stable	307.2	2900	250	5.7	0.4	12	3	74	
unstable	293.1	2400	460	5.87	0.08	3	3	74	
Ammonia[b]	195.30	5270	180	4.3	0.1	10	3	116	
t-amyl alcohol	264.61	8900	590	1.35	0.09	0	1	45	
Anethole	295.7	4930	90	2.80	0.04	10	3	15	
Aniline	266.8	5352	34	2.339	0.009	11	12	19	45, 114
Benzylaniline	310.2	4500	100	2.81	0.06	14	3	15	
Dimethylaniline	274.7	4500	450	2.2	0.2	9	2	100	45
p-nitroanisole	325.7	4700	200	2.8	0.1	8	3	94	93
p-azophenol ethyl carbonate[h]	369.2			A = 34.7 ± 0.1			1	97	
p-azoxyanisole[h]	391.0			A = 30.8 ± 0.2			3	96	
p-azoxybenzoate, ethyl[h]	386.2			A = 40.7 ± 1.3			1	97	
p-azoxyphenetol[h]	401.65			A = 27.0 ± 0.2			0.3	64	
p-azoxyphenol, ethyl carbonate[h]	375.0			A = 39.1 ± 0.1			1	94	
Benzene	278.8	3600	80	2.60	0.04	12	6 (12)	115	19, 30, 45, 48, 49, 50, 64, 75, 93, 102, 106, 115, 118
Bromobenzene	242.1	4800	40	2.46	0.01	17	12	20	47, 15
p-dibromobenzene	360.5	3600	480	2.6	0.3	2	1	47	
Chlorobenzene I	227.7	4980	30	2.42	0.01	12	12	20	30
II[g]	303.2	10 300	90	1.83	0.01	7	9.81–25	30	
p-dichlorobenzene	326.31	3200	1300	2.8	1.1	6	1	47	15
Nitrobenzene	278.8	6100	100	1.93	0.02	24	12	19	45, 76, 102, 115
Benzoic anhydride	316.2	7250	70	1.65	0.02	1.5	3	51	
Methyl benzoate	261.06			A = 49.6 ± 0.3			1	45	
Benzonitrile	260.0	10 800	800	1.18	0.08	1	1 (12)	45	115
Benzophenone	320.93	4720	20	2.350	0.007	4	12	20	45, 64, 102
Dibenzyl	324.5	2700	360	3.3	0.4	7	1.5	47	75
Benzyl alcohol	257.9			A = 65.0 ± 0.2			1	47	
Betol	368.2	1770	160	5.6	0.4	26	3	51	
Monobromoacetic acid III[g]	328.0			A = 54.2 ± 1.3			2.3	56	
Bromoform	280.94	5340	70	2.05	0.02	20	11	20	
2-butanol–2–methyl	264.8	693	190	12.8	1.6	170	3	102	103, 106
n-butyl alcohol	183.4	5160	140	2.40	0.03	130	35	30	
t-butyl alcohol	298.7	1290	150	5.6	0.64	36	3	102	45, 104
n-butyric acid	267.66			A = 52.29 ± 0.08			1	45	
Camphor	449			A = 7.855 ± 0.004			0.3	64	
Caproic acid	289.46			A = 52.984 ± 0.003			1	45	
Caprylic acid	289.46			A = 48.186 ± 0.003			1	45	
Carbon tetrabromide	363.3			A = 27 ± 6 (impure)			0.1	119	
Carbon tetrachloride[i]	250.6	2919	30	2.12	0.01	14	9	19	9, 45, 102
Carbon monoxide	68.146			A = 45.27 ± 0.09			0.250	43	117
Carbon dioxide	216.56	4000	40	2.60	0.01	19	12	19	83, 103, 112
Carbon disulfide	161.6	8250	220	1.50	0.02	120	35	30	113
Carbonyl sulfide	134.31			A = 76.5 ± 0.2			0.013	41	
Monochloroacetic acid	335.69	4900	1400	3.95	0.72	73	9	19	64, 74, 114
unstable	334.3	2000	300	7.47	0.9	18	1.8	74	
Dichloroacetic acid[g]	388.4			A = 46 ± 1			2.2	56	
Cesium chloride II	933	8400	(600)	2.3	(0.1)	...	0.95–25	39	
Cetyl alcohol	322.26	5200	470	2.6	0.2	2	1	46	
iodide	295.6			A = 54.6 ± 0.1			1	46	
unstable	294.31	9350	1300	1.9	0.3	1.5	1	46	

Table I. (*Continued*)

Substance	T_0 (°K)	a (bars)	$\sigma(a)$ (bars)	c (A bars/°C)	$\sigma(c)$	Fit (bars)	$P_{\max}$ (kbars)	Reference	Other references
Cholesterol acetate[h]	387.5			$A = 31.90 \pm 0.09$			1	97	
benzoate[h]	419.2			$A = 21.4 \pm 0.7$			0.3	64	
butyrate[h]	371.8			$A = 21.7 \pm 3.5$			1	97	
caproate[h]	362.2			$A = 27.1 \pm 0.2$			1	97	
chloride[h]	370.0			$A = 24.19 \pm 0.04$			1	97	
ethyl carbonate[h]	356.4			$A = 29.22 \pm 0.02$			1	97	
formate[h]	270.4			$A = 29.09 \pm 0.2$			1	97	
methyl carbonate[h]	387.2			$A = 30.56 \pm 0.02$			1	97	
propionate[h]	369.1			$A = 26.56 \pm 0.07$			1	97	
propyl carbonate[h]	372.2			$A = 32.52 \pm 0.02$			1	97	
valerianate[h]	364.8			$A = 26.31 \pm 0.06$			1	97	
Chloroform	209.7	8330	230	1.52	0.02	70	25	30	19
o-cresol I	303.56	2700	370	6.2	0.75	4	1 (8)	47	19, 114
II	376.4	9060	660	2.8	0.2	25	6.1–12	19	
m-cresol	285.06	17 900	...	1.16	...	...	1	47	45
p-cresol	307.0	7000	440	1.9	0.1	8	3	114	
Crotonic acid	344			$A = 26.82 \pm 0.08$			0.3	64	
Cyclobutanone	222.2	4550	800	2.00	0.3	21	4.5	115	
Cyclohexane	279.71	3640	175	1.42	0.06	2	1	45	30[k]
methyl[b]	146.8	9600	...	2.15	...	0	19	30	
Cyclohexanol	298.61			$A = 24.5 \pm 0.1$			1	47	87
Methylcyclopentanol	308.76			$A = 54.53 \pm 0.05$			1	46	
1, 4-Dioxane	284.5	7300	900	3.3	0.3	40	6	76	46
unstable	273.05			$A = 32.2$			1	46	
Dodecane	263.65	3550	90	3.05	0.05	21	8	88	
Dotriacontane	343.16			$A = 43.0 \pm 0.1$			1	46	
Enanthic acid	265.66			$A = 54.73 \pm 0.05$			1	45	
Ethane[i]	90.35			$A = 61.4 \pm 0.2$			0.04	41	
Pentachloroethane	244.2			$A = 44.334 \pm 0.0003$			1	45	
Ethyl alcohol	155.9	10 600	180	1.61	0.015	73	35	30	
Ethyl acetate	189.6	7600	5200	2.2	0.8	1500	30	30	
Ethyl bromide	154.2	5400	300	2.27	0.07	200	30	30	
Ethyl ether	157.2			$A = 73.2$			3	113	
2,2-Dichloroethyl sulfide	286.7	7280	60	2.66	0.02	1	2	8	
Ethyl stearate	306.6			$A = 46.35 \pm 0.01$			1	47	
unstable	304.06	4200	950	3.24	0.7	6	1	47	
Ethylene[j]	103.97			$A = 70 \pm 2$			0.01	41	
bromide	283.11			$A = 39.541 \pm .005$			1	45	103
chloride	239.7	7400	560	1.65	0.1	25	5.5	115	
Erucic acid	306.7	4600	130	3.10	0.07	5	3	114	
Erythritol	399.2	4270	255	11.3	0.55	11	3	51	
Fenchyl alcohol	314.7			$A = 42.0 \pm 0.1$			1	47	
Formanilide	320.7	2980	140	4.9	0.2	11	3	114	
Formamide	275.71	10 700	3600	2.7	0.9	2	1	45	
Formic acid	281.6	4100	490	5.2	0.5	23	3	114	45
Guaiacol	301.2	4100	140	3.9	0.1	21	3	51	
Indium antimonide II	608			$A = 437$			19.4–50	66	
Hydrocyanic acid	259.2	3080	170	3.6	0.15	12	3	103	
Lauric acid	321.2	3240	140	4.0	0.1	31	3	114	
Lithium chloride	878	14 500	(1000)	2.5	(0.1)	...	25	39	
Menthol	315.7	2650	150	4.6	0.2	14	3	15	62, 64
unstable	308.7			$A = 41.2 \pm 0.2$			0.3	64	
Methane, CH_4[j]	90.667			$A = 36.629 \pm 0.00007$			0.115 (3)	41	99
CH_3D[j]	90.417			$A = 38.41 \pm 0.02$			0.077	41	
CD_4[j]	89.777			$A = 39.179 \pm 0.0003$			0.17	41	

Nitromethane	244.6			$A = 71.45 \pm 0.03$			1	45	
Diphenylmethane	300.2	900	170	5.5	0.6	71	3	15	
Triphenylmethane	365.7	2670	130	3.6	0.1	12	3	51	
Methyl alcohol	175.4			$A = 163$			3	113	
siloxanes dimer	205.2	3808	80	1.67	0.03	7	4	31	
trimer	189.2	4550	360	1.8	0.1	41	6	31	
tetramer	197.2	4400	30	1.621	0.008	3	5	31	
Methylisothiocyanate	308.82			$A = 39.1 \pm 0.1$			1.7	103	
Methylene chloride	176.5	10 590	570	1.495	0.05	183	30	30	
iodide	279.26			$A = 53.07 \pm 0.02$			1	46	107
unstable II	278.76			$A = 53.5 \pm 0.2$			1	46	107
III	287.16			$A = 44 \pm 1$			1	46	107
Myristic acid	331.2	3080	160	4.2	0.2	12	3	114	
Napthalene	353.17	3600	100	2.49	0.06	18	0.6	48	13, 44, 64, 103, 106
, 1-bromo	279.26			$A = 36.34 \pm 0.04$			1	47	
, 1-nitro	332			$A = 230$ (impure)			3.5	62	44, 64
1-Napthylamine	323.2			$A = 203$			0.3	64	44, 50, 81
1-Naphthol	369.2	7600	180	1.98	0.02	5	3	79	
Nitric oxide	109.487			$A = 82.29 \pm 0.26$			0.075	42	
n-nonane I	219.7	10 300	. . .	1.60	. . .	. . .	5	88	
II^g	288.71	11 650	. . .	2.53	. . .	. . .	67.9	88	
n-octadecane	300.95	3450	26	3.39	0.02	4	6	88	
Methyl oxalate	327.40	6760	40	2.131	0.008	4	8	20	
Palmitic acid	337.2	9560	60	1.70	0.01	0	1.8	114	62
n-pentadecane^g I	283.1	2700	300	3.3	0.3	. . .	1.4	88	
II	333.15	4600	700	4.2	0.5	71	2.735–9	88	
Phenol I	314.03	2670	140	8.0	0.3	5	2	21	45, 64, 93, 108, 110
II	337.2	6600	190	2.54	0.05	11	2.085–12	21	93, 108, 110
, *m*-bromonitro	326.8			$A = 42.72 \pm 0.02$			2.5	92	
, *m*-chloronitro	317.7	7700	1400	1.7	0.3	20	2	92	
o- nitrophenol	319.2	10 300	900	1.4	0.1	10	4	53	62
m-	368.9	9300	1200	2.0	0.2	9	3	53	
p-	385.6	4700	130	3.01	0.07	17	4	53	20
Diphenylamine	327.2	4750	90	2.46	0.03	17	8	19	15, 44, 62, 81, 93, 94, 114
Phosphine^j	139.4	330	160	15	7	0	0.025	41	
o-phosphoric acid	315.5			$A = 123$			3	114	
Phosphonium chloride	299.2	3700	100	2.67	0.05	7.6	3	114	
Phthalide	346.2	5650	100	2.08	0.03	2	3	74	
Piperidine	262.06			$A = 57.8 \pm 0.2$			1	45	
Potassium chloride I	1043	6900	(700)	5.7	(0.05)	. . .	30	39	
II	1315	12 100	. . .	4	. . .	. . .	18.95–30	39	
— thiocyanate	444.4			$A = 45.81$			1.5	21	
Propionic acid	252.4	3300	800	3.4	0.7	7	1	45	22^k
1,2-Dibromopropionic									
acid stable	337.2			$A = 52 \pm 2$			1	119	
unstable	323.2			$A = 53 \pm 2$			1	119	
n-propyl bromide	163.2	7350	100	1.74	0.01	90	40	30	
Resorcinol	383.2	3100	180	7.9	0.3	12	3	52	
Rubidium chloride I	990.5	6600	(700)	6	(0.3)	. . .	8	39	
II	1127	7200	(1000)	4	(0.3)	. . .	7.8–30	39	
Salol	314.86	7600	300	1.54	0.07	0	1	46	51
unstable I	312.0			$A = 38.2 \pm 0.1$			1	46	
unstable IV	286.1			$A = 64 \pm 3$			1	46	
Silicon tetrachloride^b	205	4620	30	1.420	0.005	9	12	20	
Silver nitrate	485			$A = 110$			15	89b	
Sodium bromide	1014	12 200	(500)	2.9	(0.1)	. . .	20	39	
chloride	1073.5	16 700	(900)	2.7	(0.1)	. . .	20	39	
fluoride	1265	14 300	(3000)	5.5	(1)	. . .	12	39	

TABLE I. (*Continued*)

Substance	T_0 (°K)	a (bars)	$\sigma(a)$ (bars)	c (A bars/°C)	$\sigma(c)$	Fit (bars)	$P_{\max}$ (kbars)	Reference	Other references
Sodium iodide	928	10 100	(400)	2.8	(0.1)	...	30	39	
tungstate	695.5			$A = 46 \pm 1$			1	59	
Stearic acid	331.53			$A = 40.3 \pm 0.1$			0.3	64	62
Succinotrile	330.1			$A = 49.995 \pm 0.02$			1	47	
n-tetracosane I	323.5	4500	...	2.84	...	...	0.4	88	
II	352.59	4240	270	3.87	0.19	9	1.27–45	88	
Thiophene	234.6	1300	1000	3.3	0.2	18	5	115	
Thymol	324.7	2090	170	6.8	0.4	22	3	15	64
o- toluidine,	257.06			$A = 53.2 \pm 0.2$			1	46	
unstable	248.7			$A = 59.72 \pm 0.06$				45	
p-	316.8	6200	300	2.00	0.08	44	8	20	44, 45, 50, 62, 64, 74, 75, 81, 93
Bromotoluene	311.2	4000	≈100	2.50	≈0.04	4	3	15	
Chlorotoluene	281.0	4075	120	2.48	0.06	6	3	15	
Iodotoluene	308.2	4120	100	2.37	0.05	15	3	15	
o- nitrotoluene,	269.99	8740	670	1.5	0.1	0	1 (6)	46	76
unstable	263.89	4140	970	3.0	0.6	5	1	46	
m-	289.21			$A = 40.28 \pm 0.05$			1	45	
p-	324.81	4300	600	2.6	0.3	4	1	45	
n-tridecane[g] I	283.1	2500	...	4.57	...	...	1	88	
II	310.93	7970	100	2.62	0.03	2	2.43–7	88	
Urethan I	321.06	2000	30	1.4	0.2	2	2	21	93, 94, 75
II	339.4	1900	400	22.2	3.9	19	2.35–4.23	21	93
III	350.0	10 000	300	2.77	0.07	18	4.23–12	21	
Valeric acid	238.7			$A = 61.6 \pm 0.1$			1	45	
Veratrole	295.7			$A = 51.6 \pm 0.1$			1 (3)	47	15
unstable	294.1			$A = 55.66 \pm 0.07$			0.8	47	
Water, H_2O III	251.2	620	90	60	5	14	2.115–3.5	18	105, 109, 110, 111
V	256.2	4100	1000	8.1	1.5	32	3.53–6.38	18	
VI	273.32	7070	180	4.46	0.07	66	6.38–22.4	18, 29	30
VII	354.8	12 980	190	3.11	0.03	27	22.4–40 (20a)	29	30, 89c
D_2O III	254.41	1610	110	36	1.9	6	2.245–3.555	28	
IV	255.26	4160	80	6.4	0.1	0	4–5.5	28	
V	258.86	4480	80	7.6	0.1	3	3.555–6.405	28	
VI[g]	263.15	1400	400	11.2	2.0	104	4.956–8.5	28	
o- xylene,	248.2			$A = 42.49 \pm 0.04$			1	45	101
m-	227.7			$A = 48.86 \pm 0.03$			2.7	101	
p-	286.51	4640	190	1.76	0.07	0	1	45	47, 101

[a] Thermocouple corrections lacking.

[b] T_0 from *American Institute of Physics Handbook*, edited by D. E. Gray (McGraw-Hill Book Company, Inc., New York, 1957).

[c] Still provisional.

[d] Data include thermocouple corrections.

[e] Pressure scale adjusted from original publications.

[f] The deviations below 200 bars lie outside the experimental error and the points below 200 bars may be represented by a different set of constants. The original publication should be consulted for details.

[g] T_0 not triple point.

[h] Liquid crystal transition also run.

[i] Transition overlooked within P range.

[j] Some thermometer errors not corrected.

[k] The phase transition which is designated as melting in this paper is actually a I–II solid–solid transition.

TABLE Ia. Falling melting curves.

Substance	T_0 (°K)	a (bars)	$\sigma(a)$ (bars)	c (A bars/°C)	$\sigma(c)$	Fit (bars)	$P_{\max}$ (kbars)	Reference	Other references
Antimony	903.7	−29 400	1000	60	4	450	26	37	
	903.7	−91 000	26 000	17	7	4200	50	73	
Bismuth I	544.2	−27 250	280	5.60	0.07	17	12 (18)	20	12, 27, 36, 68, 89a, 108, 110, 111
Cesium II	?	?	?	7.7	1 (see text)			73	
Gallium I	303.01	−57 500	4800	2.5	0.2	50	12	23	27, 47, 95, 96
Germanium	1213			$A = -263$			50 (100)	65	61
Silicon[a]	1693			$A = -172$			40	67	
				COMPOUNDS					
Aluminum antimonide[a]	1333			$A = -145$			40	67	
Cadmium telluride I	1318			$A = -50$			13	65	
II	1041	−3400	2000	16	1.4	480	13.1–50	65	
Copper chloride (ous)	703	−55 000	2500	11	0.8	1210	50	65	
Gallium antimonide	973			$A = -200$			50	65	
Gallium arsenide	1411			$A = -294$			40	67	
Indium arsenide	1213			$A = -233$			50	65	
Indium antimonide I	1298			$A = -100$			20	66	55
Indium phosphide	1333			$A = -344$			40	67	
Potassium tetrasilicate	1038			$A = -166$			3	58	
Water, H_2O I	273.15	−3952	77	9.0	0.2	4	2	18	10, 52, 25, 77, 103, 105, 110
D_2O I	276.97	−4596	100	7.75	0.3	19	2	28	

[a] Still provisional

the Simon equation does not apply and many interesting phenomena are encountered. A fair cross section of the work along these lines, as well as earlier references, may be found in some recent articles.[134–138]

TABLE II. Substances for which fragmentary information is available.

Substance	Reference
Acetone	19, 122
Ammonium nitrate	123
Diethylamine	103
i-amyl decane	125
n-amyl ether	30, 125, 128
Diethylaniline	125
Antimony tri-iodide	20
2, 2 Dimethyl butane	126
2, 3 Dimethyl butane	126
Carbamide	22
Carbon	131, 131a
Cineole	125
Tri-o-cresyl phosphate	127
n-decane	128
Ethylene glycol	127
n-heptane	128
n-hexadecane	128
n-hexane	125, 126
Mesitylene	113, 128
Methyl alcohol	30
Methyl oleate	127
Tetrahydronapthalene	128, 130
i-octane	127
n-octane	128
Oleic acid	125
Phosphorus (black)	129
Styrene	128
Toluene	124

Another area of omission is the recent work on melting of substances of geophysical interest. The transition is quite sluggish for these substances, and this, coupled with the necessarily high temperatures reduces the attainable accuracy. There are a number of recent papers in which these melting relations are discussed.[139–143]

One should also mention the work of Jencel and Rinkens[144] on various molecular weight polyesters. These substances do not seem to be well enough characterized to include.

The numbers after Bridgman's papers correspond to the list of his publications which is given in his book.[145]

COMMENTS UPON INDIVIDUAL SUBSTANCES

Bismuth. The various polymorphic transitions of bismuth have been investigated essentially four times. The first of these was by Bridgman. His investigations did not actually include Bi II, but volume measurements on the *L* I and the *I* II transitions in the neighborhood gave a normal slope for this phase. Since then there have been three investigations, two of which have shown a negative slope. Both of these investigations have been with superpressure, quasi-hydrostatic-pressure apparatus. The total change across the region of stability of Bi II is small, being only 2–7°K. Butuzov *et al.*[36] directly determine the melting curve of Bi II and obtained a positive value, the total change in temperature being 3 to 4 times higher than their possible experimental error. Thus, it appears that the actual slope is small, but positive. It is not inconceivable that the shear present in the superpressure apparatus depresses this transition somewhat, thus making it even more difficult to observe the rise in temperature.

[*Note added in proof.* In the recent experiments of Vereshchagin and co-workers[89a] this phase was detected, but its melting temperature was assumed constant and used for calibration purposes.]

Bi I is a phase for which the agreement between the superpressure experiments and the hydrostatic ones is apparently poor. The simple piston-cylinder types of apparatus yield a curve which runs above that obtained in hydrostatic environments, possibly due to a systematic error of the experiment. The usual course is to raise the pressure, let everything settle down, and then heat until melting is detected. Since Bi I contracts upon melting, this means that the pressure drops abruptly on the sample, and this may be sufficiently supported by the solid medium to give appreciable errors. The volume change upon melting increases with increasing pressure, which would tend to make the errors larger at higher pressures. Some further work could clear up this point.

[*Note added in proof.* In the more exotic types of superpressure apparatus, the curve runs below the hydrostatic one and has drastically incorrect curvature. This would almost certainly be due to some systematic error, which is probably a combination of the above effect plus the complex processes involved in gasket formation.]

The work of Kennedy and his co-workers[73] is still provisional at the time of writing, and thus may eventually clear up these points.

Alkali metals. The Simon equation does not fit cesium, rubidium, potassium, and possibly sodium over an extended pressure range. Cesium and rubidium have maxima in the melting curves, and potassium probably does also. Thus, the normal Simon equation does not work. It is possible to admit the possibility of a maximum by making a and c functions of either pressure or temperature.[146] The value for c for Cs II was obtained by taking increasing numbers of data points, backing away from the

II–III–*L* triple point. The value of *c* was consistently obtained, until the vicinity of the maximum was reached and the equation ceased being even a fair approximation for the curve.

Kennedy[89] and his co-workers have raised the question of the possible existence of maxima in sodium and lithium. This question must be answered experimentally at the present state of theories of melting, but it is possible to get a hint. The fits to these investigators' data over the full 50-kbar range agree rather well with Bridgman for Li and Na, but start disagreeing more with K, violently for Rb, and the equation does not fit Cs over an extended range. Therefore, this writer would be tempted to guess then neither Li nor Na will show a maximum under 100 kbar, if at all. Any further extrapolation is dangerous.

Nitrogen and argon. The number of investigations on these substances is large. The data of Mills and Grilly[85] in one case and of Michels and Prins[82] in the other have been adopted as the most recent and the most carefully run. Their papers should be consulted for analysis of agreement with other workers.

Mercury. Mercury occupies a unique place, due to the widespread use of its freezing pressure at 0°C for calibration of Manganin-wire pressure guages. The comparison of the mercury melting curves run by different investigators has led to some conclusions concerning Bridgman's pressure scale. This has been discussed by the author in a forthcoming paper.[147] Roughly, his 12 000 kg/cm² is off by a linear amount, and the melting pressure at 0°C is closer to 7716 kg/cm² than to his value of 7640. Bridgman's 12 000 scale may also be shown to be somewhat nonlinear, and the highest points are not always as good as the lower ones. This may be seen in Tables III and V, where the 12 000 kg/cm² point is clearly out of line. For all substances where the correction for the error in the mercury point is applicable, the correction is included in the value given in the tables.

TABLE III. Bismuth ($a = -29\,670$ bars; $c = 5.77$).

T (°K)	P_{exp} (bars)	P_{calc} (bars)	Error (bars)
544.2	0	0	0
540.7	991	975	16
537.0	1982	1975	7
533.2	2974	2967	7
529.2	3965	3974	− 9
525.1	4956	4972	−16
520.8	5948	5979	−31
516.4	6939	6981	−42
511.8	7930	7961	−31
507.0	8922	8951	−29
502.0	9913	9938	−25
496.8	10 904	10 915	−11
491.5	11 895	11 862	33

Tellurium I. This substance has been run recently by Kennedy and his co-workers[72] and shows a flat maximum. The scatter in the points is too great to fit a Simon equation in the portion where it might apply. The initial slope of the curve (A) is 200 bars/deg.

TABLE IV. Antimony

T (°K)	P_{exp} (bars)	P_{calc} (bars)	Error (bars)
($a = -30\,000$ bars; $c = 60$) (Ponyatovskii).			
903.7	0	0	0
902.2	2255	2792	− 537
901.2	4120	4945	− 825
899.2	7845	7639	− 206
896.2	12 307	10 973	−1334
891.2	16 769	16 692	− 77
886.7	19 514	20 005	489
880.2	23 731	23 363	− 368
874.7	25 300	25 264	− 36
($a = -91.000$ bars; $c = 17$) (Kennedy)			
903.7	0	0	0
895	5100	13 806	−8706
892	10 900	18 082	−7982
892	21 000	18 082	2918
889	27 200	22 142	5058
883	32 600	29 627	2973
876	38 200	37 290	810
870	43 800	43 310	590
868	46 300	45 130	1170
863	49 100	49 400	− 300
860	51 600	51 800	− 200
854	54 500	56 215	−1715

[*Note added in proof. Carbon.* Bundy[131a] has quite recently published a phase diagram for carbon which shows the melting curve of carbon passing through a maximum, and diamond as having a falling melting curve. No actual experiments have been carried out on the diamond part of this curve.]

CHARACTERISTICS OF THE SIMON EQUATION

The Simon equation gives a form of the melting curve which rises indefinitely with increasing pressure for constant positive *a* and *c*. From this one may not conclude that this is the eventual course of the curve. By a careful study of the way the equation extrapolates, one may conclude that the equation is valid only over a limited range of temperatures and pressures. This range is roughly an order of magnitude greater than the value of *a* given by the lower pressure fits. These arguments have become superfluous since Kennedy and his co-workers[73,89] and Bundy[34] have found maxima in the melting curves of Cs, Rb, and Te. This work has partially answered the old questions about the eventual course of the melting curve and has raised some new ones.

For all melting curves (with the single known exception of He^3 in the vicinity of 0°K) the concavity is toward the pressure axis. This means that c is by necessity greater than 1. The constant c has received considerably more attention than a. This is partially due to the fact that c is independent of the units in which pressure is measured, and thus, of any errors in calibration of the pressure measuring devices. The value of c is sensitive to nonlinear errors in the pressure scale, however.

The slope of the melting curve at T_0 is given by ac/T_0. The standard deviation of this quantity is given by: $[\sigma(a)\ c - \sigma(c)\ a]/T_0$, so that the slope is known considerably better than either a or c, as one would expect.

The application of the Simon equation to falling melting curves is apparently unique. The only discussions of this are by Voronel,[148,149] but his derivation is in error. He takes a derivative of the equation, applies the derivative where the original didn't apply, and integrates to get an equation which is different from the one he started with. Predictions based upon this treatment have not been found to hold. There is no theoretical justification for the use of a Simon equation for falling melting curves, although some of Gilvarry's work[150] may be interpreted as implying that such an equation would work.

The quality of a Simon-equation fit to a normal and to an abnormal substance may be seen by examining Tables III and V, where fits to Bridgman's data for potassium and bismuth are given. The fit is quite good, for both cases, but it should be remembered that Bridgman always smoothed his values before publication.

Table V. Potassium (a = 4266 bars; c = 4.44).

T (°K)	P_{exp} (bars)	P_{calc} (bars)	Error (bars)
335.7	0	0	0
351.9	991	993	2
365.6	1982	1907	−75
377.9	2974	2949	−25
389.0	3965	3938	−27
399.2	4956	4938	−18
408.6	5948	5942	− 6
417.3	6939	6939	0
425.7	7930	7974	44
433.3	8922	8975	53
440.2	9913	9937	24
446.8	10 904	10 907	3
452.8	11 985	11 832	−63

In Table IV the fit to antimony is given for two different investigations. Here the equation quite clearly does not fit the data.

Attempts to fit the equation to falling melting curves with a negative c led to very poor fits. The least-squares fit always yielded negative values of a. The scatter in this value from one investigator to another is considerably larger than for the normal substances.

Table VI. Effects of fitting technique.

Criterion	c	a(bars)
Potassium		
least squares	4.43	4266
sum deviations vanish	4.41	4313
?	4.53	...
Taylor's series expansion	4.38	4360
Sodium		
least squares	3.53	11 970
sum deviations vanish	3.47	12 240
?	3.56	...

PRECISION OF THE CONSTANTS

The comparison of the experimental values of the Simon-equation constants with the theoretical expressions for their values will be considered in a forthcoming paper,[151] the discussion being somewhat lengthy.

As has been previously noted, the standard deviations of the constants are somewhat higher than most previous estimates. These standard deviations only represent statistical uncertainties resulting from scatter in the original data. The values of these constants are also somewhat sensitive to the criteria of a fit. This may be seen from Table VI, where fits according to two different criteria are compared with previously published values[152] for potassium and sodium. For these substances the scatter of the data is rather small, so the constants are fairly close together. These fits are to the identical data. For many other substances, a slightly different criterion for a good fit could drastically alter the results, without seriously imparing the representation of the data by the Simon equation. The deviations between values of c are about the same as the $\sigma(c)$ given by the table for potassium, but greater than $\sigma(c)$ for sodium.

The standard deviations were calculated, as already noted, by assuming that the temperature measurements were perfect. This is never achieved in practice, so the assumption needs investigation. For most of the nonmetallic substances, the slopes of the melting curves lie between 20 and 50 bars per deg. Assuming that a Manganin guage is used, the usual sensitivity is about 0.1%. Thus accuracies on the order of 0.1° are sufficient for a large pressure range. For metals, the slopes are usually at least an order of magnitude higher, and the temperatures are materially higher, so that the error in the temperature measurement is usually considerably in excess of 0.1°. Here the assumption is definitely false.

The assumption of perfect accuracy of the temperatures is not too serious, however. As an example, consider some data of indium. The standard deviations given in Table I for this data are 4 kbars for *a* and 0.23 for *c*. If one calculates the standard deviations assuming that the temperatures are in error and the pressures perfect (a much more reasonable assumption in this case), then one obtains the values of 1.5 kbars for *a* and 0.101 for *c*. These values are distinctly smaller than the ones given by the original assumption. Consequently, in this case, one might say that the uncertainties given are generous estimates.

This illustration is a little misleading, since there are very few substances given for which the temperature errors mask the pressure errors. In an ideal case, one should weigh the errors from both causes by evaluating the various sources of errors in the two measurements. This requires a fairly intimate knowledge of the experimental arrangement, and is rarely attempted. Thus all standard deviations should, at worst, be within a factor of about 2 of the best values that could be calculated for them. Most of them are within a few percent.

It should perhaps be emphasized that the Simon equation is to be considered only as a very useful and simple interpolation equation. For many of the substances listed in Table I, the deviations of the measured values from the best fit lie outside the experimental error. These deviations show regularities, as may be seen from Tables II and III. Thus, though the equation is also useful for some theoretical discussions, it should not be considered to be an exact representation of the melting curve.

[*Note added in proof.* Perhaps one further note of caution should be emphasized. Many of the numbers given in Tables I and Ia are still more characteristic of the experiment than the substance. There are a number of substances, such as mercury and argon, where the melting curves have been very carefully run, and different investigators agree on the values of *a* and *c* to well within their experimental uncertainties. For many others the difficulties with technique are such that mild systematic errors in the experiment introduce drastic errors in the final answer.]

CONCLUSIONS

The values of the parameters in the Simon equation have been given for all substances known to the author for which sufficient data are known. Their probable precision is discussed.

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APPENDIX

The equations for calculation of the standard deviations using the notation and procedure of Deming[153] of *a* and *c* are

$$\sigma^2(a) = C_{aa}\sigma^2\ , \quad \sigma^2(c) = C_{cc}\sigma^2$$

with the following definitions:

$$C_{aa} = \frac{[cc]}{\Delta}\ , \quad C_{cc} = \frac{[aa]}{\Delta}\ , \quad \Delta = \begin{vmatrix} [aa] & [ac] \\ [ac] & [cc] \end{vmatrix}\ ,$$

where the bracketed quantities are defined by:

$$[ac] = \sum \left[\frac{(\partial F/\partial a)(\partial F/\partial c)}{L} \right], \text{etc.},$$

$$L = \frac{(\partial F/\partial P)^2}{W_P} + \frac{(\partial F/\partial T)^2}{W_T}$$

and σ is defined by

$$\sigma^2 = S/(N-2)\ .$$

Here S is given by the expression

$$S = \frac{1}{\Delta} \begin{vmatrix} [aa] & [ac] & [ao] \\ [ac] & [cc] & [co] \\ [ao] & [co] & [oc] \end{vmatrix}$$

$$= [oo] + [ao] \frac{\begin{vmatrix} [ac] & [cc] \\ [ao] & [co] \end{vmatrix}}{\Delta} - [co] \frac{\begin{vmatrix} [cc] & [ac] \\ [ao] & [co] \end{vmatrix}}{\Delta}$$

in which the last two terms are always small. Here $[oo] = \sum F^2/L$, etc.

For the case of the Simon equation,

$$F = P - ax_i\ , \quad x_i = (T/T_0)^c - 1\ .$$

The value of L is, therefore,

$$L = \frac{1}{W_P} + \left[\frac{ac}{T_0} \left(\frac{T}{T_0} \right)^{c-1} \right]^2 \frac{1}{W_T}\ ,$$

which takes the two values

$$1 \text{ for } \begin{matrix} T \text{ perfect} \\ W_P = 1 \end{matrix}\text{; and } \left[\frac{ac}{T_0}\left(\frac{T}{T_0}\right)^{c-1}\right]^2 \text{ for } \begin{matrix} P \text{ perfect} \\ W_T = 1 \end{matrix}.$$

In the following the pressures are assumed to be the source of error, so $L = 1$. Then:

$$\begin{aligned}
[cc] &= \sum a^2 (T_i/T_0)^{2c} \ln (T_i/T_0) \\
[aa] &= \sum x_i^2 \\
[ac] &= \sum a (T_i/T_0)^c x_i \ln (T_i/T_0) \\
[oo] &= \sum (P_i - ax_i)^2 \\
[oc] &= \sum (P_i - ax_i) a (T_i/T_0)^c \ln (T_i/T_0) \\
[oa] &= \sum (P_i - ax_i) x_i \,.
\end{aligned}$$

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