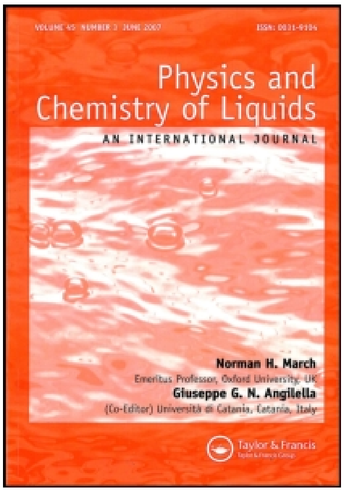

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Critical temperatures of elements from their boiling points

Y. P. Varshni[a]
[a] Department of Physics, University of Ottawa, Ottawa, Canada K1N 6N5

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Critical temperatures of elements from their boiling points

Y. P. VARSHNI*

Department of Physics, University of Ottawa, Ottawa, Canada K1N 6N5

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A linear relation between critical temperature and boiling point is proposed for elements belonging to the same group in the periodic table. The validity of the relationship is demonstrated for the alkalies and the groups 16, 17 and 18. From this the critical temperature of tellurium is predicted as 2325 K and that for polonium as 2277 K.

Keywords: Elements; Critical temperature; Boiling point

1. Introduction

The developments in space science and modern technology require knowledge of materials at high temperatures and pressures. In addition there is of course an intrinsic interest to understand the physics of various materials at high temperatures and pressures.

Experimental measurement of critical temperatures for most elements is difficult and only in recent years has an increasing amount of data become available [1]. Consequently over the years quite a few attempts have been made to estimate the critical temperatures of elements by a variety of methods. Throughout this article all temperatures will be expressed in K. Guldberg [2] connected the critical temperature (T_c) with the boiling point (T_b) with the following relation:

$$\frac{T_b}{T_c} = 0.567 \tag{1}$$

Meissner and Redding [3] proposed the following relation for organic compounds which have boiling points below 235 K:

$$T_c = 1.70T_b - 2 \tag{2}$$

In a short paragraph they state that the relation is also applicable to the few elements for which data were available at that time (i.e., 1942) except hydrogen and helium.

*Tel.: (613) 562-5800, ext. 6769. Email: ypvsj@uottawa.ca

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Gates and Thodos [4] suggested the following relation:

$$T_c = 1.4732 T_b^{1.0313} \tag{3}$$

There have been several other attempts to estimate critical temperatures of elements [5–17]. A short summary of some of these attempts may be found in [17].

2. Linear relation for different groups

In the present article we wish to show that a linear relation of the following form

$$T_c = aT_b + b \tag{4}$$

where a and b are constants, when applied to each group of the periodic table separately can give very good values for the critical temperatures of elements.

3. Results and discussion

Experimental values of the critical temperatures of elements are available only for about 34 elements, of which only 15 have accurate data. The total experimental data are shown in tables 1–3. All boiling points are from [18]. Sources for critical temperatures are given in certain cases, where none is given which are from [18]. Figure 1 shows T_c *versus* T_b for this whole data; experimental uncertainties are not shown to avoid cluttering the diagram. The solid line represents a least squares solution of equation (4)

Table 1. Experimental values of boiling points and critical temperatures for all other elements which are not included in tables 2 and 3. All temperatures are in K.

Z	Element	T_b expt.	T_c expt.	Reference
1	H	20.28	32.97	[18]
7	N	77.36	126.21	[18]
15	P	553.65	994	[18]
80	Hg	629.88	1750	[18]
23	V	3680	6396	[19]
26	Fe	3134	9250 ± 1110	[20]
			9250 ± 700	[21]
27	Co	3200	10,384 ± 830	[22]
			10,400 ± 700	[21]
30	Zn	1180	3600 ± 360	[33]
			3600 ± 500	[21, 23]
34	Se	958	1863 ± 20	[24]
42	Mo	4912	10,400 ± 267	[25]
49	In	2345	7000 ± 490	[26]
74	W	5930	13,400 ± 1400	[27]
			16,000 ± 1000	[28]
77	Ir	4701	10,335	[19]
78	Pt	4098	9285	[29]
79	Au	3129	7400 ± 1100	[30]
80	Hg	630	1753 ± 15	[31]
			1750	[32]
82	Pb	2022	5400 ± 400	[33]

and the dashed line represents equation (2). We notice that a single line is only a very approximate representation of the correlation between T_c and T_b. Further equation (2) is valid for only a few elements. Next we consider individual groups. Figure 2 shows the alkalies, figure 3 group 16 elements, figure 4 group 17 elements and figure 5 group 18 elements. In each case the solid line represents a least squares solution of equation (4) from the experimental values. The values of a and b are summarized in table 4. The experimental values of boiling points and critical temperatures of alkalies are given in table 2. It will be noticed from table 2 and figure 2 that there are considerable

Table 2. Boiling points and critical temperatures of alkalies. All temperatures are in K.

Z	Element	T_b expt.	T_c expt.	Ref.	T_c	Diff.
3	Li	1615	3344	[34]	3312	−32
			3223 ± 600	[35]	3312	89
11	Na	1156	2485 ± 15	[34]	2444	−41
			2573 ± 350	[35]	2444	−129
			2429	[1]	2444	15
19	K	1032	2198 ± 30	[34]	2210	12
			2223 ± 600	[35]	2210	−13
			2280	[32]	2210	−70
37	Rb	961	2017 ± 10	[34]	2076	59
			2093 ± 25	[35]	2076	−17
			2090	[32]	2076	−14
55	Cs	944	1924 ± 10	[34]	2044	120
			2057 ± 40	[35]	2044	−13
			2010	[32]	2044	34

Table 3. Experimental values of boiling points and critical temperatures together with the calculated values of T_c for Groups 16, 17 and 18 elements. All experimental values are from [18]. The last column shows the difference between the calculated and experimental values of T_c. All temperatures are in K. The values of a and b are given in table 4.

Z	Element	T_b expt.	T_c expt.	T_c Calcd	Difference
GROUP 16					
8	O	90.20	154.59	153.6	−1.0
16	S	717.75	1314	1317.7	3.7
34	Se	958	1766	1763.3	−2.7
52	Te	1261		2325.4	
84	Po	1235		2277.2	
GROUP 17					
9	F	85.03	144.13	141.5	−2.6
17	Cl	239.11	416.95	420.8	3.9
35	Br	331.95	588.15	589.1	1.0
53	I	457.55	819.00	816.8	− 2.2
GROUP 18					
2	He	4.22	5.19	3.5	−1.7
10	Ne	27.07	44.45	44.4	−0.1
18	Ar	87.30	150.87	152.2	1.4
36	Kr	119.93	209.41	210.7	1.2
54	Xe	165.11	289.73	291.5	1.8
86	Rn	211.45	377.15	374.5	−2.6

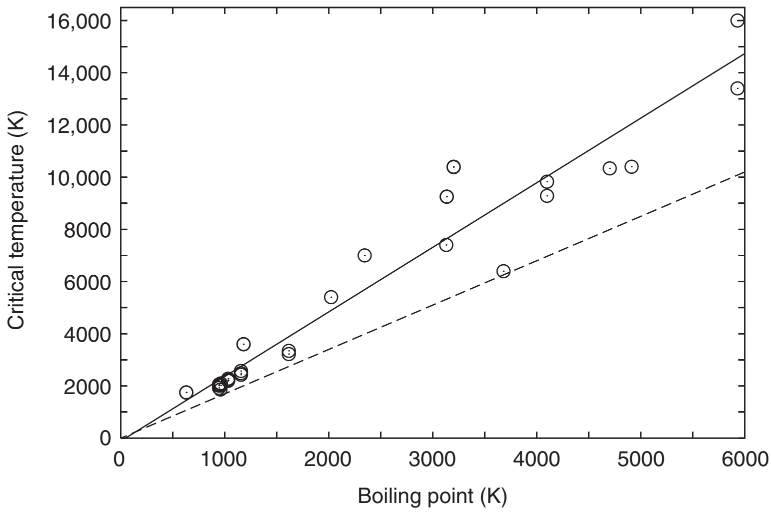

Figure 1. T_c (K) *vs.* T_b (K) for all elements for which experimental data for T_c are available. In other words the data given in tables 1 to 3. Error bars for experimental values of T_c are not shown to avoid cluttering the diagram. The solid line represents a least squares solution of equation (4) and the dashed line represents equation (2).

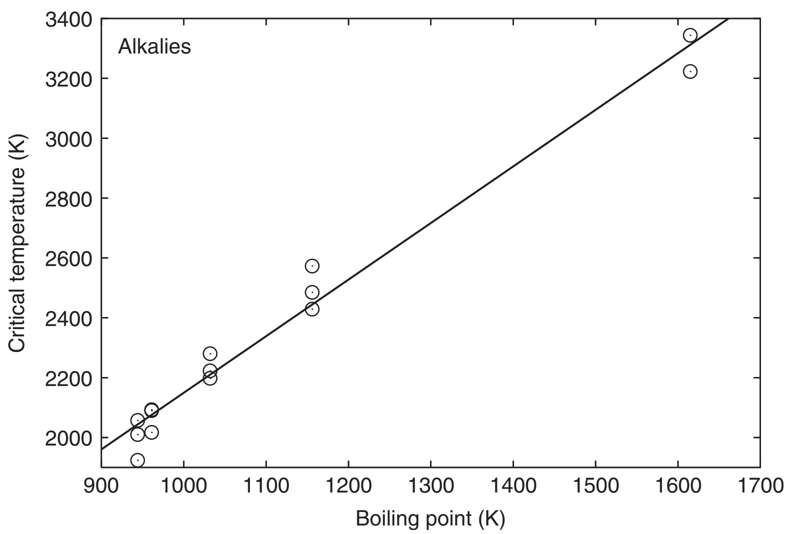

Figure 2. T_c (K) *vs.* T_b (K) for the alkalies. The solid line represents equation (4) with a and b values as given in table 4.

differences between the experimental values of T_c as reported by different workers, and there are considerable uncertainties in each of these (table 2). Allowing for these factors the straight line is a reasonable representation of the data. The differences between the experimental and calculated values T_c are usually less than the uncertainties in the experimental data.

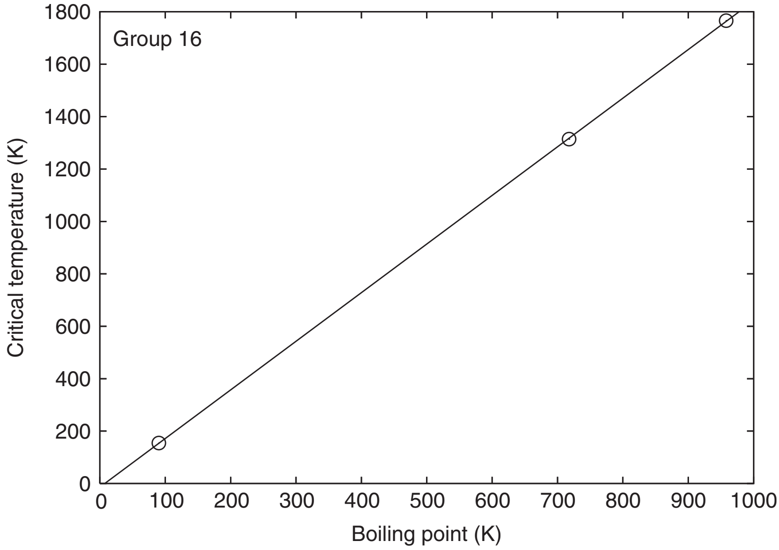

Figure 3. T_c (K) *vs.* T_b (K) for elements of group 16. The solid line represents equation (4) with *a* and *b* values as given in table 4.

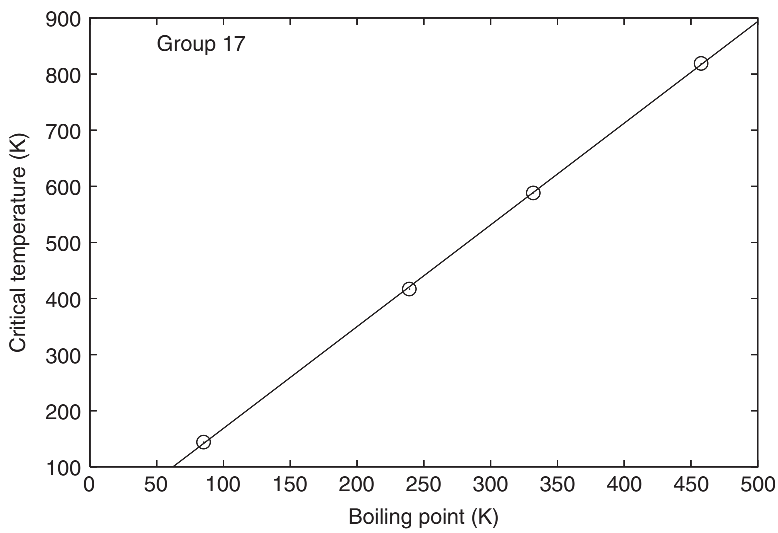

Figure 4. T_c (K) *vs.* T_b (K) for elements of group 17. The solid line represents equation (4) with *a* and *b* values as given in table 4.

The experimental values of boiling points and critical temperatures of elements of Groups 16, 17 and 18 are given in table 3. It will be noticed from figures 3, 4 and 5 and table 3 that the straight lines are in excellent agreement with the experimental values. Table 3 shows that the difference between the calculated and experimental values is within ±4. From equation (4) for Group 16 we predict the following critical temperatures: T_c for tellurium = 2325 ± 4 K, T_c for polonium = 2277 ± 4 K.

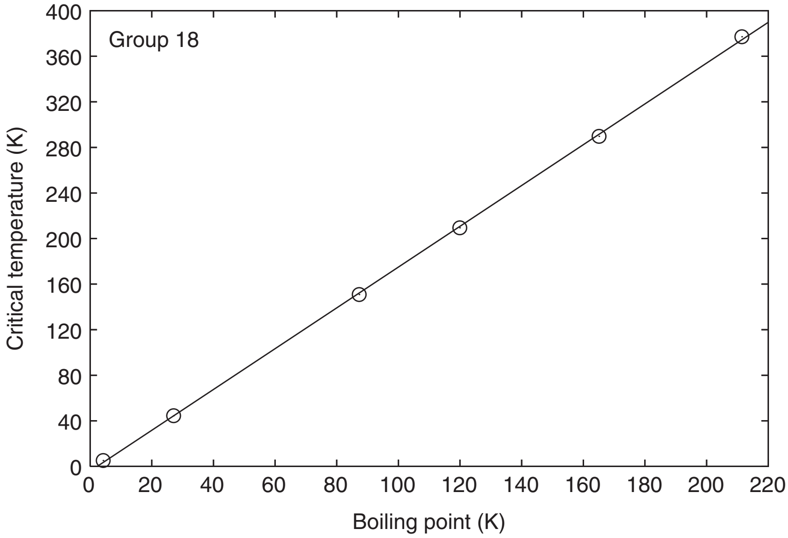

Figure 5. T_c (K) *vs.* T_b (K) for elements of group 18. The solid line represents equation (4) with a and b values as given in table 4.

Table 4. Values of the constants a and b for the alkalies and groups 16, 17 and 18.

Group	a	b (K)
Alkalies	1.8903	259.21
16	1.8545	−13.75
17	1.8126	−12.59
18	1.7904	−4.08

For checking equation (4) we need at least three points. However, this requirement is not fulfilled by any other group. A note concerning the situation about group 15 is in order. The critical temperatures of nitrogen and phosphorus are known, but arsenic sublimates and does not liquify. Critical temperatures of antimony and bismuth are not known. When boiling points of francium and astatine are measured, it would be possible to predict their critical temperatures from the relation given here.

It will be noticed from table 4 that there is a regular variation in the constants a and b as we go from Group 18 to Group 16. However, the alkalies constants do not follow this trend. At present it is unclear if it is due to uncertainties in the experimental data.

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