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PHYSICOCHEMICAL STUDIES OF SYSTEMS AND PROCESSES

Calculation of the Critical Parameters of Inorganic Compounds by the Additive Method

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Abstract—A set of 100 substances was studied to obtain data that would allow application of the additive method to calculation of critical parameters of inorganic compounds. An additive scheme that makes it possible to improve the accuracy of calculation of the critical pressure of inorganic compounds was suggested.

At present, methods of the thermodynamic similarity theory are widely used to prognosticate physicochemical properties of substances [1, 2]. In this case, the critical parameters of substances serve as input data for a calculation. Published data on critical parameters are rather scarce. Experimental determination of critical parameters involves severe difficulties. Of particular practical importance in this context is determining the critical parameters by calculation.

A possible way to calculate the critical parameters is to sum up the corresponding increments for the elements constituting the molecule of a compound. This method is attractive in that it is based on the minimum amount of information about the substance under study, which frequently does not include any data except the stoichiometric formula.

The additive method for calculation of critical parameters is widely used for prognosticating the critical parameters of organic substances [1, 3]. The potentialities of this technique, as applied to determination of the critical parameters of molecular inorganic compounds, are unknown. This is because the increments are available in the literature for less than 10 elements. These are nonmetals (C, H, O, S, N, F, Cl, Br, I), which constitute molecules of organic substances. However, data on the increments for metals contained in molecules of inorganic and organometallic substances are lacking completely.

The goals of this study were as follows: (a) to obtain missing information about the increments of metals from experimental data on critical parameters and (b) to determine, using the data obtained, the accuracy of calculation of the critical parameters by the additive method for inorganic and organometallic compounds.

The most widely used in the literature is the additive scheme suggested by Leadersen [1]. In this technique, atomic constituents (increments) of the reduced temperature at the boiling point are summed up for determining the critical temperature:

$$\theta = T_{boil}/T_{cr}, \quad (1)$$

where T_{boil} and T_{cr} are, respectively, the temperatures at the normal-boiling and critical points.

The calculational formula for determining θ for a binary compound of the AB_n type has the form

$$\theta = 0.576 + \Sigma\Delta_T - (\Sigma\Delta_T)^2, \quad (2)$$

$$\Sigma\Delta_T = \Delta_T(A) + n\Delta_T(B), \quad (3)$$

where $\Delta_T(A)$ and $\Delta_T(B)$ are the increments of the reduced boiling point θ for elements A and B, respectively; and n is the number of B atoms in compound AB_n.

The critical volume is found in the Leadersen method by the formula

$$V_{cr} = 40 + \Sigma\Delta_V. \quad (4)$$

The critical pressure (MPa) is given by

$$P_{cr} = 0.101325M/(\Sigma\Delta_P + 0.34)^2, \quad (5)$$

where M is the molecular weight of the compound.

In Eqs. (4) and (5), the sum of increments Δ_V and Δ_P is calculated in accordance with Eq. (3).

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Table 1. Increments of the critical temperature (K), critical volume, and Van der Waals constant ($cm^3\ mol^{-1}$)

Element	Δ_T	Δ_V	Δ_P	Element	Δ_T	Δ_V	Δ_P
H^{1-}	0	5	5.8	$S^{2+,\ 4+}$	0.006	47*	30
H^{1+}	–0.005	2	8.6	S^{6+}	–0.023	47*	22.8
F	0.018*	18*	11	Se^{2-}	0.032	65	35
Cl	0.017*	49*	26.4**	Se^{4+}	–0.006	55	30
Br	0.010*	70*	34	Se^{6+}	–0.028	66	31
I	0.012*	95*	45	Te^{2-}	0.016	99	43
Hg^{2+}	–0.002	33	26	Te^{4+}	0.028	74	21
B^{3+}	0.032	30	13.4	Te^{6+}	–0.006	92	41
C^{4+}	0.022	37	19.3	Cr^{6+}	0.004	80	33
Si^{4+}	0.035	81	36.5	$Mo^{5+,\ 6+}$	–0.020	83	33.6
Ge^{4+}	0.033	84	42.5	$W^{5+,\ 6+}$	–0.008	89	34.6
Sn^{4+}	0.034	110	53	Tc^{6+}	–0.036	78	34
Pb^{4+}	0.017	110	52	Re^{6+}	–0.028	82	37
Ti^{4+}	0.019	86	45	$Os^{5+,\ 6+}$	–0.040	84	37.5
V^{4+}	–0.005	92	35	Os^{8+}	–0.048	94	28
$N^{1+,\ 2+,\ 3+}$	0.008	28	19	$Ir^{5+,\ 6+}$	–0.028	92	36
P^{3+}	0.006	56	36	Pt^{6+}	–0.033	82	37
P^{5+}	0.025	80	37	$Ru^{5+,\ 6+}$	–0.037	70	33
As^{3+}	–0.012	60	36	Ru^{8+}	–0.026	90	25
Sb^{3+}	0.011	61	39	U^{6+}	–0.025	107	48
Sb^{5+}	–0.005	110	43	Np^{6+}	–0.026	102	45
Bi^{3+}	–0.012	63	31	CH_3***	0.022	68	33
O	0.020*	11*	13.4**	C_2H_5***	0.028	126	56

* Calculation by Leadersen [1].

** Calculation by Heukelom [6].

*** Increments for the CH_3 and C_2H_5 radicals were determined for organometallic compounds.

Table 2. Increments of the critical parameters of silicon, obtained for various silicon compounds

Compound	Δ_T	Δ_V	Δ_P	Compound	Δ_T	Δ_V	Δ_P
$SiCl_4$	0.026	90.0	0.529	$SiCl_2F_2$	0.025	68.0	0.564
$SiBr_4$	0.042	62.0	0.628	$SiCl_3F$	0.024	75.0	0.560
$SiHCl_3$	0.025	81.0	0.394	$SiBrCl_3$	0.036	89.0	0.610
$SiHBr_3$	0.054	75.1	0.539	$SiBr_2Cl_2$	0.032	86.0	0.643
$SiClF_3$	0.034	60.0	0.547	$SiBr_3Cl$	0.043	85.0	0.665

In the first stage, it was necessary to find the increments Δ_T, Δ_V, and Δ_P for elements-metals. For this purpose, substances with known critical parameters were chosen and Δ(A) (increment for the element-metal A) was found by an inverse calculation by Eqs. (1)–(5) from the known Δ(B) (increment for element B in compound AB_n).

The values of the critical parameters were taken from the reference book [4], with only experimental data used. The data array under study included experimental values of the boiling point and critical parameters for 100 molecular inorganic compounds, 90% of which were compounds of the AB_n type. The resulting values of the increments are listed in Table 1. For most of elements, the increments were determined for several compounds.

As an example of the scatter of increments obtained for different compounds of the same element, Table 2 lists increments of critical parameters for silicon. Use of averaged values of the increments for silicon

Table 3. Average error in calculation of the critical parameters

Data array	Average calculation error, %				Data array	Average calculation error, %			
	T_{cr}	V_{cr}	P_{cr}			T_{cr}	V_{cr}	P_{cr}	
			by Leadersen	this study				by Leadersen	this study
10*	0.9	3.5	6.9	2.1	100**	1.5	3.6	11.8	3.0

* Silicon compounds listed in Table 2.

** All the inorganic compounds considered in this study.

Table 4. Calculation of the critical parameters* of compounds with a complex stoichiometry and organometallic compounds

Compound	Reference	T_{cr}, K		V_{cr}, $cm^3\ mol^{-1}$		P_{cr}, MPa	
		found	error, %	found	error, %	found	error, %
$SiHCl_3$	[7]	479.0	–1.3	268.0	0.2	4.17	1.1
Si_2Cl_6O	[7]	578.0	–2.3	560.0	9.7	2.35	2.1
PCl_2OF	[4]	510.0	–0.1	247.0	0.1	4.79	–0.2
$Si(CH_3)_3Cl$	[8]	497.8	–0.3	365.6	2.3	3.21	–0.7
$Si(CH_3)_2Cl_2$	[8]	520.4	–1.1	349.9	1.5	3.48	–1.0
$SiCH_3Cl_3$	[9]	517.8	–1.4	339.8	–1.1	3.51	1.7
$Si(C_2H_5)_3Cl$	[10]	600.0	1.5	520.0	5.4	2.84	–3.5
$Si(C_2H_5)_2Cl_2$	[10]	595.8	0.2	455.0	3.5	3.06	0.7
$SiC_2H_5Cl_3$	[10]	560.8	–0.8	402.7	–2.2	3.33	1.1

* T_{cr}, critical temperature; V_{cr}, critical volume; and P_{cr}, critical pressure.

(Table 1) leads to calculation errors of the critical parameters of silicon compounds, listed in Table 3.

Table 3 also presents the error of the Leadersen method for a set of 100 molecular inorganic compounds. It should be noted for comparison that the accuracy of the Leadersen method (average error) for organic substances is less than 2% for the critical temperature [1], 3.2% for the critical volume [5], and 3.8% for the critical pressure [1]. Thus, the data on the critical temperature and critical volume, obtained for inorganic substances, are in a good agreement with those for organic substances.

It can be seen from Table 3 that, as applied to inorganic compounds, the Leadersen method provides a high accuracy of prognostication of the critical temperature and a satisfactory accuracy of prognostication of the critical volume.

At the same time, the calculation error is unacceptable in the case of the critical pressure. An additive scheme that allows reliable prognostication of the critical pressure of inorganic compounds was developed in this study. The essence of the additive scheme suggested is in the following.

The critical pressure was calculated from the Van der Waals constant b:

$$P_{cr} = RT_{cr}/8b. \quad (6)$$

The critical temperature in Eq. (6) was calculated by the Leadersen equations (1)–(3), and the Van der Waals constant was found using the conventional additivity rule:

$$b = \Sigma\Delta_b = \Delta_b(a) + n\Delta_b(B).$$

The increments of the Van der Waals constant, determined in the study, are listed in Table 1.

As can be seen in Table 3, the method suggested provides a significantly improved accuracy of prognostication of the critical pressure.

The increments obtained in this study make it possible to reliably prognosticate the critical parameters of molecular inorganic compounds with any stoichiometry, as well as those of organometallic compounds (Table 4).

CONCLUSIONS

(1) Data were obtained, which allow application of the additive method to calculation of the critical parameters of inorganic compounds.

(2) The accuracy of prognostication of the critical parameters was established for a set of 100 compounds.

(3) It was shown that the accuracy of data on the critical temperature and critical volume exactly coincides with that of published data for organic compounds.

(4) It was found that the additive scheme suggested makes it possible to improve the accuracy of calculation of the critical pressure for inorganic compounds.

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