Journal of Chemical and Engineering Data

Method of Extending Tables of *P*, *v*, *T* – Data for a liquid to the Region of Metastable States

Yermakov German Viktorovith., Sharipova Zemfira Asgatovna, Yankovskaya Olga Pavlovna

Institute of Thermophysics, Ural Division Russian Academy of Science,

Pervomaiskaya Str., 91, GSP-828, Ekaterinburg, 620219, Russia

E-mail: eson@ensb.pssr.ru

Experimental investigation of the equations of state of superheated liquids is connected with a number of difficulties, and the available methods of its analytical construction are too cumbersome and labour consuming to make it possible to calculate rapidly, but with a sufficient accuracy the *P*, *v*, *T* values for the metastable region [1]. Below is a procedure that allows solving this problem.

To describe *P, v* – isotherms a simple relation based on the expansion of free energy into a series in the vicinity of the spinodal has been suggested [2, 3]:

$$P = P_{sp} + l \cdot \left(v - v_{sp}\right)^3, \tag{1}$$

where P_{sp} and v_{sp} are the pressure and the specific volume on the spinodal, l is the expansion coefficient. Relation (1) gives value of the specific volumes of n-hexane, diethyl ether and argon, which do not differ by more than 0.5% from the data of reference [1] in a wide range of temperatures and pressures [2]. In this case it is assumed that the spinodal parameters are known, and the constant l is determined by the *P*, *v*, *T* – data of the saturation line or by the derivative $\left(\partial P/\partial v\right)_T$. With the use of relations of the thermodynamic similarity theory formula (1) makes it possible to

perform calculation by minimum initial information with an accuracy sufficient for most applications.

To determine the pressure on the spinodal we use generalization of the Fiirth formula in the framework of the one-parametric theory of thermodynamic similarity [4, 5].

$$\tau = 1 - \alpha^{-1} \cdot (1 - \pi) + Q(1 - \pi)^q , \tag{2}$$

$$\alpha = 8.07 - 3.983 \lg A \tag{3}$$

$$Q = 0.03795 + 0.01841 A - 0.0019 A^2 \tag{4}$$

Here $\tau = T/T_{cr}$ is the reduced temperature, $\pi = P/P_{cr}$ is the reduced pressure, $A = 100\pi_{1.6}$ is the criterion of thermodynamic similarity, q=1.2233.

The remaining constants in Equation (1) will be determined from tabulated data. We shall assume that at a given temperature the pressure of saturated vapor P_s and the specific volume of the liquid phase on the saturation line v_s, and also N values of the P, v –quantities in the stable region are known. Then for every point of the isotherm we can write:

$$a_i = \frac{P_i - P_{sp}}{P_s - P_{sp}} = \frac{(v_i - v_{sp})^3}{(v_s - v_{sp})^3} \quad (i = 1, \ldots, N) \tag{5}$$

After resolving (5) with respect to v_{sp}, summing over i and dividing by the number of points in the stable region N we shall obtain

$$v_{sp} = \frac{v_s \langle \sqrt[3]{a} \rangle - \langle v \rangle}{\langle \sqrt[3]{a} \rangle - 1} \tag{6}$$

where $\langle \sqrt[3]{a} \rangle$ and $\langle v \rangle$ are the average values of the corresponding quantities. For the coefficient l from (1) it follows:

$$l = \left(P_s - P_{sp}\right) / \left(v_s - v_{sp}\right)^3 . \tag{7}$$

Table 1 gives absolute (Δv, cm^3/g) and relative ($\Delta v/v$,%) discrepancies between the specific volumes obtained by the suggested methods and the data from the paper [1] by isotherms for n-hexane, diethyl ether, argon. Table 2 presents the values of the complex

$$\frac{\Delta v}{v} = \frac{\sqrt{\sum_1^L \left(v_p - v_T\right)^2 / L}}{v_s}, \% \tag{8}$$

characterizing the integral degree of co-ordination of the methods, for the same liquids at the same temperatures. Summation is made by all the points of the isotherm L to the depth of penetration into the metastable region described in the table by the parameter ε - degree of metastability:

$$\varepsilon = \frac{P_s - P}{P_s - P_{sp}}, \% \tag{9}$$

As may be seen, differences in the determination of the specific volume between the methods under consideration in the vicinity of the saturation line are from 0.03% to 0.5%. Table 2 also gives discrepancies with [1] in the determination of the pressure on the spinodal ΔP_{sp} by formulae (2)-(4) and the specific volume by formula (6) - $\Delta v_{sp}/v_{sp}$. From Table 1 and 2 it follow that in the vicinity of the spinodal differences in the determination of the specific volume may reach 2%.

Tables of twenty organic liquids [6-14] have been extended to the metastable region to illustrate the above-mentioned methods.

The work has been done with a financial support of the Russian Foundation of Fundamental Investigations, project № 98-02-17503.

Degree of coordinatyion of methods.

Table 1.

n-hexane														
T=120			T=130			T=140			T=150			T=160		
P	ΔV	ΔV/V %	P	ΔV	ΔV/V %	P	ΔV	ΔV/V %	P	ΔV	ΔV/V %	P	ΔV	ΔV/V %
30	0,00069	0,04	30	0,00202	0,11	30	0,00029	0,02	30	0,00007	0,004	30	0,00155	0,08
25	0,00008	0,004	25	0,00115	0,06	25	0,00006	0,003	25	0,00016	0,01	25	0,00046	0,02
20	0,00037	0,02	20	0,00013	0,01	20	0,0004	0,02	20	0,00011	0,01	20	0,00008	0,01
15	0,00043	0,02	15	0,00004	0,002	15	0,00034	0,02	15	0,00025	0,01	15	0,00114	0,06
10	0,00034	0,02	10	0,00137	0,08	10	0,00029	0,02	10	0,00005	0,01	10	0,00079	0,04
5	0,00036	0,02	5	0,00189	0,1	5	0,00049	0,03	5	0,00005	0,003	5	0,00113	0,06
0	0,0005	0,03	0	0,0016	0,09	0	0,00002	0,001	0	0,00041	0,02	0	0,00129	0,06
-5	0,00077	0,04	-5	0,00254	0,14	-5	0,00024	0,01	-5	0,00135	0,07	-5	0,00042	0,02
-10	0,00118	0,07	-10	0,00271	0,15	-10	0,00112	0,06	-10	0,0017	0,09	-10	0,00025	0,01
-15	0,00075	0,04	-15	0,00314	0,17	-15	0,0016	0,08	-15	0,00235	0,12	-15	0,0014	0,07
-20	0,00048	0,03	-20	0,00387	0,21	-20	0,00264	0,14	-20	0,00414	0,21	-20	0,05655	2,68
-60	0,00401	0,22	-50	0,00318	0,17	-30	0,00507	0,26	-30	0,00828	0,41	-30	0,11408	5,15
-100	0,02998	1,53	-80	0,00997	0,49	-50	0,01515	0,77	-40	0,01602	0,79	-40	0,0316	1,45
						-70	0,04498	2,17	-50	0,03145	1,51			

Table 1(continuation).

n-hexane														
T=170			T=180			T=190			T=200			T=210		
P	DV	DVV %	P	DV	DVV %	P	DV	DVV %	P	DV	DVV %	P	DV	DVV %
30	0,00066	0,03	30	0,00018	0,01	30	0,00136	0,06	35	0,00114	0,05	35	0,00238	0,11
25	0,00042	0,02	25	0,00005	0,003	25	0,00054	0,03	30	0,00061	0,05	30	0,00095	0,04
20	0,00015	0,01	20	0,00012	0,01	20	0,00082	0,04	25	0,001	0,05	25	0,00143	0,06
15	0,00093	0,05	15	0,00035	0,02	15	0,00028	0,01	20	0,00048	0,02	20	0,00392	0,16
10	0,00178	0,09	10	0,00197	0,09	10	0,00179	0,08	15	0,00501	0,22	15	0,02785	1,08
5	0,00349	0,17	5	0,00414	0,19	5	0,00594	0,26	10	0,01599	0,67			
0	0,00578	0,28	0	0,00894	0,41	0	0,01548	0,67	5	0,0503	1,99			
-5	0,00823	0,39	-5	0,01461	0,66	-5	0,04221	1,73						
-10	0,01317	0,62	-10	0,02536	1,13									
-15	0,01949	0,91	-15	0,04751	2,03									
-20	0,02887	1,32												
-30	0,11227	4,88												

Table 1(continuation).

Ether											
T=100			T=110			T=120			T=130		
P	ΔV	ΔV/V %	P	ΔV	ΔV/V %	P	ΔV	ΔV/V %	P	ΔV	ΔV/V %
40	0,00018	0,01	40	0,00046	0,03	40	0,00019	0,01	40	0,00196	0,08
30	0,00017	0,01	30	0,00026	0,02	30	0,00004	0,003	30	0,00016	0,01
20	0,00009	0,01	20	0,00037	0,02	20	0,00014	0,01	20	0,00162	0,09
10	0,0001	0,01	10	0,00035	0,02	5	0,00037	0,02	10	0,00232	0,13
0	0,00019	0,01	5	0,00005	0,003	0	0,00019	0,01	5	0,00258	0,14
-10	0,00012	0,01	0	0,00054	0,03	-10	0,00006	0,003	0	0,0036	0,2
-20	0,00016	0,01	-5	0,00078	0,05	-20	0,00068	0,04	-10	0,0046	0,25
-40	0,00012	0,01	-10	0,00076	0,05	-40	0,00177	0,09	-20	0,00655	0,35
-60	0,00105	0,06	-20	0,00077	0,05	-50	0,00727	0,39	-40	0,03592	1,84
-80	0,00666	0,38	-40	0,00044	0,03						
-90	0,01539	0,86	-70	0,00988	0,54						

Table 1(continuation).

Ether											
T=140			T=150			T=160			T=160		
P	ΔV	ΔV/V %	P	ΔV	ΔV/V %	P	ΔV	ΔV/V %	P	ΔV	ΔV/V %
40	0,00172	0,09	40	0,0011	0,06	40	0,00059	0,03	40	0,00432	0,21
30	0,00048	0,03	30	0,00076	0,04	35	0,00038	0,02	35	0,00049	0,02
20	0,00125	0,07	20	0,00035	0,02	30	0,00033	0,02	30	0,00188	0,09
10	0,00259	0,14	10	0,00049	0,03	25	0,00011	0,01	25	0,00293	0,14
5	0,00363	0,19	5	0,0012	0,06	20	0,00094	0,05	20	0,00163	0,07
0	0,00339	0,18	0	0,0034	0,17	15	0,00334	0,16	15	0,03312	1,41
-10	0,00478	0,25	-5	0,0064	0,31	10	0,00836	0,39			
-20	0,0092	0,46	-10	0,00587	0,28	5	0,02029	0,9			

Table 1(end).

Ether											
T=-168			T=-158			T=-148			T=-138		
P	ΔV	ΔV/V %	P	ΔV	ΔV/V %	P	ΔV	ΔV/V %	P	ΔV	ΔV/V %
45	0,00005	0,01	45	0,00018	0,02	50	0,00027	0,03	70	0,00031	0,03
40	0,00007	0,01	40	0,00015	0,02	45	0,00023	0,03	60	0,00017	0,02
35	0,00009	0,12	35	0,00017	0,02	40	0,00019	0,02	50	0,00043	0,05
30	0,00002	0,003	30	0,00004	0,004	35	0,00008	0,01	45	0,00032	0,03
25	0,00002	0,004	25	0,00005	0,01	30	0,00011	0,01	40	0,00016	0,02
20	0,00005	0,01	20	0,00009	0,11	25	0,00024	0,03	35	0,00016	0,02
15	0,00005	0,01	15	0,00018	0,02	20	0,00042	0,05	30	0,00062	0,06
10	0,00014	0,02	10	0,00031	0,04	15	0,00002	0,002	25	0,00007	0,01
1	0,00003	0,004	5	0,00008	0,01	10	0,00032	0,04	20	0,00107	0,11
-50	0,00115	0,14	1	0,00002	0,02	5	0,00059	0,07	15	0,00266	0,26
-80	0,00363	0,45	-10	0,00059	0,07	1	0,00119	0,13	10	0,00501	0,49
-100	0,00483	0,59	-30	0,00^48	0,17	-10	0,00269	0,29	5	0,00809	0,77
			-50	0,00363	0,42	-30	0,00665	0,69			
			-80	0,00834	0,93						

Degree of co-ordinatyion of calculations of spinodal parameters and average values of discrepancies with [1] on isoterms.

Table 2.

T,°C	P_T	P_P	ΔP_{sp}	V_T	V_P	ΔV_{sp}	$\Delta V_{sp}/V_{sp}$ %	ε	ΔV/ V%
1	2	3	4	5	6	7	8	9	10
n-hexane									
120	-108,1	-108,16	-0,06	2,116	2,078	-0,04	-1,89	22	0,03
130	-89,8	-89,55	0,25	2,167	2,157	-0,01	-0,46	26	0,12
140	-72,9	-72,76	0,14	2,222	2,174	-0,05	-2,25	46	0,09
150	-57,4	-57,33	0,07	2,281	2,237	-0,04	-1,75	58	0,15
160	-43,1	-43,26	-0,16	2,346	2,323	-0,02	-0,85	75	1,86
170	-30	-30,28	-0,28	2,418	2,363	-0,06	-2,48	75	0,58
180	-17,9	-18,35	-0,45	2,499	2,459	-0,04	-1,6	89	0,85
190	-6,8	-7,34	-0,54	2,593	2,581	-0,01	-0,46	89	0,74
200	3,3	2,74	-0,56	2,705	2,683	-0,02	-0,81	85	0,88
210	12,5	11,94	-0,56	2,844	2,841	-0,003	-0,11	67	0,52

Table 2 (end).

T,°C	P_T	P_P	ΔP_{sp}	V_T	V_P	ΔV_{sp}	$\Delta V_{sp}/V_{sp}$ %	ε	ΔV/ V%
1	2	3	4	5	6	7	8	9	10
Ether									
110	-90	-78,26	11,74	1,984	1,947	-0,04	-2,02	56	0,03
120	-67,6	59,25	8,35	2,038	2,008	-0,03	-1,47	72	0,04
130	-47,3	-41,97	5,33	2,099	2,092	-0,01	-0,48	96	0,69
140	-29,1	-26,13	2,97	2,17	2,166	-0,004	-0,18	85	0,23
150	-12,8	-11,75	1,05	2,253	2,241	-0,01	-0,44	94	0,18
160	1,6	1,39	-0,21	2,353	2,35	-0,003	-0,13	81	0,39
170	14,1	13,34	-0,76	2,48	2,519	0,04	1,61	87	0,64
Argone									
-168	-185,1	-200,37	-15,27	0,97	0,962	-0,008	-0,01	51	0,23
-158	-113	-117,65	-4,65	1,008	1,008	-0,0002	-0,02	70	0,29
-148	-53,4	-55,07	-1,6	1.077.	1,074	-0,003	-0,27	36	0,23
-138	-5,2	-5,89	-0,69	1,18	1,169	-0,011	-0,01	49	0,29

References

1. Skripov V.P., Sinitsin E.N., Pavlov P.A. et al. Thermal Properties of Liquids in Metastable State. – M.: Atomizdat, 1980. -208p.
2. Yermakov G.V. Stability Boundary and Equation of State of Liquid in the Vicinity of the Saturation Line. – journal of Phys. Chem., 1982, v.58, no.4, pp. 841-844.
3. Ermakov G.V. Similitude Relationships in the Vicinity of the Spinodal. Teplofizika Visokikh Temperatur (Thermal Physics of High Temperatures), 1983, v.21, No. 5, pp. 1018-1021.
4. Fiirt R. Proc. Cambridge Philos. Soc., 1941, v.37, p.252.
5. Sinitsin E.N., Vinogradov V.E. Approximation of the Spinodal of Normal Liquids. - Teplofizika Visokikh Temperatur, 1980, v.18, No.5, pp. 1101-1103.