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PREDICTION AND CORRECTION OF THE PVT-DATA OF VARIOUS SUBSTANCES ALONG THE SATURATION LINE

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The occurrence of three similarity points (T_{mel}, T_m, T_{cr}) in vapors at saturation has allowed one to develop, along with polynomial expansions, a method for predicting and correcting the PVT-data of the vapor phase. The curve of the vapor branch of saturation was described by the function $y(x)=P_sV_s\left(\frac{2}{3}RT_{cr}\right)^{-1}$. *Theoretical values of y(x) were determined with the aid of Legendre polynomials.*

Introduction. Similarity theory serves to correlate experimental thermodynamic properties of various substances and as such allows one to determine the parameters of substances which have not been investigated as yet.

One of the most important empirical laws of similarity theory is the law of corresponding states. According to this law, any dimensionless combination is a universal function of two, out of three, reduced variables.

In the present work the function

$$y(x) = P_sV_s/P_mV_m,$$

is a universal function, where the product P_mV_m can be replaced by $(2/3)RT_{cr}$.

Depending on the reduced temperature τ, the values of this function were determined with the aid of steam (H_2O), which is the most studied substance in the experimental sense. Processing of the experimental values of y(x) for H_2O steam by Legendre, Chebyshev and other polynomials of different degrees has shown that the least discrepancy between experimental and theoretical values of y(x) in the region τ_{mel}- τ_{cr} is obtained with the use of tenth-degree Legendre polynomials.

Methods of predicting the thermodynamic properties of substances based on similarity theory are given in [1, 2]. In [3, 4] it was found that at the saturation line all substances have a maximum of the product P_sV_s in the vapor phase and that the PVT-data obey the laws

$$T_m = 0{,}785\ T_{cr}, \tag{1}$$

$$P_mV_m \simeq \frac{2}{3} RT_{cr}. \tag{2}$$

Expression (1) is valid for all substances without exception, whereas Eq. (2) is in poor agreement with experimental data only for substances with the most pronounced quantum properties (He, H_2, Ne, etc.).

In [5, 6] it was found that the value of the product P_sV_s at the melting temperature (T_{mel}) at saturation is rather accurately equal to RT_{mel}, since at T_{mel} the saturated gas is close in its state to ideal:

$$(P_sV_s)_{mel} \simeq RT_{mel} \tag{3}$$

Consequently, the temperatures T_{mel} and T_m , along with the generally adopted similarity point T_{cr}, can be used to plot a generalized curve with the help of which one can predict the PVT-data of substances at saturation.

Knowing T_{cr} and the values of $y(x) = P_sV_s(2/3\cdot RT_{cr})^{-1}$, we can find values of P_sV_s from the available values of y(x) and T_{cr} at any temperature on the gas saturation line. To obtain the form of the generalized curve, we used

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a standard program with the subprogram PROIZ. The unknown value of y(x) is a function of the independent variable τ ($\tau = x$). The independent variable τ was reduced to the interval [-1, 1], over which the Legendre polynomials were specified. Reduction to the interval indicated was achieved by introducing the normalized variable

$$\tau(x) = \frac{2x - (x_L + x_R)}{x_R - x_L},$$

where x_R is the right end and x_L, is the left end.

The quantity $y(x) = \mathcal{P}(x)/Q(x)$ where $\mathcal{P}(x)$ and Q(x) are the values of functions expanded in Legendre polynomials, calculated using the numerator and denominator coefficients. Calculations of $y(x) = \sum_{i=1}^{N} C_j \mathcal{P}_{i-1}$ were made by means of direct recursion with the use of the recurrent relationship between Legendre polynomials:

$$\mathcal{P}_{n+1}(x) = 2x\mathcal{P}_n(x) - \mathcal{P}_{(n-1)}(x) - \frac{[x\mathcal{P}_n(x) - \mathcal{P}_{(n-1)}(x)]^2}{(n+1)}.$$

The coeficients C_i (given below) were determined from the condition of the minimum of the sum of the squares of deviations

$$\Sigma[f(x) - y(x)]^2 = \min,$$

where the values of f(x) were determined from reference data for steam [7].

The values of the numerator coefficients (the order of the numerator is 10) are: 0.8620709777; 0.5120719969 E-01; 0.2556379437 E-03; -0.1002099514; -0.4173399881 E-01; -0.2951799706 E-01; -0.2386539802 E-01; -0.1901349798 E-01; -0.1566849649 E-01; -0.1329379901 E-01.

The values of the denominator coefficients (the order of the denominator is 10) are: 1.00000000; -0.6945669884 E-04; 0.6266618147 E-03; 0.1897429902 E-03; -0.5058019269 E-05; -0.5911609624 E-03; -0.1052689971 E-02; -0.1740339911 E-02; -0.1553919865 E-02; 0.2223069916 E-03.

Processing of the PVT-data for steam [7] yields that the sum of the squares of deviations is equal to

$$\Sigma[f(x) - y(x)]^2 = 0{,}0104.$$

Since the number of points used in the work is of the order of 400, the deviation between f(x) and y(x) is equal on the average to $5 \cdot 10^{-3}$. This has the consequence that some of the values of y(x) are larger than unity (Table 1). From this table it is seen that substantial discrepancies between f(x) and y(x) are observed under edge conditions. Especially large deviations of f(x) from y(x) are noted in the range $0.98 \leq \tau \leq 1$ (at $\tau = 1$ the discrepancy attains 20%). If the interval τ_{mel}-τ_{cr} is partitioned into parts, then for the interval$0.43 \leq \tau \leq 0.785$ the deviation of f(x) from y(x) does not exceed 0.1%; for the interval $0.43 \leq \tau \leq 0.93$ the difference of f(x) from y(x) is not higher than 0.2%; for the interval $0.422 \leq \tau \leq 0.98$ this difference is no more than 1%.

In Tables 2-5 reference and calculated data are given for the products P_sV_s, $J \cdot mole^{-1}$. They were determined by the method suggested in the present work. In Table 6 values of P_sV_s are given for ammonia, sulfur dioxide and n-hexane calculated by the Redlich-Quong equation modified by Wilson [2], as well as values of P_sV_s found for n-hexane from equations (5.62) and (5.78) in [1]. Values of P_sV_s for n-hexane calculated by our method are listed in the last column and are denoted by an asterisk.

In Table 2 the PV-data for Ar, Xe, Cl_2 are analyzed. The ratios P_mV_m/RT_{cr} for Ar, Xe and Cl_2 are equal to 0.645; 0.650 and 0.664, respectively. The deviations of the values of the ratio P_mV_m/RT_{cr} for Ar and Xe from 2/3 are due to the relatively high values of the zero energy [4] (with respect to the interaction energy). Consequently, the calculated values of P_sV_s for Ar and Xe are larger than the reference data near $\tau = 0.785$. Generally, for Ar and Xe in the intervals τ_{mel}- 0.961 (argon) and τ_{mel}- 0.950 (xenon) the discrepancies between $(P_sV_s)_r$ and $(P_sV_s)_c$ do not exceed 3.5%. The value of the ratio P_mV_m/RT_{cr} for Cl_2 is virtually equal to 2/3; therefore the reference and calculated values of P_sV_s practically coincide in the range $0.439 \leq \tau \leq 0.839$.

TABLE 1. Calculated y(x) and Reference f(x) Values of the Function of the Form P_sV_s/P_mV_m

τ	f(x)	y(x)	τ	f(x)	y(x)
0.4220	0.6305	0.6360	0.7495	0.9957	0.9940
0.4297	0.6419	0.6413	0.7604	0.9982	0.9970
0.4498	0.6716	0.6687	0.7820	1.0000	1.0003
0.4700	0.7010	0.7014	0.7851	0.9998	1.0004
0.4899	0.7302	0.7321	0.7866	0.9998	1.0004
0.5101	0.7589	0.7598	0.7912	0.9992	1.0003
0.5302	0.7870	0.7859	0.8098	0.9949	0.9973
0.5502	0.8143	0.8119	0.8300	0.9859	0.9882
0.5703	0.8407	0.8381	0.8500	0.9709	0.8722
0.5904	0.8659	0.8644	0.8700	0.9502	0.9490
0.6105	0.8896	0.8898	0.8901	0.9217	0.9190
0.6306	0.9118	0.9132	0.9102	0.8852	0.8831
0.6507	0.9320	0.9339	0.9303	0.8387	0.8403
0.6707	0.9501	0.9515	0.9504	0.7778	0.7843
0.6908	0.9659	0.9660	0.9705	0.6943	0.6969
0.7109	0.9790	0.9778	0.9797	0.6413	0.6360
0.7310	0.9891	0.9872	0.9906	0.5557	0.5372
0.7743	0.9998	0.9996	0.9999	0.3480	0.4160

TABLE 2. Reference and Calculated Values of the Product P_sV_s for Argon, Xenon and Chlorine

Ar			Xe			Cl_2		
τ	$(P_sV_s)_r$	$(P_sV_s)_c$	τ	$(P_sV_s)_r$	$(P_sV_s)_c$	τ	$(P_sV_s)_r$	$(P_sV_s)_c$
0.555	678	684	0.557	1306	1318	0.439	1530	1509
0.557	679	686	0.570	1330	1346	0.466	1603	1607
0.579	700	711	0.585	1358	1377	0.519	1784	1785
0.603	722	737	0.600	1384	1408	0.599	2013	2025
0.650	758	780	0.650	1456	1491	0.652	2148	2163
0.696	785	810	0.700	1514	1560	0.705	2243	2254
0.749	805	831	0.750	1547	1597	0.732	2273	2284
0.775	809	836	0.775	1554	1606	0.759	2295	2305
0.782	809	836	0.785	1554	1607	0.785	2302	2314
0.795	809	836	0.800	1553	1605	0.812	2296	2305
9.855	791	809	0.850	1525	1562	0.839	2272	2271
0.895	760	762	0.900	1445	1449	0.892	2160	2118
0.961	642	622	0.950	1292	1262	0.945	1914	1853
0.994	478	416	0.994	963	800	0.998	1156	1029
1.000	365	348	1.000	695	688	1.000	854	962

In Table 3 the data for benzene (C_6H_6), sulfur dioxide (SO_2) and chlorobenzene (C_6H_5Cl) are analyzed. The data on chlorobenzene are incomplete; therefore instead of the reference data for P_sV_s Table 3 cites the values of the volume of chlorobenzene determined with the aid of $(P_sV_s)_c$ and reference pressure values. Knowing the critical parameters of chlorobenzene [8], we found that the calculated value of the critical volume differs from the reference

TABLE 3. Reference and Calculated Values of P_sV_s for Benzene, Sulfur Dioxide and Chlorobenzene

C_6H_6			SO_2			C_6H_5Cl		
τ	$(P_sV_s)_r$	$(P_sV_s)_c$	τ	$(P_sV_s)_r$	$(P_sV_s)_c$	τ	V_p, m^3/mole	
0.498	2322	2317	0.472	1692	1682	0.432	6.7178	2257
0.533	2467	2463	0.494	—	1762	0.464	2.0756	2224
0.569	2636	2607	0.525	—	1859	0.495	0.7472	2590
0.604	2776	2750	0.611	—	2124	0.527	0.3138	2742
0.640	2906	2878	0.658	2229	2246	0.558	0.1493	2882
0.675	3020	2978	0.681	2276	2289	0.590	0.07769	3031
0.711	3113	3050	0.704	2331	2325	0.622	0.03693	3165
0.746	3183	3096	0.727	2348	2354	0.653	0.02624	3284
0.782	3224	3118	0.750	2352	2373	0.685	0.01650	3372
0.791	3229	3118	0.774	2359	2387	0.717	0.01089	3439
0.800	3263	3115	0.785	2369	2387	0.748	$7.42\cdot10^{-3}$	3483
0.853	3202	3022	0.797	2368	2387	0.780	$5.20\cdot10^{-3}$	3507
0.889	3120	2872	0.808	2371	2282	0.796	$4.39\cdot10^{-3}$	3506
0.924	2966	2666	0.866	2317	2277	0.812	$3.70\cdot10^{-3}$	3495
0.960	2695	2332	0.936	1992	1972	0.843	$2.67\cdot10^{-3}$	3428
1.000	1265	1297	0.959	1792	1795	0.859	$2.26\cdot10^{-3}$	3375
—	—	—	0.983	1500	1467	0.953	$8.56\cdot10^{-4}$	2731
—	—	—	0.994	1266	1189	1.000	$3.22\cdot10^{-4}$	1458
—	—	—	1.000	962	992	—	—	—

Note: The value of P_sV_s for sulfur dioxide at $\tau = 0.472$ was found from the relation $(P_sV_s)_{mel} = RT_{mel}$.

TABLE 4. Reference and Calculated Values of P_sV_s for Ammonia, Freon-22 and Freon-113

NH_3			Freon-22			Freon-113		
τ	$(P_sV_s)_r$	$(P_sV_s)_c$	τ	$(P_sV_s)_r$	$(P_sV_s)_c$	τ	$(P_sV_s)_r$	$(P_sV_s)_c$
0.482	—	1620	0.469	1438	1432	0.499	2014	2012
0.493	1644	1656	0.510	1555	1555	0.520	2094	2088
0.567	1872	1875	0.550	1668	1661	0.540	2172	2158
0.592	1939	1948	0.591	1772	1770	0.561	2247	2231
0.641	2055	2078	0.632	1866	1872	0.581	2320	2302
0.690	2142	2171	0.672	1941	1948	0.602	2388	2376
0.740	2195	2228	0.713	1999	2003	0.622	2454	2441
0.764	2201	2244	0.740	2024	2046	0.643	2515	2503
0.789	2191	2250	0.783	2042	2046	0.663	2574	2553
0.814	2180	2240	0.785	2043	2046	0.684	2624	2597
0.863	2091	2154	0.789	2042	2046	0.704	2669	2631
0.912	1908	1978	0.821	2029	2032	0.725	2712	2660
0.937	1767	1852	0.859	1982	1962	0.785	—	2703
0.962	1571	1663	0.902	1877	1839	0.962	—	1998
0.986	1280	1311	0.946	1686	1633	0.986	—	1576
1.000	819	935	1.000	841	851	1.000	1109	1123

TABLE 5. Reference and Calculated Values of P_sV_s for Mercury, Air and Dowtherm

Hg			Air			Dowtherm		
τ	$(P_sV_s)_r$	$(P_sV_s)_c$	τ	$(P_sV_s)_r$	$(P_sV_s)_c$	τ	$(P_sV_s)_r$	$(P_sV_s)_c$
0.427	6193	6244	0.463	530	530	0.466	2786	3086
0.44	6419	6450	0.528	575	575	0.491	3242	3260
0.461	6852	6978	0.573	618	619	0.516	3436	3410
0.495	7059	7222	0.619	656	661	0.565	4144	3690
0.512	7262	7446	0.664	687	695	0.591	4063	3841
0.529	7455	7662	0.709	711	718	0.616	4236	3979
0.546	7641	7877	0.739	721	727	0.665	4266	4205
0.563	7820	8101	0.770	726	734	0.703	4527	4321
0.580	7992	8316	0.785	727	735	0.729	4394	4379
0.597	8155	8531	0.800	726	734	0.765	4373	4432
0.609	8261	8678	0.845	714	718	0.790	4392	4441
0.785	—	9772	0.890	683	673	0.803	4373	4436
0.908	—	8668	0.935	627	609	0.828	4239	4392
0.964	—	7134	0.981	524	460	0.840	4151	4357
1.000	5505	4065	1.000	349	306	1.000	—	1847

one by 4.5%. Analysis of the data for benzene shows that the calculated and reference values of P_sV_s in the interval τ_{mel} - 0.791 differ by no more than 3.5%, with the difference increasing to 13% (in the interval τ_{mel}- 0.96). It should be noted that the discrepancy between the calculated and reference values seems to be due to errors in the PVT-data, since for benzene both the ratio P_mV_m/RT_{cr} and the value of T_m are much higher than the corresponding values found from Eqs. (1) and (2).

For sulfur dioxide the reference and calculated values virtually coincide in the temperature interval τ_{mel}-0.959.

Table 4 presents P_sV_s-data for ammonia and two Freons. The value of P_mV_m/RT_{cr} for Freon-22 is equal to 0.665. The magnitude of this ratio for ammonia is equal to 0.653. The data on P_sV_s for Freon-113 are given in [8] only up to the temperature $0.725\tau_{cr}$. The low values of P_mV_m/RT_{cr} and T_m (0.653 and 0.76, respectively) that were obtained by us for ammonia are due to the fact that the PVT-data for ammonia are given over 10°. Interpolation of the PV-data for ammonia shows that the temperature T_m should be near 318.4 K. The difference between the P_sV_s values in the interval τ_{mel}- 0.863 does not exceed 3%, whereas the maximum discrepancy between the reference and calculated values of P_sV_s in the interval τ_{mel} - 0.986 does not exceed 6%. The magnitude of the ratio P_mV_m/RT_{cr} for Freon-22 is equal to 0.666, and $T_m = 0.785T_{cr}$; therefore the discrepancy between the calculated and reference values of P_sV_s also does not exceed 1% in the interval τ_{mel}-0.859 and 3.1% in the interval τ_{mel}-0.946. The prediction of the PVT-data for Freon-113 shows that the discrepancy between the values studied is not higher than 1.9% in the interval τ_{mel} -0.725.

In Table 5 the PVT-data are analyzed for mercury and two mixtures (air and dowtherm). The PVT-data for mercury are available only up to the temperature $0.609T_{cr}$, and for dowtherm only up to the temperature $0.840T_{cr}$.

Comparison of the products P_sV_s for dowtherm shows that in approximately half the cases the discrepancy does not exceed 1.5%. In the other half, the discrepancy lies in the interval 2.2-11%. Over the studied portion of the saturation curve for dowtherm (a eutectic mixture consisting of 73.5% diphenyl ether and 26.5% diphenyl) three maxima are observed (at 0.565, 0.703 and 0.790 τ_{cr}). The most intense of these lies at 0.703 τ_{cr}. The absence of any trend in the discrepancy between the reference and calculated values of P_sV_s indicates that the reference data for dowtherm need correction.

Analysis of P_sV_s data for mercury shows that the calculated results are higher than the reference data and that the discrepancy increases, reaching 5%, with rise in the reduced temperature.

TABLE 6. Reference and Calculated Values of P_sV_s for NH_3, SO_2 and C_6H_{14}

τ	NH_3 [2]	τ	SO_2 [2]	τ	C_6H_{14}—P_sV_s			
					[2]	[1]	[8]	*
0.493	1639	0.658	2264	0.538	2233	2259	2597	2240
0.567	1875	0.681	2321	0.577	2382	2401	2316	2382
0.592	1949	0.704	2372	0.617	2522	2470	2464	2526
0.641	2087	0.727	2414	0.656	2647	2631	2738	2643
0.690	2204	0.750	2442	0.695	2749	2790	2751	2727
0.740	2289	0.774	2468	0.735	2822	2834	2811	2783
0.764	2316	0.785	2475	0.774	2863	2887	2858	2814
0.789	2330	0.797	2480	0.814	2859	2882	2830	2804
0.814	2329	0.808	2481	0.853	2801	2838	2748	2728
0.863	2266	0.866	2648	0.892	2679	2734	2637	2573
0.912	2085	0.936	2115	0.932	2471	2543	2454	2355
0.937	1926	0.959	1895	0.971	2090	2181	2090	1961
0.962	1690	1.000	964	1.000	1123	—	1114	1171
0.986	1318	—	—					
1.000	856	—	—					

Analysis of P_sV_s values for air shows that in the temperature interval τ_{mel}- 0.890 the investigated values do not deviate by more than 1.2%, whereas in the interval τ_{mel}- 0.935 the discrepancy does not exceed 2.9%. It should be noted that the maximum of the product P_sV_s for air lies near $0.785T_{cr}$, and the value of the ratio P_mV_m/RT_{cr} is equal to 0.660.

Analysis of the reference and calculated values of P_sV_s (Tables 2-5) demonstrates that our method "works" successfully in the range 0.43-0.785 τ_{cr} (the averaged maximum discrepancy, except for dowtherm, does not exceed 1.8%), and in the majority of cases the maximum discrepancy in the averaged range τ_{mel}-0.95 τ_{cr} is not higher than 3%. The temperature range $0.95\text{-})_{cr}$ for correcting and predicting PVT-data is practically inapplicable, since the critical temperature is a "bad" similarity point.

In Table 6 our method is compared with some widely known methods for calculating and predicting PVT-data [1, 2].

Using the modified Redlich-Quong equation, we calculated the P_sV_s values for Ar, Xe, H_2O, SO_2, NH_3, and C_6H_{14} (the data on Ar, Xe and H_2O were not included in the paper because of length restrictions). Comparison of the P_sV_s values found from the Redlich-Quong equation and by our method (Tables 2-4, 6) showed that in the range τ_{mel}-0.96 our method represents well the PVT-data for H_2O, NH_3, SO_2 and less satisfactorily the data for Ar, Xe and C_6H_{14}. According to our method the mean deviations of the results of calculations from those of experiment $\left[\frac{1}{n}\sum_{i=1}^{n}\left(\frac{\Delta x_i}{x_i}\right)\right]$ in the range τ_{mel} - 0.96 for H_2O, NH_3, SO_2, Ar and Xe are equal to -0.3, 2.3, 0.2, 1.5 and 2.0%, respectively. The corresponding deviations in the modified Redlich-Quong method are equal to 1.5, 4.8, 4.8, 0.7, and 1.1%, respectively.

The relatively large deviations in our method for Ar and Xe are explained by the method being sensitive to quantum effects [4], which is reflected in the value of the ratio P_mV_m/RT_{cr}.

In the last column of Table 6 reference values [8] for n-hexane are compared with results obtained by three different methods:

1) P_sV_s values found from the modified Redlich-Quong equation;
2) P_sV_s values found by multiplying P_s by V_s, as given in [1];
3) P_sV_s values found by the present method.

Analysis of the P_sV_s values for n-hexane indicates that these values are most adequately described by the Redlich-Quong equation. Deviations in the other two methods have almost the same absolute errors, which are opposite, however, in sign.

The advantage of our method is its universality, its simplicity and the minimum of information needed. For determining P_sV_s, our method requires knowledge of only one parameter (T_{cr}), whereas the modified Redlich-Quang equation needs T_{cr}, P_{cr}, the vapor volume over the entire region of determination and the vapor pressure at the temperature $T = 0.7T_{cr}$.

The simplicity and universality of our method with a minimum of information about the substance and a rather high accuracy of the results allow one to hope that the method will find application in engineering calculations.

Conclusion. A method has been developed for predicting and correcting the PVT-data of different substances. The method is based on the use of three similarity points and polynomial expansion.

The concept behind the method is that knowing the value of y(x), we can determine the values of P_sV_s along the saturation line or only the values of V_s if the values of P_s are known beforehand.

The method suggested in the present work allows the determination of P_sV_s in the range τ_{mel}-0.95 with a mean error of 3%. However, if the value of P_mV_m virtually coincides with $(2/3)RT_{cr}$, then the degree of reliability of the results of prediction in this range are much higher.

NOTATION

P, pressure; V, volume; T, temperature, K; P_s, pressure at saturation; V_s, volume at saturation; P_m, pressure at the point of the maximum of P_s/V_s; V_m, volume at the point of the maximum of the product P_s/V_s; T_m, temperature at the point of the maximum of the product P_s/V_s; T_{cr}, critical temperature; τ, reduced temperature; A, critical compressibility factor; R, universal gas constant.

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