Saturation and Metastable Properties of the van der Waals Fluid

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Modern applications require accurate thermodynamic equations of state that portray stable and metastable states of fluids. Earlier work has shown that the famous van der Waals equation, contrary to widely held views, finds its natural niche in the rank of real substances ordered according to their values of the acentric factor. In this note, the saturated and metastable state properties of a van der Waals fluid are presented in the form of a temperature table and a pressure table. A comparison of these results with the available data for mercury is made and it is established that mercury is approximated rather well as a van der Waals fluid.

Les applications modernes exigent l'emploi d'équations d'état thermodynamiques exactes décrivant les états stable et métastable des fluides. Un travail antérieur a montré que la fameuse équation de van der Waals, contrairement à certains points de vue exprimés, trouve une place naturelle dans la classe des substances réelles ordonnées selon leurs valeurs du facteur "d'acentricité". On présente les propriétés à l'état saturé et métastable d'un fluide de van der Waals, sous forme d'un tableau de température et d'un tableau de pression. On a comparé ces résultats avec les données disponibles pour le mercure et l'on a établi que le mercure est assez bien représenté par un fluide de van der Waals.

There has been strong recent interest in the formulation of equations of state, driven in part by the problems of dealing with the superheated liquids and supercooled vapors that arise in many modern heat transfer processes. Such problems arise in nuclear reactors, light hydrocarbon spills, and in the expansion of vapors in turbines. It is no longer enough to have equations that will only model stable equilibrium states.Today, there is a serious need for equations that will also represent the metastable liquid and vapor states (sometimes, although incorrectly, called non-equilibrium states.)

Most existing equations of state are inherently capable of correctly reproducing metastable states, at least qualitatively. This is particularly true of the many different algebraic equations of state whose parameters are determined with the use of very few experimental results — for example, those based on the critical quantities and a known boiling point. It is well known that many such equations are valid only for substances with a specific value of the critical compressibility, Z_c. The best known simple equation of state, the van der Waals equation, gives $Z_c = 3/8$. The one most often quoted by chemical engineers, the Redlich-Kwong equation, gives $Z_c = 1/3$. This value is much closer to the Z_c of most inorganic gases and hydrocarbons; thus the Redlich-Kwong equation is better suited for these substances than is the van der Waals equation. The common inference from these — that the Redlich-Kwong equation is more accurate than the van der Waals equation — is misleading since an equation of state should only represent those substances whose Z_c lies close to the Z_c of the equation.

This train of thought was pursued convincingly by Peck (1982), whose compilation and analysis shows that the van der Waals substance, i.e., one with $Z_c = 3/8$, finds its natural niche in the rank of real substances when they are ordered by their values of Z_c. Actually, Peck used a more effective characterization of molecular structure than Z_c, namely the Pitzer acentric factor, $\omega = -[1 + \log p$ $(T = 0.7)]$. ($\omega = -0.302$ for a van der Waals fluid, or 0.058 for a Redlich-Kwong fluid.)

Peck's conclusion (which we endorse) is, in effect, that if a real substance with $Z_c = 3/8$ or $\omega = -0.302$ were to be discovered, it would obey the van der Waals equation and would conform to all conclusions based upon that equation. This statement rested only upon circumstantial evidence, for we do not know of a van der Waals substance. Further evidence supporting Peck's conclusion will be given in this paper. This evidence involves data for mercury, which has a value of Z_c close to 3/8, and ω close to −0.302.

Once it is accepted that the van der Waals substance, with mercury being a conceivable example thereof, has its place in the hierarchy of real substances, it follows that, in formulating new equations of state applicable to substances with a range of values of Z_c, the properties of the van der Waals substance should be used as constraints. It should be possible to recover the properties of the van der Waals substance by substituting 3/8 for Z_c in the new equations. Lienhard (1982) has shown that including the van der Waals equation in this way leads to improved results.

In the program we have undertaken for formulating such equations, we have often felt the need for a tabulation of the properties of a van der Waals substance. No such tabulation is available within the knowledge of the authors, although the calculations leading to such a table are, in the main, simple. Graphical presentations of this or that individual property of the van der Waals substance are scattered in numerous papers. In this paper, we present a pair of complete tables of properties of the saturated and metastable van der Waals fluid, calculated with high precision. A new analytical approximation for the vapor pressure at low temperatures is also supplied.

Calculations

All physical properties in the following dicussion are *reduced* quantities.
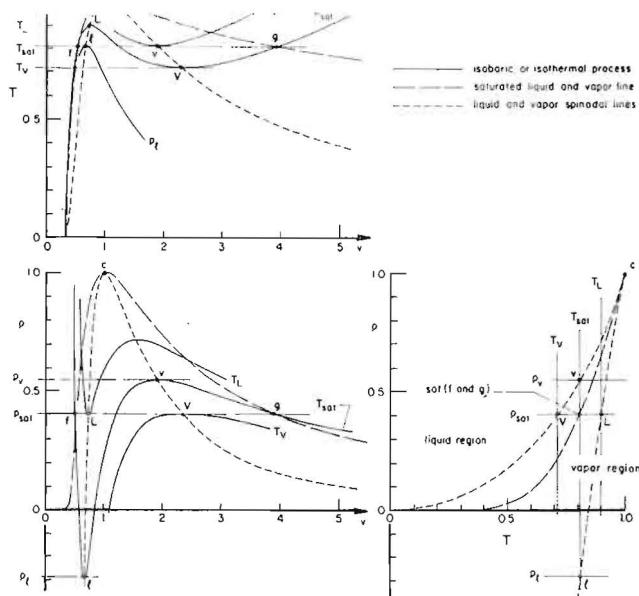
Figure 1 — van der Waals p-v-T surface.

Figure 2 — Comparison of some typical v_f/v_g curves for fluids with different Pitzer "acentric" factors.

The coexistence curve is best calculated using Rowlinson's (1958) technique. The advantage of his method over the alternative procedure described by Peck (1982) is that no cubic equations have to be solved. Over a wide range of temperatures and pressures, the coefficients of the cubic equation would span several orders of magnitude, and the roots could be widely separated, calling for care in the numerical work. Rowlinson's method gives values of T, p_{sat}, v_f and v_g for a given value of the parameter $r \equiv (3v_f - 1)/(3v_g - 1)$. To obtain tables with regular values of p or T, as we desire, it is necessary to build an iteration scheme around Rowlinson's sequence of calculations. We employed the secant method.

To facilitate the calculations, we supply a set of equations that will furnish an estimate of the parameter r with which the iterations are to be started:

$$r_{est} = (p_{sat}/22)(1 + 10 \, p_{sat}) \dots \dots \dots \dots (1)$$

If T is the primary variable, it becomes necessary to estimate p_{sat} before using this equation. The following approximations are recommended.

For $T > 0.3$,

$$\ln p_{sat} \cong 4.5267 - 5.1227/(T + 0.1317) \dots \dots (2)$$

For $T \leq 0.3$,

$$-\ln (p_{sat}/27) \cong 1 + 729/[8T(8T + 27)] \dots \dots (3)$$

The medium-high temperature approximation (2) is an Antoine correlation developed by Lienhard (1976). The low-temperature approximation (3) is new, and was obtained by developing series expansions of the governing equations at low pressures. The correlation (1) is also new.

Spinodal points are found by applying the condition $(\partial p/\partial v)_T = 0$ to the van der Waals equation. The result may be written in either of two forms:

$$4Tv^3 - (3v - 1)^2 = 0 \quad \text{or} \quad pv^3 - 3v + 2 = 0 \quad \dots (4)$$

The spinodal volumes are the two larger roots of these equations.

Internal energy, enthalpy, and entropy are related to their ideal gas values (marked*) by the relations

$$u^* - u = 9/8v \dots \dots \dots \dots \dots \dots \dots \dots \dots \dots \dots (5)$$

$$h^* - h = 9/8v + T-(3/8)pv \dots \dots \dots \dots \dots (6)$$

$$s^* - s = -\ln (1 - 3v) \dots \dots \dots \dots \dots \dots (7)$$

The use of these equations bypasses the use of the Clausius-Clapeyron equation to find u_{fg}, h_{fg} and s_{fg}. Thus, we avoid introducing the inaccuracy associated with finding the slope of the vapor pressure curve.

Figure 1 is used to explain the notation for the various states. With reference to the figure, the following enthalpy differences are calculated using Equation (6):

Isothermal differences:

$$\Delta h_l \equiv h_l - h_f, \qquad \Delta h_v \equiv h_g - h_v \dots \dots \dots \dots (8)$$

Isobaric differences:

$$\Delta h_L \equiv h_L - h_f, \qquad \Delta h_V \equiv h_g - h_V \dots \dots \dots \dots (9)$$

The availability, Δa, of a spinodal state with reference to its neighbouring saturation state is of interest because it indicates how much damage a flashing liquid could possibly accomplish. The following four availabilities are based on the reference temperature being T_{sat}, with $a = h - T_{sat}s$:

Isothermal availabilities:

$$\Delta a_l \equiv a_{sat} - a_l, \qquad \Delta a_v = a_v - a_{sat} \dots \dots \dots \dots (10)$$

Isobaric availabilites:

$$\Delta a_L \equiv a_L - a_{sat}, \qquad \Delta a_V = a_V - a_{sat} \dots \dots \dots \dots (11)$$

Here, note that $a_{sat} = a_f = a_g$. In calculating the isobaric differences in equations (9) and (11), we have used $c_p/R = 5/2$.

Table 1
van der Waals Saturation and Spinodal Properties: Temperature Table

T	p_{sat}	v_f	v_g	v_{fg}	h_{fg}	s_{fg}	u_{fg}	v_ℓ	v_v	Δp_ℓ	Δp_v	Δh_ℓ	Δh_v	Δa_ℓ	Δa_v
1	1	1	1	0	0	0	0	1	1	0	0	0	0	0	0
0.98	0.92191	0.77554	1.3761	0.6006	0.8407	0.8579	0.6331	0.85611	1.1892	0.01616	0.01018	0.15919	0.18851	0.00484	0.00501
0.96	0.84762	0.70819	1.6118	0.9936	1.1778	1.2269	0.3906	0.80593	1.2867	0.04951	0.02557	0.20875	0.26736	0.01367	0.01433
0.94	0.77707	0.66369	1.8438	1.1831	1.4288	1.5200	1.3849	0.77040	1.3715	0.09649	0.04256	0.23799	0.32587	0.02511	0.02661
0.92	0.71021	0.63022	2.0869	1.4567	1.6340	1.7760	1.2460	0.74221	1.4511	0.15591	0.05993	0.25577	0.37268	0.03868	0.04137
0.90	0.64700	0.60340	2.3488	1.7454	1.8090	2.0100	1.3855	0.71860	1.5285	0.22716	0.07701	0.26562	0.41194	0.05411	0.05838
0.88	0.58736	0.58106	2.6360	2.0549	1.9619	2.2295	1.5093	0.69814	1.6052	0.30985	0.09340	0.26937	0.44490	0.07124	0.07746
0.86	0.53175	0.56195	2.9545	2.3925	2.0978	2.4393	1.5212	0.68003	1.6821	0.40375	0.10880	0.26817	0.47238	0.08993	0.09852
0.84	0.47859	0.54530	3.3113	2.7659	2.2197	2.6425	1.7233	0.66373	1.7601	0.50872	0.12301	0.26273	0.49663	0.11009	0.12147
0.82	0.42932	0.53053	3.7141	3.1835	2.3299	2.8414	1.3174	0.64888	1.8396	0.62467	0.13590	0.25360	0.51667	0.13167	0.14627
0.80	0.38336	0.51741	4.1725	3.6550	2.4301	3.0377	1.9047	0.63521	1.9212	0.75155	0.14737	0.24114	0.53340	0.15460	0.17287
0.78	0.34064	0.50552	4.6978	4.1922	2.5215	3.2327	1.9860	0.62254	2.0053	0.88937	0.15736	0.22565	0.54712	0.17884	0.20126
0.76	0.30108	0.49469	5.3041	4.8094	2.6050	3.4277	2.3620	0.61071	2.0924	1.03814	0.16582	0.20736	0.55807	0.20436	0.23141
0.74	0.26459	0.48473	6.0092	5.5244	2.6816	3.6238	2.1334	0.59960	2.1828	1.19793	0.17274	0.18643	0.56644	0.23113	0.26333
0.72	0.23108	0.47555	6.8354	6.3597	2.7517	3.8218	2.2006	0.58912	2.2770	1.36881	0.17812	0.16302	0.57239	0.25914	0.29702
0.70	0.20046	0.46719	7.8111	7.3439	2.8160	4.0229	2.2640	0.57920	2.3755	1.55087	0.18197	0.13724	0.57606	0.28836	0.33249
0.68	0.17262	0.45933	8.9734	8.5141	2.8750	4.2279	2.3238	0.56977	2.4787	1.74426	0.18433	0.10917	0.57756	0.31881	0.36974
0.66	0.14745	0.45200	10.370	9.9185	2.9289	4.4377	2.3805	0.56077	2.5872	1.94911	0.18524	0.07890	0.57700	0.35046	0.40879
0.64	0.12485	0.44511	12.066	11.621	2.9782	4.6534	2.4341	0.55215	2.7016	2.16560	0.18475	0.04647	0.57447	0.38332	0.44968
0.62	0.10470	0.43863	14.147	13.708	3.0232	4.8761	2.4850	0.54389	2.8225	2.39393	0.18293	0.01194	0.57006	0.41740	0.49243
0.60	0.86869-1	0.43261	16.729	16.296	3.0641	5.1068	2.5333	0.53595	2.9506	2.63432	0.17987	-0.02467	0.56385	0.45271	0.53708
0.58	0.71229-1	0.42687	19.974	19.547	3.1012	5.3470	2.5791	0.52828	3.0867	2.88705	0.17564	-0.06333	0.55591	0.48926	0.58365
0.56	0.57645-1	0.42145	24.110	23.689	3.1348	5.5979	2.6227	0.52088	3.2318	3.15240	0.17034	-0.10404	0.54634	0.52706	0.63221
0.54	0.45975-1	0.41630	29.465	29.049	3.1650	5.8611	2.5642	0.51371	3.3869	3.43071	0.16408	-0.14678	0.53520	0.56616	0.68279
0.52	0.36073-1	0.41141	36.517	36.106	3.1921	6.1387	2.7037	0.50676	3.5532	3.72236	0.15697	-0.19157	0.52258	0.60657	0.73544
0.50	0.27789-1	0.40675	45.984	45.577	3.2163	6.4326	2.7413	0.50000	3.7321	4.02779	0.14913	-0.23844	0.50857	0.64833	0.79024
0.48	0.20967-1	0.40231	58.969	58.567	3.2377	6.7453	2.7772	0.49342	3.9252	4.34748	0.14068	-0.28739	0.49325	0.69150	0.84724
0.46	0.15451-1	0.39807	77.219	76.821	3.2567	7.0797	2.8115	0.48700	4.1344	4.68201	0.13176	-0.33849	0.47673	0.73611	0.90651
0.44	0.11084-1	0.39402	103.58	103.19	3.2733	7.4392	2.8443	0.48073	4.3619	5.03202	0.12249	-0.39178	0.45912	0.78224	0.96813
0.42	0.77097-2	0.39013	142.89	142.50	3.2877	7.8279	2.3757	0.47459	4.6105	5.39826	0.11301	-0.44733	0.44052	0.82997	1.03218
0.40	0.51745-2	0.38641	203.63	203.24	3.3003	8.2507	2.9059	0.46857	4.8833	5.78159	0.10346	-0.50523	0.42106	0.87937	1.09876
0.38	0.33318-2	0.38283	301.49	301.11	3.3111	8.7135	2.9349	0.46265	5.1841	6.18301	0.09394	-0.56558	0.40086	0.93055	1.16796
0.36	0.20435-2	0.37939	466.97	466.59	3.3204	9.2235	2.9629	0.45685	5.5177	6.60369	0.08459	-0.62850	0.38007	0.98365	1.23989
0.34	0.11834-2	0.37607	763.14	762.76	3.3285	9.7896	2.9900	0.45112	5.8898	7.04500	0.07551	-0.69415	0.35882	1.03880	1.31467
0.32	0.64005-3	0.37288	1330.0	1329.7	3.3353	10.423	3.0162	0.44545	6.3078	7.50853	0.06679	-0.76271	0.33724	1.09617	1.39243
0.30	0.31882-3	0.36980	2505.9	2505.5	3.3413	11.138	3.0417	0.43985	6.7807	7.99620	0.05851	-0.83441	0.31545	1.15599	1.47332
0.28	0.14367-3	0.36682	5193.2	5192.9	3.3464	11.952	3.0667	0.43430	7.3206	8.51025	0.05074	-0.90951	0.29358	1.21849	1.55749
0.26	0.57229-4	0.36395	12111.		3.3509	12.888	3.0910	0.42878	7.9427	9.05341	0.04350	-0.98833	0.27171	1.28398	1.64513
0.24	0.19533-4	0.36116	32760.		3.3549	13.979	3.1149	0.42327	8.6678	9.62894	0.03684	-1.07128	0.24992	1.35283	1.73646
0.22	0.54768-5	0.35845	0.10711+06		3.3584	15.265	3.1384	0.41777	9.5239	10.2408	0.03075	-1.15883	0.22825	1.42547	1.83172
0.20	0.11891-5	0.35584	0.44852+06		3.3615	16.807	3.1615	0.41225	10.550	10.8941	0.02525	-1.25159	0.20673	1.50246	1.93120
0.18	0.18358-6	0.35331	0.26147+07		3.3642	18.690	3.1842	0.40669	11.804	11.5948	0.02031	-1.35033	0.18538	1.58451	2.03525
0.16	0.17734-7	0.35084	0.24059+08		3.3666	21.041	3.2066	0.40105	13.370	12.3512	0.01595	-1.45605	0.16420	1.67253	2.14432
0.14	0.87689-9	0.34844	0.43575+09		3.3687	24.062	3.2287	0.39534	15.382	13.1738	0.01213	-1.57005	0.14317	1.76771	2.25896
0.12	0.15878-10	0.34611	0.20153+11		3.3704	28.087	3.2504	0.38945	18.064	14.0772	0.00885	-1.69415	0.12230	1.87174	2.37986
0.10	0.57631-13	0.34384	0.46271+13		3.3718	33.718	3.2718	0.38338	21.818	15.0825	0.00611	-1.83096	0.10158	1.98703	2.50799
0.08	0.12561-16	0.34163	0.16984+17		3.3730	42.163	3.2930	0.37698	27.446	16.2221	0.00389	-1.98452	0.08100	2.11731	2.64469
0.06	0.98727-23	0.33943	0.16206+23		3.3739	56.232	3.3139	0.37010	36.824	17.5502	0.00217	-2.16157	0.06055	2.26890	2.79200
0	0	1/3	∞		27/8	∞	27/8	1/3	∞	27	0	-27/8	0	27/8	27/8

Table 2
van der Waals Saturation and Spinodal Properties: Pressure Table

p	T_{sat}	v_f	v_g	v_{fg}	h_{fg}	s_{fg}	u_{fg}	v_L	v_V	ΔT_L	ΔT_V	Δh_L	Δh_V	Δa_L	Δa_V
1	1	1	1	0	0	0	0	1	1	0	0	0	0	0	0
0.98	0.99497	0.87437	1.1623	0.2879	0.4246	0.4267	0.3187	0.92630	1.0917	0.00041	0.00041	0.0918	0.0891	0.00003	0.00003
0.96	0.98988	0.83034	1.2448	0.4147	0.6009	0.6070	0.4516	0.89976	1.1369	0.00116	0.00119	0.1319	0.1264	0.00010	0.00010
0.94	0.98472	0.79848	1.3159	0.5175	0.7364	0.7479	0.5540	0.88072	1.1751	0.00214	0.00220	0.1638	0.1554	0.00024	0.00024
0.92	0.97950	0.77333	1.3823	0.6090	0.8510	0.8688	0.6439	0.86547	1.2102	0.00332	0.00343	0.1916	0.1803	0.00044	0.00043
0.90	0.97421	0.75218	1.4464	0.6942	0.9522	0.9774	0.7179	0.85260	1.2435	0.00467	0.00484	0.2171	0.2027	0.00070	0.00068
0.88	0.96884	0.73380	1.5096	0.7758	1.0439	1.0774	0.7879	0.84139	1.2758	0.00618	0.00642	0.2408	0.2233	0.00103	0.00100
0.86	0.96340	0.71748	1.5726	0.8551	1.1284	1.1712	0.8526	0.83142	1.3076	0.00785	0.00817	0.2634	0.2426	0.00143	0.00140
0.84	0.95789	0.70274	1.6361	0.9334	1.2073	1.2603	0.9133	0.82242	1.3393	0.00960	0.01008	0.2852	0.2610	0.00191	0.00186
0.82	0.95230	0.68928	1.7005	1.0113	1.2815	1.3457	0.9706	0.81420	1.3709	0.01162	0.01215	0.3062	0.2786	0.00247	0.00241
0.80	0.94662	0.67686	1.7663	1.0895	1.3520	1.4282	1.0252	0.80661	1.4028	0.01372	0.01437	0.3269	0.2957	0.00312	0.00304
0.78	0.94085	0.66532	1.8338	1.1585	1.4192	1.5084	1.0774	0.79957	1.4351	0.01596	0.01675	0.3471	0.3122	0.00387	0.00376
0.76	0.93500	0.65452	1.9032	1.2487	1.4836	1.5868	1.1277	0.79300	1.4678	0.01834	0.01928	0.3671	0.3284	0.00471	0.00458
0.74	0.92905	0.64435	1.9750	1.3307	1.5456	1.6636	1.1763	0.78682	1.5013	0.02087	0.02196	0.3870	0.3442	0.00566	0.00551
0.72	0.92300	0.63474	2.0494	1.4147	1.6054	1.7393	1.2234	0.78100	1.5354	0.02354	0.02480	0.4067	0.3597	0.00672	0.00654
0.70	0.91684	0.62562	2.1268	1.5012	1.6633	1.8142	1.2692	0.77548	1.5705	0.02636	0.02779	0.4264	0.3751	0.00791	0.00770
0.68	0.91058	0.61693	2.2075	1.5906	1.7195	1.8884	1.3139	0.77025	1.6066	0.02932	0.03095	0.4461	0.3903	0.00923	0.00898
0.66	0.90421	0.60862	2.2918	1.6832	1.7742	1.9621	1.3576	0.76526	1.6438	0.03244	0.03426	0.4658	0.4053	0.01068	0.01040
0.64	0.89771	0.60065	2.3803	1.7796	1.8275	2.0357	1.4003	0.76050	1.6822	0.03571	0.03774	0.4856	0.4203	0.01229	0.01197
0.62	0.89109	0.59299	2.4732	1.8803	1.8795	2.1092	1.4423	0.75594	1.7221	0.03915	0.04138	0.5056	0.4351	0.01406	0.01371
0.60	0.88434	0.58560	2.5712	1.9856	1.9303	2.1828	1.4836	0.75157	1.7635	0.04275	0.04520	0.5257	0.4500	0.01600	0.01561
0.58	0.87744	0.57846	2.6748	2.0963	1.9802	2.2568	1.5242	0.74738	1.8066	0.04652	0.04919	0.5461	0.4648	0.01813	0.01771
0.56	0.87040	0.57154	2.7845	2.2130	2.0291	2.3312	1.5643	0.74334	1.8516	0.05047	0.05336	0.5667	0.4795	0.02046	0.02001
0.54	0.86320	0.56483	2.9011	2.3363	2.0771	2.4062	1.6040	0.73944	1.8986	0.05461	0.05773	0.5876	0.4943	0.02301	0.02253
0.52	0.85584	0.55831	3.0254	2.4671	2.1243	2.4821	1.6432	0.73568	1.9480	0.05895	0.06228	0.6088	0.5092	0.02580	0.02530
0.50	0.84829	0.55195	3.1583	2.6063	2.1707	2.5589	1.6820	0.73205	2.0000	0.06349	0.06704	0.6305	0.5240	0.02885	0.02834
0.48	0.84055	0.54574	3.3008	2.7551	2.2165	2.6370	1.7206	0.72854	2.0548	0.06825	0.07201	0.6525	0.5390	0.03218	0.03166
0.46	0.83261	0.53966	3.4542	2.9146	2.2617	2.7164	1.7589	0.72513	2.1128	0.07324	0.07719	0.6750	0.5540	0.03582	0.03531
0.44	0.82445	0.53371	3.6200	3.0862	2.3063	2.7974	1.7971	0.72183	2.1743	0.07847	0.08261	0.6981	0.5691	0.03980	0.03932
0.42	0.81606	0.52787	3.7997	3.2719	2.3504	2.8802	1.8351	0.71862	2.2398	0.08396	0.08826	0.7217	0.5843	0.04415	0.04372
0.40	0.80741	0.52213	3.9956	3.4734	2.3941	2.9652	1.8731	0.71551	2.3098	0.08974	0.09417	0.7460	0.5996	0.04891	0.04856
0.38	0.79848	0.51646	4.2099	3.6934	2.4374	3.0525	1.9111	0.71248	2.3849	0.09581	0.10034	0.7709	0.6151	0.05413	0.05389
0.36	0.78925	0.51087	4.4457	3.9348	2.4803	3.1426	1.9491	0.70953	2.4658	0.10221	0.10680	0.7967	0.6307	0.05986	0.05977
0.34	0.77969	0.50534	4.7066	4.2012	2.5229	3.2357	1.9872	0.70666	2.5534	0.10896	0.11356	0.8233	0.6464	0.06616	0.06627
0.32	0.76976	0.49985	4.9970	4.4972	2.5652	3.3325	2.0255	0.70386	2.6486	0.11610	0.12063	0.8510	0.6624	0.07310	0.07348
0.30	0.75943	0.49440	5.3227	4.8283	2.6073	3.4333	2.0641	0.70113	2.7529	0.12366	0.12805	0.8797	0.6785	0.03076	0.08149
0.28	0.74865	0.48896	5.6909	5.2919	2.6493	3.5388	2.1031	0.69847	2.8677	0.13169	0.13584	0.9097	0.6948	0.08925	0.09044
0.26	0.73736	0.48353	6.1108	5.6273	2.6912	3.6498	2.1425	0.69587	2.9950	0.14025	0.14403	0.9410	0.7114	0.09870	0.10047
0.24	0.72550	0.47808	6.5948	6.1167	2.7330	3.7671	2.1825	0.69333	3.1375	0.14941	0.15265	0.9740	0.7281	0.10925	0.11177
0.22	0.71297	0.47260	7.1594	6.6868	2.7750	3.8921	2.2233	0.69085	3.2985	0.15924	0.16175	1.0089	0.7451	0.12111	0.12459
0.20	0.69969	0.46707	7.8278	7.3608	2.8170	4.0261	2.2649	0.68842	3.4826	0.16985	0.17138	1.0459	0.7623	0.13450	0.13922
0.18	0.68550	0.46144	8.6328	8.1713	2.8593	4.1711	2.3077	0.68604	3.6960	0.18139	0.18159	1.0854	0.7797	0.14977	0.15608
0.16	0.67023	0.45569	9.6229	9.1672	2.9019	4.3297	2.3519	0.68371	3.9476	0.19402	0.19246	1.1281	0.7973	0.16733	0.17572
0.14	0.65364	0.44977	10.873	10.424	2.9451	4.5056	2.3978	0.68143	4.2506	0.20798	0.20407	1.1745	0.8150	0.18779	0.19892
0.12	0.63539	0.44361	12.508	12.064	2.9889	4.7041	2.4461	0.67920	4.6257	0.22363	0.21656	1.2257	0.8328	0.21200	0.22682
0.10	0.61497	0.43712	14.744	14.307	3.0339	4.9334	2.4974	0.67701	5.1072	0.24147	0.23005	1.2831	0.8504	0.24128	0.26119
0.08	0.59155	0.43015	18.008	17.578	3.0802	5.2071	2.5529	0.67486	5.7583	0.26232	0.24474	1.3492	0.8675	0.27779	0.30499
0.06	0.56369	0.42242	23.268	22.845	3.1289	5.5507	2.6148	0.67276	6.7106	0.28763	0.26088	1.4281	0.8832	0.32547	0.36372
0.04	0.52835	0.41342	33.329	32.915	3.1812	6.0210	2.6874	0.67069	8.3054	0.32043	0.27875	1.5283	0.8952	0.39287	0.44961
0.02	0.47680	0.40162	61.480	61.078	3.2409	6.7973	2.7828	0.66866	11.899	0.36946	0.29816	1.6749	0.8953	0.50578	0.60075
0.01	0.43414	0.39286	113.47	113.08	3.2777	7.5498	2.8537	0.66766	16.977	0.41086	0.30676	1.7959	0.8783	0.61306	0.75224
0	0	1/3	∞	∞	27/8	∞	27/8	2/3	∞	27/32	0	27/8	0	27/8	0

and pressure differences are useful.

Isobaric differences:

$$\Delta T_L \equiv T_L - T_{sat}, \qquad \Delta T_V \equiv T_{sat} - T_V \dots\dots\dots (12)$$

Isothermal differences:

$$\Delta p_l \equiv p_{sat} - p_l, \qquad \Delta p_v \equiv p_v - p_{sat} \dots\dots\dots\dots (13)$$

Results and discussion

The results of the calculation are displayed in Table 1, a temperature table, and Table 2, a pressure table. To complete the tables, the limiting values at $T = 0$ (or $p = 0$) were calculated analytically. These limits are shown at the foot of each table.

To enable the reader to assess the practical usefulness of the results in the tables, the results will be compared to "data" for mercury (Vargaftik 1975 and Reynolds, 1979). Mercury is the only known substance whose estimated value of Z_c is close to the van der Waals value of 3/8. Now, we do not have complete and accurate data for mercury. All the liquid metals have high critical temperatures, some of which have only been estimated. The numbers stated for T_c by various authorities show some scatter. There is much more uncertainty regarding the critical pressures and critical volumes of the liquid metals. Therefore, we have chosen a plot for comparing the results to the data which uses ony the critical temperature and avoids using the uncertain critical pressure. This is a plot of the ratio v_f/v_g against reduced temperature. This correlation may not be as widely known as the vapor-pressure curve, the Cailletet-Mathias plot (of the mean of the reduced densities of liquid and vapor against reduced temperature), etc., but it does have the advantage stated. A set of such curves was correlated as a function of ω in Lienhard (1982).

Six such curves are shown in Figure 2. The saturation data available to us for mercury stop at a temperature far short of the critical temperature. The van der Waals results, extracted from Table 1, are also shown. The closeness of the two curves, and their considerable separation from the curves for various other substances, based on the tables of Reynolds (1979), makes us expect that mercury, is indeed, close to being a van der Waals substance. To show how the ratio v_f/v_g varies over the spectrum of substances at any given temperature, a plot of the ratio against the Pitzer factor for $T = 0.7$ is shown in the inset in Figure 2. It is clear from the inset that the van der Waals equation is a legitimate member of the family of real fluids and mercury is very close to it in behavior.

Even the saturation tables of mercury and other liquid metals are incomplete. There is no liquid superheat data for any of these, and their critical constants are not accurately known. Nevertheless, the comparison made above leads to the surmise that mercury, at least, might be approximated rather well as a van der Waals fluid.

Conclusions

Tables of saturation and spinodal thermodynamic properties of the van der Waals fluid have been made available.

mercury is quite close to being a van der Waals fluid.

Nomenclature

h	=	specific enthalpy $\div RT_c$
p	=	absolute pressure $\div p_c$
p_c	=	critical pressure (Pa)
R	=	ideal gas constant (J/kg-mole-K)
s	=	specific entropy $\div R$
T	=	absolute temperature $\div T_c$
T_c	=	critical temperature (K)
u	=	specific internal energy $\div RT_c$
v	=	specific volume $\div v_c$
v_c	=	critical volume (m^3/kg)
Z_c	=	$p_c v_c / RT_c$
ω	=	Pitzer factor, $-[1 + \log p(T = 0.7)]$
Δa	=	specific availability $\div RT_c$ (see Equations (10) and (11))
Δh	=	see definitions in Equations (8) and (9)
Δp	=	see definitions in Equation (13)
ΔT	=	see definitions in Equation (12)

Subscripts

f,g	=	saturated liquid and vapor states respectively
fg	=	change of a property from saturated liquid to saturated vapor state at the same T_{sat} and p_{sat}
l, L	=	liquid spinodal points defined in Figure 1
sat	=	saturation pressure or temperature
v, V	=	vapor spinodal points defined in Figure 1

Superscript

*	=	ideal gas

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