

TEST OF SUITABILITY OF VAPOUR PRESSURE EQUATIONS FOR TEMPERATURES ABOVE NORMAL BOILING POINT

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Some equations used for expressing the temperature dependence of saturated vapour pressures of pure liquids within the range from normal boiling point up to the critical temperature are critically evaluated in the paper. Their suitability is evaluated on the basis of a statistical treatment of a set of published direct experimental data. The corresponding numerical values are summarized in tables to serve as a measure of the suitability of the correlation relations for a given type of substance and a temperature range.

Saturated vapour pressure is a significant thermodynamic property of a two-phase one-component system. It is easily accessible experimentally and therefore it is often used for the quantitative description of phase equilibrium. To express the temperature dependence of saturated vapour pressures a number of relations (for their review see ¹⁻³) was proposed. A critical evaluation of some reduced and semi-reduced equations for the range of normal and low pressures was carried out by Miller¹.

TABLE I
Equations Tested

Ref.	Symbol	Number of constants	Form of equation
4	M	4	$\log P = A + B/T + CT + DT^2$
5	FK	4	$\log P = A + B/T + C \log T + DP/T^2$
6	RW	4	$\log P_r = A + B/T_r + C \log T_r + DT_r^6$
7	RM	2	$\ln P_r = 0.9076(1 + a) \ln T_r + B(36/T_r + 42 \ln T_r - T_r^6 - 35)$
1	RPM	2	$\log P_r = A(T_r - 1/T_r) + B(1 - T_r)^3/T_r$
8	RPME	2	$\log P_r = A(T_r - 1/T_r) + B(3 + T_r)(1 - T_r)^3/T_r$
9	RFK	1	$\log P_r = (5C/9 - 40/27)(1/T_r - 1) + C \log T_r + 0.1832(P_r/T_r - 1)$
7	RK	1	$\log P_r = A(1 - 1/T_r)$

TABLE II
Substances Used and Their Critical Constants

Number	Substance	T_c K	P_c atm	Ref. T_c, P_c	Ref. data
1	Ar	150.69	48.02	10	10
2	Kr	209.46	54.48	11	11
3	Xe	289.75	58.0	12	12
4	N ₂	126.20	33.56	10	10
5	O ₂	154.33	49.71	13	13
6	H ₂ O	647.14	217.6	14	14
7	D ₂ O	643.95	213.8	15	15
8	CO ₂	304.19	72.91	16	16
9	N ₂ O	309.54	71.40	17	17
10	NO ₂	431.15	100.0	18	18
11	SF ₆	318.69	37.10	19	19
12	CH ₄	190.77	45.66	20	20
13	C ₂ H ₆	305.33	48.08	21	21
14	C ₃ H ₈	369.82	41.94	22	23
15	n-C ₄ H ₁₀	425.12	37.35	24	24
16	CH ₃ C(CH ₃) ₂ CH ₃	433.75	31.55	25	25
17	cyclo-C ₃ H ₆	389.30	55.06	26	26
18	C ₆ H ₆	562.09	48.34	22	27
19	C ₂ H ₅ CH ₂ OH	536.71	51.02	28	28
20	C ₃ H ₇ CH ₂ OH	562.98	43.55	28	28
21	CH ₃ COCH ₃	508.15	46.96	27	27
22	CH ₂ F ₂	351.65	57.54	29	29
23	CH ₃ Cl	416.25	65.9	22	30
24	CCl ₄	556.30	44.98	31	31
25	CCl ₂ F ₂	384.95	40.71	32	32
26	C ₂ F ₄ Cl ₂	418.86	32.20	33	33
27	C ₃ F ₈	345.05	26.45	22	34
28	C ₆ F ₁₄	451.0	18.1	35	35
29	2-CF ₃ C ₅ F ₁₁	452.7	18.0	35	35
30	3-CF ₃ C ₅ F ₁₁	450.0	16.7	35	35
31	C ₆ F ₆	516.67	32.30	36	36
32	C ₆ F ₅ H	531.95	34.7	37	37
33	C ₆ F ₅ Cl	570.95	31.8	37	37
34	C ₆ F ₅ CH ₃	566.52	30.85	38	38
35	CF ₃ COCF ₃	357.25	28.04	39	39
36	CF ₃ COCF ₂ Cl	410.65	28.40	39	39

TABLE III
Summary of Test Results

Symbol	Mean maximum deviation $\bar{\sigma}_{\max}$ (%) in substance groups					
	7 hydro- carbons	3 polar organic	15 halogen. organic	overall 25 organic	11 inorganic	overall 36 substances
M	0.20	0.47	0.43	0.36	0.19	0.32
FK	0.17 ^a	0.50	0.46	0.38	0.27	0.35
RW	0.19	0.45	0.42	0.35	0.16	0.30
RM	0.36	0.67	0.63	0.55	0.34	0.50
RPM	0.41	0.87	0.68 ^b	0.65	0.68	0.66
RPME	0.39	0.80	0.70	0.63	0.56	0.60
RFK	0.76	3.01	0.96	1.57	1.40	1.53
RK	1.80	4.33	1.63	2.59	2.28	2.51

^a With the exception of C_3H_8 — anomalous, ^b with the exception of CH_3Cl — anomalous.

In this work, the test of eight equations (two of them non-reduced and six reduced) is carried out which are used for correlation in the high pressure region. The form of the correlation relations is summarized in Table I. Constants of the equations were evaluated by the least square method using a statistical weight

$$w = [(\partial Y/\partial P)_T^2 \Delta P^2 + (\partial Y/\partial T)_P^2 \Delta T^2]^{-1}, \quad (1)$$

where $Y(T, P) = 0$ is the corresponding vapour pressure equation, w is the statistical weight, and ΔT or ΔP is an average error in temperature or pressure measurement, respectively. For testing, a set of 36 substances was used comprising 11 inorganic and 25 organic ones. The organic substance group consisted of 7 hydrocarbons, 2 alcohols, 1 ketone, 13 halogenated hydrocarbons, and 2 halogenated ketones. The substances used are listed in Table II. In the data of some substances, evident erroneous points were found by comparing the results of all the equations tested and these points distorted considerably the resultant deviations. These points were therefore discarded and the data were correlated once more. The summary of the test results is presented in Table III. Tables IV–X include the calculated constants of equations for the substances considered. All the data given were obtained using temperature in K and pressure in atm. The percent deviation σ was calculated from the relation

$$\sigma(\%) = 100(|P_{\text{calc}} - P_{\text{exp}}|)/P_{\text{exp}}. \quad (2)$$

TABLE IV
Values of Constants of the FK Equation

Sub- stance	$A \cdot 10^{-1}$	$-B \cdot 10^{-3}$	$-C \cdot 10^{-1}$	$D \cdot 10^{-2}$	σ_{\max} %	σ_{mean} %
1	1.05624	0.448645	0.280024	0.923351	0.11	0.04
2	1.15796	0.636703	0.302007	1.65978	0.07	0.03
3	0.997325	0.824419	0.224731	2.40502	0.26	0.10
4	1.15215	0.409404	0.330652	0.927382	0.09	0.03
5	1.25657	0.503076	0.358255	1.09672	0.57	0.14
6	1.89602	2.86645	0.438649	2.64483	0.11	0.05
7	2.34822	3.18456	0.582806	3.17574	0.14	0.03
8	2.93788	1.69566	0.894385	3.39025	0.03	0.01
9	5.03636	2.47681	1.64399	5.89045	1.24	0.14
10	-0.231356	1.38494	-0.284261	0.666376	0.12	0.03
11	4.66030	2.42199	1.51166	11.1884	0.20	0.11
12	1.43432	0.648250	0.418319	2.02603	0.21	0.06
13	1.73620	1.18504	0.483841	4.33184	0.03	0.02
14	—	—	—	—	—	—
15	2.37187	2.02367	0.670287	11.2431	0.02	0.01
16	2.23434	1.99781	0.624095	13.1348	0.04	0.01
17	1.86421	1.60478	0.503368	6.23324	0.10	0.04
18	-0.502392	0.975062	-0.308510	-2.77243	0.61	0.24
19	4.63455	4.40286	1.34176	10.8422	0.36	0.12
20	5.43328	5.02905	1.60017	18.3522	0.34	0.13
21	3.98023	3.41633	1.17169	16.4794	0.79	0.31
22	1.76646	1.51672	0.461575	3.42546	0.64	0.22
23	-0.450667	0.692596	-0.306833	-1.25511	0.12	0.03
24	1.70982	2.20746	0.424329	11.7816	0.49	0.19
25	2.42287	1.83963	0.699899	9.28280	0.12	0.05
26	4.46380	3.01208	1.38561	21.4170	1.39	0.50
27	2.54663	1.85155	0.743811	8.93458	0.45	0.17
28	4.77424	3.63885	1.45922	35.3626	0.84	0.41
29	3.46325	2.97353	1.01842	27.0934	0.36	0.19
30	3.08924	2.78902	0.892112	23.8290	0.12	0.09
31	2.48996	2.75093	0.672109	14.0232	0.09	0.03
32	1.09331	1.99122	0.209892	5.64657	0.57	0.21
33	2.88912	3.20887	0.798055	24.4846	0.86	0.55
34	2.38904	2.97257	0.628650	16.0244	0.22	0.05
35	2.83303	2.05504	0.835954	9.65448	0.36	0.13
36	3.03070	2.41097	0.888162	13.6583	0.30	0.10

TABLE V
Values of Constants of the M Equation

Sub- stance	$A \cdot 10^{-1}$	$-B \cdot 10^{-3}$	$-C \cdot 10^1$	$D \cdot 10^4$	σ_{\max} %	σ_{mean} %
1	0.548680	0.399901	0.141360	0.430797	0.10	0.04
2	0.568052	0.564046	0.109787	0.238825	0.08	0.03
3	0.514898	0.739929	0.054945	0.090096	0.21	0.09
4	0.585850	0.363329	0.205428	0.714695	0.12	0.04
5	0.615587	0.442741	0.187840	0.549069	0.65	0.14
6	0.962083	0.275302	0.078354	0.048750	0.16	0.08
7	1.18579	3.18588	0.117065	0.071343	0.17	0.04
8	1.92313	2.18985	0.530113	0.643647	0.04	0.01
9	10.8183	11.0655	3.50105	3.94409	0.07	0.02
10	0.654465	1.76903	0.035235	0.057895	0.14	0.04
11	4.39647	4.76311	1.35042	1.53458	0.34	0.18
12	0.688218	0.584948	0.199116	0.451175	0.18	0.07
13	0.850777	1.13322	0.171763	0.228464	0.05	0.03
14	-0.864168	-0.493778	-0.374670	-0.360506	0.33	0.14
15	1.20321	2.11273	0.210916	0.192348	0.05	0.03
16	1.03083	1.94123	0.164138	0.148035	0.07	0.03
17	0.832724	1.47034	0.122602	0.125312	0.14	0.05
18	0.187911	1.09469	-0.046012	-0.026448	0.57	0.22
19	1.63409	3.81265	0.214243	0.137771	0.36	0.12
20	1.83957	4.31847	0.248250	0.154297	0.34	0.12
21	1.39373	2.92126	0.205777	0.152666	0.72	0.27
22	0.868493	1.41903	0.138083	0.158979	0.66	0.22
23	0.255041	0.848602	-0.044908	-0.032453	0.13	0.03
24	0.759426	2.00900	0.071269	0.052770	0.52	0.18
25	1.11854	1.79097	0.210914	0.215636	0.19	0.07
26	1.72592	2.76162	0.355253	0.326119	0.73	0.29
27	1.04878	1.65509	0.199829	0.220436	0.47	0.17
28	2.16841	3.75954	0.431595	0.362490	0.74	0.38
29	1.57910	2.95916	0.287740	0.245188	0.41	0.20
30	1.52657	2.90845	0.270732	0.227204	0.10	0.06
31	1.12106	2.62001	0.146066	0.109244	0.19	0.05
32	0.618543	1.87831	0.035590	0.027415	0.53	0.21
33	1.07167	2.76886	0.127795	0.090144	0.94	0.50
34	1.16224	2.96776	0.140373	0.095268	0.25	0.05
35	1.22869	1.91361	0.248460	0.265956	0.42	0.13
36	1.35501	2.33791	0.252433	0.235048	0.29	0.08

TABLE VI
Values of Constants of the RW Equation

Sub- stance	$A \cdot 10^{-1}$	$-B \cdot 10^{-1}$	$-C$	$D \cdot 10$	σ_{\max} %	σ_{mean} %
1	0.245911	0.251893	0.869297	0.596940	0.09	0.02
2	0.248274	0.254575	0.952190	0.629317	0.07	0.03
3	0.237296	0.242439	0.505968	0.479920	0.16	0.06
4	0.266893	0.273269	1.22734	0.634606	0.08	0.03
5	0.261467	0.269210	1.25674	0.769913	0.58	0.13
6	0.407486	0.417918	3.48038	1.03866	0.10	0.04
7	0.445840	0.457991	4.54834	1.22140	0.15	0.03
8	0.590311	0.609172	9.75136	1.88413	0.03	0.01
9	2.95305	3.05891	78.2399	10.5866	0.07	0.03
10	0.334420	0.341472	-2.10239	0.708481	0.12	0.03
11	1.02019	1.05949	22.7842	3.90836	0.29	0.15
12	0.265737	0.273597	1.48462	0.784893	0.19	0.07
13	0.318554	0.327200	2.43391	0.862868	0.04	0.02
14	-0.089629	-0.105736	-10.8198	-1.64737	0.33	0.14
15	0.422467	0.455301	4.97756	1.28280	0.04	0.02
16	0.391090	0.401919	3.99076	1.07922	0.06	0.02
17	0.329063	0.337780	2.54356	0.868607	0.12	0.04
18	0.182263	0.179609	-2.83295	-0.274702	0.58	0.23
19	0.721382	0.735765	10.7323	1.43318	0.35	0.12
20	0.769235	0.787043	12.5487	1.78603	0.35	0.13
21	0.530274	0.545487	7.35116	1.54497	0.75	0.28
22	0.385149	0.395328	3.27428	1.01208	0.61	0.22
23	0.189267	0.187665	-2.31093	-0.162886	0.14	0.03
24	0.335208	0.343284	2.25693	0.792372	0.50	0.19
25	0.405334	0.418262	4.65378	1.28924	0.17	0.06
26	0.526293	0.546091	8.04072	1.97230	0.75	0.32
27	0.461552	0.473302	5.19615	1.15947	0.45	0.16
28	0.764106	0.794697	14.0942	3.04963	0.79	0.37
29	0.578154	0.598431	8.31842	2.00772	0.40	0.19
30	0.576592	0.593903	7.99822	1.70815	0.11	0.07
31	0.482435	0.495492	5.43700	1.30509	0.12	0.03
32	0.340101	0.344105	1.07278	0.368239	0.52	0.21
33	0.448638	0.462297	4.64636	1.44550	0.92	0.50
34	0.469208	0.480738	4.81686	1.15100	0.21	0.05
35	0.509904	0.524709	6.55954	1.49010	0.33	0.12
36	0.521087	0.537041	7.05754	1.60771	0.30	0.09

TABLE VII
Values of Constants of the RM Equation

Substance	$a \cdot 10^{-1}$	$-B$	σ_{\max} %	σ_{mean} %
1	0.540358	0.167339	0.23	0.11
2	0.541118	0.168273	0.19	0.08
3	0.548479	0.163319	0.64	0.20
4	0.562196	0.183146	0.27	0.09
5	0.561124	0.169906	0.69	0.14
6	0.742541	0.274942	0.25	0.10
7	0.746886	0.305529	0.23	0.07
8	0.655796	0.285857	0.08	0.04
9	0.627866	0.345754	0.21	0.09
10	1.11805	0.245040	0.21	0.09
11	0.667582	0.123153	0.75	0.35
12	0.549298	0.171238	0.19	0.07
13	0.595347	0.216294	0.06	0.03
14	0.621951	0.227039	0.71	0.25
15	0.649414	0.259459	0.07	0.03
16	0.646526	0.260688	0.10	0.03
17	0.612372	0.224471	0.11	0.05
18	0.664508	0.189529	1.25	0.56
19	0.826672	0.564268	0.60	0.24
20	0.799535	0.570484	0.58	0.23
21	0.701822	0.360398	0.82	0.32
22	0.701720	0.258695	0.68	0.22
23	0.633869	0.214567	0.67	0.33
24	0.653180	0.231993	0.49	0.22
25	0.641315	0.240964	0.30	0.06
26	0.688471	0.237374	0.99	0.35
27	0.714990	0.314511	0.49	0.18
28	0.794537	0.392371	1.24	0.64
29	0.805012	0.284424	0.71	0.39
30	0.789916	0.349786	0.64	0.27
31	0.760067	0.324596	0.10	0.04
32	0.743026	0.277377	0.86	0.31
33	0.758601	0.303407	1.21	0.60
34	0.770762	0.340169	0.31	0.07
35	0.732123	0.334462	0.36	0.15
36	0.721933	0.334408	0.34	0.13

TABLE VIII
Values of Constants of the RPM Equation

Substance	$A \cdot 10^{-1}$	$-B \cdot 10^{-1}$	σ_{\max} %	σ_{mean} %
1	0.127100	0.177562	1.11	0.36
2	0.127339	0.178675	0.57	0.30
3	0.128771	0.171906	0.88	0.35
4	0.131432	0.201609	0.92	0.28
5	0.131365	0.179631	0.56	0.25
6	0.167300	0.315369	1.28	0.33
7	0.167255	0.401704	0.41	0.11
8	0.149014	0.419251	0.08	0.04
9	0.143485	0.531927	0.21	0.09
10	0.240697	0.266123	0.34	0.19
11	0.151289	0.151974	0.75	0.35
12	0.128396	0.199953	0.25	0.08
13	0.137278	0.281513	0.11	0.04
14	0.142377	0.311155	0.71	0.25
15	0.147895	0.351388	0.05	0.03
16	0.147374	0.349631	0.10	0.04
17	0.140791	0.282334	0.25	0.09
18	0.150980	0.220087	1.39	0.68
19	0.183320	0.791900	0.90	0.33
20	0.177944	0.802264	0.86	0.35
21	0.158597	0.481734	0.85	0.35
22	0.159271	0.296261	1.02	0.37
23	—	—	—	—
24	0.149126	0.275353	0.78	0.27
25	0.146429	0.311907	0.26	0.06
26	0.155711	0.304439	0.95	0.34
27	0.161447	0.396615	0.63	0.25
28	0.177704	0.494524	0.89	0.56
29	0.178896	0.358924	0.65	0.37
30	0.175910	0.463628	0.64	0.23
31	0.170577	0.401232	0.39	0.14
32	0.166681	0.344445	1.08	0.39
33	0.169921	0.380894	1.37	0.65
34	0.171950	0.459094	0.37	0.11
35	0.164933	0.419963	0.65	0.25
36	0.162640	0.434597	0.39	0.15

TABLE IX
Values of Constants of the RPME Equation

Substance	$A \cdot 10^{-1}$	$-B$	σ_{\max} %	σ_{mean} %
1	0.126743	0.503278	0.93	0.27
2	0.127031	0.502979	0.42	0.23
3	0.128473	0.483333	0.70	0.29
4	0.131084	0.566186	0.74	0.22
5	0.131037	0.505091	0.60	0.19
6	0.166779	0.886890	1.08	0.24
7	0.167107	1.07906	0.34	0.10
8	0.148990	1.08380	0.08	0.04
9	0.143483	1.35506	0.21	0.09
10	0.240519	0.724582	0.30	0.16
11	0.151290	0.390377	0.75	0.35
12	0.128270	0.545137	0.22	0.07
13	0.137202	0.750636	0.09	0.04
14	0.142328	0.820722	0.71	0.25
15	0.147837	0.928956	0.05	0.03
16	0.147297	0.928424	0.09	0.04
17	0.140655	0.762626	0.21	0.08
18	0.150700	0.612236	1.35	0.65
19	0.182966	2.13263	0.84	0.29
20	0.177590	2.16175	0.75	0.31
21	0.158369	1.30079	0.82	0.34
22	0.158835	0.828129	0.89	0.30
23	0.144626	0.742516	1.06	0.38
24	0.148904	0.756511	0.66	0.25
25	0.146338	0.833166	0.27	0.05
26	0.155673	0.801843	0.96	0.35
27	0.161132	1.08518	0.57	0.23
28	0.177550	1.32913	0.95	0.58
29	0.178843	0.952870	0.66	0.38
30	0.175800	1.23506	0.64	0.24
31	0.170215	1.10099	0.29	0.10
32	0.166411	0.943890	0.99	0.36
33	0.169609	1.04264	1.29	0.63
34	0.171816	1.22727	0.34	0.10
35	0.164566	1.15375	0.54	0.21
36	0.162430	1.17534	0.37	0.14

TABLE X
Values of Constants of the RFK and RK Equations

Substance	RFK equation			RK equation		
	$-C$	σ_{\max} %	σ_{mean} %	A	σ_{\max} %	σ_{mean} %
1	2.60805	0.24	0.11	2.33302	2.99	1.46
2	2.62509	0.27	0.13	2.33166	2.31	1.49
3	2.68372	0.87	0.62	2.34947	3.01	1.73
4	3.04705	0.18	0.05	2.42621	1.81	1.04
5	2.92161	1.05	0.46	2.39720	2.84	1.32
6	6.44187	2.14	0.99	3.14821	2.78	0.74
7	6.80599	0.23	0.08	3.17665	1.11	0.43
8	5.00442	0.08	0.04	2.87928	0.57	0.24
9	4.48227	0.22	0.09	2.80827	0.28	0.19
10	13.0386	9.20	5.27	4.41740	6.14	2.99
11	5.06192	0.89	0.35	2.89274	1.20	0.63
12	2.76879	0.67	0.21	2.38267	2.12	0.90
13	3.74448	0.18	0.08	2.59824	1.30	0.59
14	4.26293	0.77	0.27	2.71083	1.41	0.62
15	4.85202	0.12	0.05	2.81939	0.88	0.57
16	4.80403	0.11	0.06	2.80648	0.96	0.58
17	4.07878	0.26	0.06	2.65358	1.29	0.73
18	4.75265	3.18	1.18	2.79305	4.67	1.43
19	9.32141	3.26	2.02	3.61959	4.57	1.56
20	8.88723	3.82	2.30	3.53705	6.43	1.76
21	6.20145	1.95	0.85	3.06001	1.98	0.47
22	5.71310	1.56	0.71	2.98884	1.88	0.87
23	4.40883	1.06	0.32	2.72053	2.46	0.81
24	4.79255	0.84	0.42	2.79641	1.63	1.00
25	4.65037	0.42	0.10	2.76938	1.24	0.69
26	5.53362	1.29	0.35	2.95439	2.11	0.86
27	6.28369	1.01	0.39	3.07991	1.36	0.66
28	8.04749	1.71	0.69	3.41640	2.20	1.18
29	7.82368	0.80	0.45	3.37407	1.79	1.02
30	7.76335	0.63	0.25	3.36260	1.08	0.64
31	7.13288	0.24	0.06	3.24782	1.34	0.39
32	6.57442	1.19	0.54	3.14780	1.47	0.78
33	6.99657	1.21	0.63	3.21937	1.65	0.51
34	7.37598	0.51	0.17	3.29111	0.79	0.47
35	6.70679	1.13	0.65	3.16494	2.46	0.83
36	6.48458	0.80	0.51	3.11689	0.93	0.43

RESULTS AND DISCUSSION

The best results were obtained with both non-reduced equations M and FK and, according to its properties, with the coinciding equation RW, too. These three relations are practically identical as to their accuracy. The most reliable from the three equations said is the RW equation which, like the M equation, in no case shows maximum deviation σ_{\max} larger than 1%. The FK equation is, from this group, the most sensitive to the quality of correlated data. The group of two-constant reduced equations RM, RPM, and RPME is very good as well. A lower accuracy in comparison with the first group is compensated by the possibility of easier and quicker computation. Relatively the worst results, especially for polar substances, are obtained in case of the RFK and RK equations. It is to be noted that the highest deviations with the RK equation occur in the region around normal boiling point and towards the critical region, the accuracy is substantially higher. Both equations contain only one constant, which simplifies considerably the computation, especially in case of the RK equation. All reduced equations require the knowledge of good critical data.

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