Density-Temperature Formulae for Coexisting Liquid and Vapor and for Freezing Liquid Parahydrogen

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A single formula is given for coexistence temperature as a continuous function of the vapor-liquid densities. With six coefficients and seven adjusted exponents, it may conveniently replace the several formulae formerly used in separate regions of the data. Freezing liquid densities are described by a simple power law in temperature, replacing more complicated formulae. Computed results are tabulated and compared with the derived data.

Key Words: Coexistence densities, freezing liquid densities, hydrogen, melting-line liquid densities, orthobaric densities, parahydrogen, vapor-liquid equilibrium.

1. Introduction

Data for densities of the coexisting phases of parahydrogen are derived, not directly experimental. They were obtained as intersections of PVT isochores and isotherms with vapor-pressure and melting-line formulae for $P(T)$ at coexistence [1, 2].[1] Any concise description of these densities is a useful computational aid, as for example, to obtain heats of transition via the Clapeyron and $P(T)$ equations. In [1], however, we had used three formulae, in three regions of the orthobaric densities, with a total of 14 coefficients and about 12 adjusted exponents. The present search for a single formula for orthobaric densities was motivated by the successful application of Ehrlich's simple formula for saturated liquid [5] to our parahydrogen data. This is reported below.

Background on fluid behavior is given by [3], and quantum effects are under study [4]. Additional references on parahydrogen are given in the monograph [6]. Useful with the Clapeyron equation are recent determinations of heats of fusion [7] and of densities of solid parahydrogen [8]. The words: coexisting; at coexistence; orthobaric; at saturation; and saturated vapor, liquid or solid, all refer to one or more of at least two phases in equilibrium. The NBS–1955 low temperature scale used here is the same as in [6], and we define one liter, L, to be 1000 cm³.

2. Ehrlich's Formula for Saturated Liquid Parahydrogen

Ehrlich's formula, eq (1), employs reduced variables, $\rho \equiv D/D_c$, $\tau \equiv T/T_c$ (where D and T are density and

temperature, with subscript c referring to the critical point),

$$(\rho - 1)^3/\rho = A \cdot (1 - \tau) + B \cdot (1 - \tau)^2. \tag{1}$$

We used iterative methods and a digital computer to find the critical constants for eq (1) which minimize the mean relative deviation between calculated densities and 46 pairs of data for $\rho(\tau)$ [1]. This form of deviation was selected because the data are not directly experimental. Largest relative deviations occur near the critical point and are tabulated in summarizing table 1, while those near the triple point are plotted in figure 1 as open circles. [We define Δ, $\% \equiv 100 \cdot (D_{calc} - D_{ref})/D_{ref}.$] Most of the remaining deviations are a mere few hundredths of 1 percent. It is seen that this formula gives an excellent representation of the data.

TABLE 1. *Ehrlich's formula for saturated liquid parahydrogen*

Constants $T_c = 32.984\ 38\ °K$, $D_c = 15.17685\ g\ mol/L$,
$A = 2.859\ 125$, $B = -0.820\ 205$

Mean deviation (46 points) = 0.0432 percent

Maximum relative deviations near critical point

T, °K	Δ, %	T, °K	Δ, %
32.914	0.000	32.363	−0.044
32.739	−0.195	32.039	−0.140
32.579	−0.110	32.000	+0.038

3. A Formula for Densities of Coexisting Vapor and Liquid

In attempting to modify Ehrlich's formula for densities below critical we note that as $\rho \to 0$ the familiar vapor-pressure and virial equations provide a relation between temperature and density,

$$P \sim P_0 \cdot \exp(-T_0/T) \sim D \cdot R \cdot T,$$

[1] Figures in brackets indicate the literature references at the end of this paper.
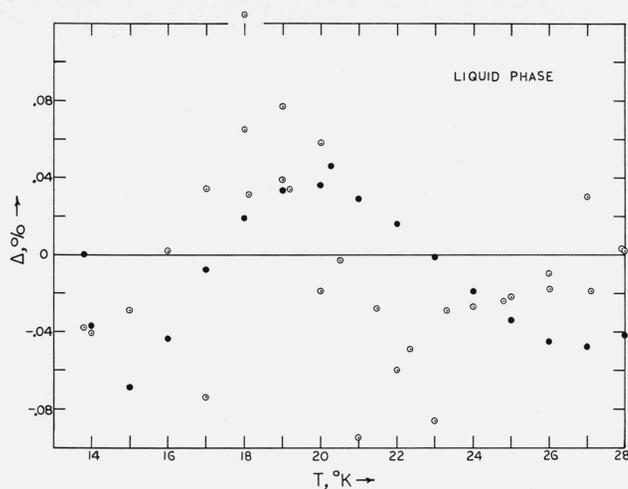
FIGURE 1. *Comparison of calculated densities.*
$\triangle \equiv 100 \cdot (D_{calc} - D_{ref})/D_{ref}$: Open circles, Ehrlich's formula with constants of table 1, using for D_{ref} the derived data of [1]; filled circles from table 4, this report.

FIGURE 2. $Y(\alpha, \beta, \rho, \tau)$ *versus* ρ *for* $\alpha = 2.97647, \beta = 8.$

where P is pressure, R is the gas constant, and P_0, T_0 are constants. At coexistence, $D \cdot R \cdot T$ may be regarded as a function only of the density. Normalizing the above exponential at the critical point in the form, $\exp[\alpha \cdot (1 - 1/\tau)]$ where α is a constant, and comparing its Taylor's series expansion about $\tau = 1$ with eq (1), we have been led to the formula,

$$\exp[\alpha \cdot (1 - 1/\tau)] = 1 - (\rho - 1)^{\beta/3}/\exp[\rho \cdot f(\rho)], \quad (2)$$

wherein $\beta/3$ replaces exponent 3 from eq (1), and $f(\rho)$ is discussed below. This is a single-valued expression for coexistence temperature as a function of the densities, constrained to a given critical point. As the variable τ ranges from 0 to +1 only, β must be an even integer. The expression $[1 - (\rho - 1)^{\beta/3}]$ becomes negative for $2 < \rho \leqslant 2.45$ where $\rho = 2.45$ is the upper limit for liquid parahydrogen at the triple point.

The exponential on the right side of eq (2) has been introduced as an empirical method for seeking representation of data. We let $f(\rho)$ be a polynomial, and search for the requisite number of terms and powers of ρ, finding coefficients by least-squares in the form $Y/\rho = f(\rho)$, where

$$Y(\alpha, \beta, \rho, \tau) \equiv \mathrm{Log}_e \{(\rho - 1)^{\beta/3}/[1 - e^{\alpha(1 - 1/\tau)}]\}.$$

For each trial β and each form, $f(\rho)$, the value of α is found by an iterative procedure with the high-speed computer. By requisite number of terms and powers of ρ in this report we mean that combination which yields deviations comparable with uncertainty of the data, and a mean relative deviation less than 0.1 percent. We have used only the critical-point constants established by [1], not to be confused with the optimizing values in table 1.

With 75 pairs of data for $\tau(\rho)$ [1], the behavior of Y versus ρ is highly sensitive to the values of α and of β. For $\beta = 6$ and for $\beta = 10$ we find that Y apparently
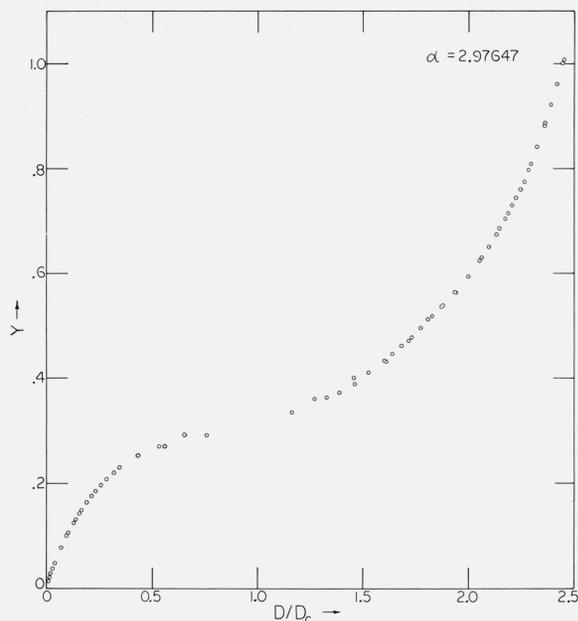
tends to infinite discontinuities as $\rho \to 1$, from below or from above, whereas for $\beta = 8$ the behavior is seen in figure 2, for which $\alpha = 2.97647$, $\beta = 8$. This plot has the qualitative behavior of an isotherm of pressure versus density at temperatures a little above critical, suggesting a cubic polynomial in the density, [or a quadratic for $f(\rho)$ in eq (2)]. Tedious exploration of forms for $f(\rho)$, however, yields

$$f(\rho) \equiv A_1 + A_2 \cdot \rho^{-1/3} + A_3 \cdot \rho^{1/3}$$
$$+ A_4 \cdot \rho^{8/3} + A_5 \cdot \rho^3 + A_6 \cdot \rho^7, \quad (3)$$

to complete eq (2) with above values for α, β. Integer exponents only were explored for the last two terms in eq (3). Mean relative deviation of temperatures using eq (3) is 0.0624 percent. As compared with a three-term expression for $f(\rho)$, we note that an additional term, $A_2 \cdot \rho^{-1/3}$, has been required for data at the lowest densities, and an opposition of similar terms, $A_4 \cdot \rho^{8/3} + A_5 \cdot \rho^{9/3}$, (with opposite signs) apparently is required for the critical region (fig. 2).

TABLE 2. *Constants for eqs (2), (3), parahydrogen*

$D_c = 15.59$ g mol/L,	$T_c = 32.976$ °K
$\alpha = 2.97647$,	$\beta = 8$,
$A_1 = +2.030\ 0583$,	$A_2 = -0.058\ 7951$,
$A_3 = -1.856\ 5706$,	$A_4 = +0.620\ 5095$,
$A_5 = -0.421\ 81139$,	$A_6 = +0.682\ 5745 \cdot 10^{-3}$

Table 2 gives constants for eqs (2) and (3). Table 3 compares calculated temperatures from eq (2) with the data. Table 4 gives densities obtained from eq (2) by an iterative method at integral temperatures, and compares them with densities calculated in [1] with

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TABLE 3. *Comparison of calculated temperatures from eq (2) with data of [1]*

DENSTY	T,DATA	T,CALC	T,DIFF	PERCNT	DENSTY	T,DATA	T,CALC	T,DIFF	PERCNT
0.0624	13.8030	13.8051	0.0021	0.0150	25.5526	30.7490	30.7516	0.0026	0.0083
0.0686	13.9900	13.9912	0.0012	0.0082	26.2284	30.3430	30.3445	0.0015	0.0049
0.1100	14.9900	14.9908	0.0008	0.0054	26.7454	30.0000	30.0049	0.0049	0.0163
0.1671	15.9900	15.9889	-0.0011	-0.0071	26.9633	29.8540	29.8543	0.0003	0.0009
0.2430	16.9900	16.9872	-0.0028	-0.0167	27.6451	29.3560	29.3534	-0.0026	-0.0089
0.3409	17.9900	17.9860	-0.0040	-0.0220	28.1314	29.0000	28.9680	-0.0320	-0.1102
0.4642	18.9900	18.9857	-0.0043	-0.0226	28.4499	28.7240	28.7026	-0.0214	-0.0744
0.6164	19.9900	19.9850	-0.0050	-0.0248	29.2443	28.0000	27.9941	-0.0059	-0.0210
0.6636	20.2680	20.2584	-0.0096	-0.0472	29.3123	27.9360	27.9303	-0.0057	-0.0204
1.0850	22.2290	22.2269	-0.0021	-0.0094	30.1841	27.0780	27.0664	-0.0116	-0.0429
1.4969	23.6510	23.6539	0.0029	0.0121	30.2437	27.0000	27.0041	0.0041	0.0153
1.6141	24.0000	24.0032	0.0032	0.0132	31.1471	26.0180	26.0086	-0.0094	-0.0360
1.9919	25.0000	25.0053	0.0053	0.0211	31.1602	26.0000	25.9935	-0.0065	-0.0252
2.1612	25.3940	25.4038	0.0098	0.0387	31.9866	25.0000	24.9917	-0.0083	-0.0332
2.4423	26.0000	26.0100	0.0100	0.0385	32.1482	24.7940	24.7853	-0.0087	-0.0353
2.5671	26.2510	26.2597	0.0087	0.0330	32.7264	24.0000	24.0169	0.0169	0.0702
2.9764	27.0000	27.0074	0.0074	0.0275	33.2393	23.3010	23.2947	-0.0063	-0.0270
3.3330	27.5760	27.5836	0.0076	0.0274	33.4635	23.0000	22.9665	-0.0335	-0.1457
3.6197	28.0000	28.0041	0.0041	0.0148	33.8838	22.3440	22.3296	-0.0144	-0.0643
3.9821	28.4870	28.4890	0.0020	0.0072	34.1067	22.0000	21.9801	-0.0199	-0.0907
4.4062	29.0000	28.9991	-0.0009	-0.0030	34.4222	21.4730	21.4706	-0.0024	-0.0113
4.9653	29.5900	29.5913	0.0013	0.0042	34.6992	21.0000	21.0085	0.0085	0.0406
5.3972	30.0000	29.9951	-0.0049	-0.0163	34.9837	20.5070	20.5189	0.0119	0.0581
6.7196	31.0000	30.9979	-0.0021	-0.0067	35.2509	19.9950	20.0445	0.0495	0.2477
6.7864	31.0480	31.0406	-0.0074	-0.0239	35.2753	20.0000	20.0005	0.0005	0.0024
8.3122	31.8470	31.8460	-0.0010	-0.0032	35.5966	19.3900	19.4087	0.0187	0.0963
8.6917	32.0000	32.0021	0.0021	0.0065	35.7845	18.9930	19.0521	0.0591	0.3111
10.1455	32.4720	32.4671	-0.0049	-0.0152	35.7945	19.0000	19.0329	0.0329	0.1731
11.8156	32.7870	32.7871	0.0001	0.0004	36.2498	18.1150	18.1336	0.0186	0.1028
18.1181	32.9140	32.9140	-0.0000	-0.0001	36.2733	18.0000	18.0858	0.0858	0.4768
19.8043	32.7390	32.7375	-0.0015	-0.0044	36.2989	17.9920	18.0336	0.0416	0.2313
20.7043	32.5790	32.5801	0.0011	0.0033	36.7931	16.9910	16.9931	0.0021	0.0121
21.6233	32.3630	32.3668	0.0038	0.0116	36.8288	17.0000	16.9155	-0.0845	-0.4973
22.7261	32.0390	32.0340	-0.0050	-0.0155	37.2633	15.9900	15.9458	-0.0442	-0.2767
22.7996	32.0000	32.0087	0.0087	0.0273	37.7102	14.9900	14.9117	-0.0783	-0.5224
23.8347	31.6020	31.6082	0.0062	0.0196	38.1286	13.9900	13.9609	-0.0291	-0.2083
24.9013	31.1040	31.1057	0.0017	0.0055	38.2029	13.8030	13.8030	0.0000	0.0002
25.0790	31.0000	31.0127	0.0127	0.0410	38.2029	13.8030	13.8030	0.0000	0.0002

MEAN DEVIATION, PERCENT = 0.0624

the more elaborate formulae. Table 5 gives temperatures from eq (2) at uniformly spaced densities and compares them with values from the monograph [6].

Deviations of temperature (table 3) are relatively large and uniform for liquid densities approaching the triple point, giving alarm that the large exponents used in eq (3) may be responsible. From [6] we find, however, that $(\rho/\tau)(d\tau/d\rho) \approx 3$ to 6 in this region, so that relative temperature deviations will be roughly fivefold greater than corresponding density deviations. We note, also, the experimentalist's estimate of 0.1 percent accuracy [9] for much of the density data used in [1]. Turning to deviations in density, we see in figure 1 that those from eq (2), filled circles, are smaller than or comparable with those from the simple formula eq (1). [To avoid a multiplicity of tables, we have compared densities from eq (2) with the sufficiently precise, calculated results from [1]; hence the relative difference also is a smooth function.] It appears highly improbable that deviations of eq (2) are due entirely to the form of $f(\rho)$ in eq (3). With data for other substances, however, we may expect that this form should be modified.

TABLE 4. *Comparison of calculated densities from eq (2) at uniform temperatures with calculated data of [1]*

CALCULATED DENSITIES, GMOL/L

T,DG.K	VAPOR PHASE			LIQUID PHASE		
	CALCLTD	REFRNCE	DIFRNCE	CALCLTD	REFRNCE	DIFRNCE
13.803	0.0623	0.0624	-0.0001	38.2030	38.2068	-0.0038
14.000	0.0689	0.0690	-0.0001	38.1105	38.1246	-0.0141
15.000	0.1104	0.1104	0.0000	37.6723	37.6984	-0.0261
16.000	0.1678	0.1678	0.0000	37.2395	37.2552	-0.0157
17.000	0.2441	0.2440	0.0001	36.7899	36.7928	-0.0029
18.000	0.3424	0.3420	0.0004	36.3153	36.3086	0.0067
19.000	0.4662	0.4653	0.0009	35.8116	35.7997	0.0119
20.000	0.6189	0.6176	0.0013	35.2755	35.2628	0.0127
20.268	0.6653	0.6636	0.0017	35.1260	35.1100	0.0160
21.000	0.8048	0.8030	0.0018	34.7042	34.6940	0.0102
22.000	1.0284	1.0273	0.0011	34.0941	34.0886	0.0055
23.000	1.2955	1.2956	-0.0001	33.4409	33.4411	-0.0002
24.000	1.6130	1.6145	-0.0015	32.7387	32.7448	-0.0061
25.000	1.9897	1.9926	-0.0029	31.9801	31.9910	-0.0109
26.000	2.4374	2.4413	-0.0039	31.1546	31.1685	-0.0139
27.000	2.9721	2.9762	-0.0041	30.2476	30.2622	-0.0146
28.000	3.6168	3.6201	-0.0033	29.2380	29.2502	-0.0122
29.000	4.4070	4.4082	-0.0012	28.0922	28.0991	-0.0069
30.000	5.4027	5.4006	0.0021	26.7526	26.7520	0.0006
31.000	6.7228	6.7170	0.0058	25.1029	25.0946	0.0083
32.000	8.6864	8.6800	0.0064	22.8246	22.8145	0.0101
32.400	9.8926	9.8880	0.0046	21.4947	21.4887	0.0060
32.700	11.2457	11.2425	0.0032	20.0459	20.0463	-0.0004
32.900	12.8997	12.8921	0.0076	18.3203	18.3247	-0.0044

TABLE 5. *Comparison of calculated temperatures from eq (2) at uniform densities with derived results from [6]*

Density	Temperature, deg. K			Density	Temperature, deg. K		
	Calculated	Reference	Difference		Calculated	Reference	Difference
0.5	19.240	19.243	− 0.003	19.5	32.780	32.780	0.000
1.0	21.882	21.887	− 0.005	20.0	32.707	32.707	0.000
1.5	23.663	23.660	0.003	20.5	32.620	32.620	0.000
2.0	25.025	25.018	0.007	21.0	32.517	32.517	0.000
2.5	26.127	26.119	0.008	21.5	32.399	32.397	0.002
3.0	27.048	27.041	0.007	22.0	32.263	32.261	0.002
3.5	27.833	27.828	0.005	22.5	32.109	32.106	0.003
4.0	28.512	28.509	0.003	23.0	31.938	31.934	0.004
4.5	29.104	29.103	0.001	23.5	31.747	31.742	0.005
5.0	29.625	29.626	− 0.001	24.0	31.536	31.532	0.004
5.5	30.085	30.087	− 0.002	24.5	31.306	31.301	0.005
6.0	30.492	30.495	− 0.003	25.0	31.054	31.050	0.004
6.5	30.853	30.856	− 0.003	25.5	30.782	30.778	0.004
7.0	31.172	31.176	− 0.004	26.0	30.487	30.484	0.003
7.5	31.455	31.459	− 0.004	26.5	30.169	30.168	0.001
8.0	31.705	31.709	− 0.004	27.0	29.828	29.829	− 0.001
8.5	31.925	31.928	− 0.003	27.5	29.464	29.466	− 0.002
9.0	32.118	32.120	− 0.002	28.0	29.075	29.080	− 0.005
9.5	32.285	32.287	− 0.002	28.5	28.660	28.668	− 0.008
10.0	32.429	32.430	− 0.001	29.0	28.219	28.229	− 0.010
10.5	32.552	32.553	− 0.001	29.5	27.752	27.764	− 0.012
11.0	32.656	32.656	− 0.000	30.0	27.256	27.270	− 0.014
11.5	32.741	32.742	− 0.001	30.5	26.732	26.747	− 0.015
12.0	32.811	32.811	− 0.000	31.0	26.178	26.194	− 0.016
12.5	32.866	32.866	− 0.000	31.5	25.592	25.608	− 0.016
13.0	32.907	32.908	− 0.001	32.0	24.975	24.988	− 0.013
13.5	32.937	32.938	− 0.001	32.5	24.323	24.334	− 0.011
14.0	32.957	32.958	− 0.001	33.0	23.637	23.642	− 0.005
14.5	32.969	32.970	− 0.001	33.5	22.912	22.912	0.000
15.0	32.975	32.975	− 0.000	34.0	22.148	22.141	0.007
15.5	32.976	32.976	− 0.000	34.5	21.342	21.327	0.015
16.0	32.976	32.975	0.001	35.0	20.490	20.469	0.021
16.5	32.972	32.972	− 0.000	35.5	19.589	19.564	0.025
17.0	32.963	32.963	− 0.000	36.0	18.633	18.612	0.021
17.5	32.946	32.947	− 0.001	36.5	17.618	17.609	0.009
18.0	32.921	32.922	− 0.001	37.0	16.539	16.556	− 0.017
18.5	32.886	32.886	0.000	37.5	15.401	15.451	− 0.050
19.0	32.839	32.840	− 0.001	38.0	14.245	14.295	− 0.050

TABLE 6. *Comparison of calculated densities of freezing liquid with derived data from [2]* [a]

T, deg. K	Publication			Above formula	
	D, data	D, calc	D, percent	D, calc	D, percent
14.171	38.50	38.51	0.03	38.516	0.042
14.416	38.70	38.72	0.05	38.722	0.056
14.764	39.00	39.00	0.01	39.010	0.024
15.247	39.39	39.40	0.01	39.401	0.029
15.375	39.50	39.50	0.01	39.504	0.009
16.006	40.00	39.99	− 0.01	40.000	0.000
16.030	40.02	40.01	− 0.02	40.019	− 0.003
16.655	40.50	40.49	− 0.02	40.497	− 0.008
16.790	40.60	40.59	− 0.01	40.598	− 0.004
17.000	40.76	40.75	− 0.02	40.755	− 0.012
17.323	41.00	40.99	− 0.02	40.994	− 0.015
17.506	41.13	41.13	− 0.01	41.128	− 0.005
18.000	41.49	41.49	− 0.00	41.485	− 0.013
18.012	41.50	41.49	− 0.01	41.493	− 0.016
18.214	41.65	41.64	− 0.02	41.637	− 0.031
18.723	42.00	42.00	− 0.01	41.995	− 0.012
18.883	42.11	42.11	− 0.01	42.106	− 0.009
19.000	42.19	42.19	− 0.00	42.187	− 0.007
19.455	42.50	42.50	0.00	42.498	− 0.005
19.585	42.58	42.59	0.02	42.586	0.014
20.000	42.86	42.87	0.02	42.864	0.009
20.203	43.00	43.00	0.00	42.999	− 0.003
20.218	43.01	43.01	0.01	43.009	− 0.003
20.879	43.44	43.44	0.00	43.440	0.000
20.976	43.50	43.50	0.01	43.503	0.006
21.000	43.52	43.52	0.00	43.518	− 0.004
21.468	43.81	43.81	0.01	43.817	0.016
21.770	44.00	44.00	0.00	44.007	0.017
22.000	44.14	44.14	0.01	44.151	0.025
23.000	44.77	44.74	− 0.05	44.765	− 0.012

[a] Densities in g mol/L.

4. A Formula for Densities of Freezing Liquid

In [2], densities of freezing liquid were derived as intersections of PVT isochores and isotherms with an analytically described $P(T)$ melting line, and given a rather complicated, empirical description. We now find that a simple power law [eq (4)] is sufficient. Variables are normalized at the triple point (subscript t):

$$(D/D_t) = (T/T_t)^\gamma. \qquad (4)$$

For parahydrogen, the constants used are $D_t = (1.0/0.026176)$ g mol/L, $T_t = 13.803$ °K [10], and we find the exponent, $\gamma = 0.310\ 4277$ by minimizing the mean relative deviation. Table 6 shows that eq (4) gives adequate representation. The first four columns are from [2].

The number of digits, given for constants in tables 1, 2, and for γ in eq (4), is more than sufficient to reproduce the calculated results, and is not the result of statistical analysis.

Mr. William J. Hall contributed the essential computer programs for iteration and for least squares.

5. References

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