ELSEVIER

Journal of Alloys and Compounds 330–332 (2002) 89–92

Journal of
ALLOYS
AND COMPOUNDS

www.elsevier.com/locate/jallcom

Useful equations of state of hydrogen and deuterium

M. Tkacz*, A. Litwiniuk

Institute of Physical Chemistry, Polish Academy of Sciences, Kasprzaka 44/52, 01-224 Warsaw, Poland

Abstract

The equations of state for hydrogen and deuterium obtained by special fitting procedure to the large number of experimental data available in literature are presented. The form of equation is very simple and allows for easy calculation of fugacities and chemical potentials of corresponding gases. Although the experimental points employed in the fitting procedure concern only the gaseous phases, the equation can be extrapolated to regions of solid phases when volume change due to fluid–solid phase transition is subtracted. Comparison of experimental data available with data obtained by extrapolation or fitting procedure is given in Tables. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Equation of state; Hydrogen; Deuterium; High pressure

1. Introduction

Calculation of the chemical potentials of hydrogen and deuterium at given pressure and temperature require knowledge of their equations of state. So far, only few experimental data have been reported [1–7] and some of them have been limited only to the certain regions of pressure–temperature variables. The most precise measurements, carried out up to 0.3 GPa, reported by Michels et al. [1], are given in polynomial form for selected temperatures only

$$pV = A + B\rho + C\rho^2 + D\rho^3 + E\rho^4 + F\rho^5 \tag{1}$$

where ρ is density expressed in Amagat unit. Corresponding coefficients for both hydrogen and deuterium are as follows: $A = 1.09086$, $B = 0.699452 \cdot 10^{-3}$, $C = 0.772450 \cdot 10^{-6}$, $D = 0.326619 \cdot 10^{-9}$, $E = 0.398361 \cdot 10^{-12}$, $F = -0.91375 \cdot 10^{-15}$ for hydrogen at $T = 298.15$ K; and $A = 1.09090$, $B = 0.677799 \cdot 10^{-3}$, $C = 0.757175 \cdot 10^{-6}$, $D = 0.267063 \cdot 10^{-9}$, $E = 0.386789 \cdot 10^{-12}$, $F = -0.092633 \cdot 10^{-15}$ for deuterium at 298.15 K.

Extrapolation of these results to higher pressures is risky due to increasing contributions from the terms corresponding to parameters in higher power. Extrapolation for temperature 273 K above 1.75 GPa or 298 K above 10 GPa shows change of sign of the second derivative in respect to density and indicates that using such data is senseless.

Equation of state presented by Mills et al. [4,5] is given below:

$$v_m = ap^{-1/3} + bp^{-2/3} + cp^{-1} \tag{2}$$

with the corresponding coefficients for hydrogen

$$\begin{aligned} a &= 36.716 + 0.0033003\,T - 22.479\,T^{-0.5} \\ b &= -17.174 - 0.00213\,T \\ c &= -8.9886 + 0.11001\,T + 69.233\,T^{-0.5} - 31.395\,T^{-1} \end{aligned} \tag{3}$$

and deuterium

$$\begin{aligned} a &= 35.283 + 0.00094704\,T + 3.2843\,T^{-0.5} \\ b &= -25.09 + 0.0063917\,T \\ c &= 13.65 + 0.069563\,T - 158.29\,T^{-0.5} + 720\,T^{-1} \end{aligned} \tag{4}$$

Eq. (2) shows large discrepancies particularly at lower pressure as compared to Michael's data. Another equation published by Hemmes et al. [6] is very inconvenient, as it is very complicated and involves 15 parameters, as presented below:

$$\left(P + \frac{a(P)}{V^{\alpha}}\right)(V - b(P)) = RT \tag{5}$$

where:

$$a(P) = \exp(a_1 + a_2 \ln(P) - \exp(a_3 + a_4 \ln(P))$$

$$b(P) = b_1 \ln(P) + b_2 \ln(P)^2 + b_3 \ln(P)^3 \cdots + b_8 \ln(P)^8$$

$$\alpha(T) = 2.9315 - 1.531 \cdot 10^{-3}\,T + 4.154 \cdot 10^{-6}\,T^2$$

Recently, the pressure–volume relationship of hydrogen

---

*Corresponding author.

0925-8388/02/$ – see front matter © 2002 Elsevier Science B.V. All rights reserved.
PII: S0925-8388(01)01488-8

has been measured by X-ray diffraction at megabar pressure at 300 K [7] and fitted to the Vinet equation of state in form of:

$$p = 3\,k_o\left(\frac{v}{v_o}\right)^{2/3}\left[1-\left(\frac{v}{v_o}\right)^{1/3}\right] \cdot \exp\left\{\frac{3}{2}(k_o')\left(1-\left(\frac{v}{v_o}\right)^{1/3}\right)\right\}$$

with corresponding parameters $v_o = 25.433$ cm^3, $k_o' = 6.813$ and $k_o = 0.162$ GPa.

In this paper, we present very useful and easy to handle equation of state for hydrogen and deuterium in the following form:

$$v = Ap^{-1/3} + Bp^{-2/3} + Cp^{-4/3} + (D + ET)p^{-1} \qquad (6)$$

H_2: v[cm^3/mole] p[MPa] T[K]

$A = 176.330$, $B = -633.675$, $C = -304.574$,
$D = 731.393$, $E = 8.59805$

D_2:

$A = 174.725$, $B = -643.463$, $C = -334.258$,
$D = 763.862$, $E = 8.63927$

This equation has been obtained by special fitting pro-

Table 1
Comparison of the experimental data for hydrogen at 298 K of Michels et al. [1] V_{exp} with the data obtained from equation given in this work V, and by Hemmes [6] V_g and Mills [4] V_m, respectively

p (MPa)	V_{exp} (cm^3/mole)	$(V_{\mathrm{exp}} - V)$ *100%/v	$(V_{\mathrm{exp}} - V_g)$ *100%/v	$(V_{\mathrm{exp}} - V_m)$ *100%/v
2.755104	1186.661	−0.977	0.014	3.166
2.652384	949.413	−0.689	0.015	3.709
3.204605	788.383	−0.430	0.016	4.119
3.755104	674.926	−0.220	0.006	4.414
4.341674	585.751	−0.024	0.005	4.655
4.931183	517.530	0.150	0.009	4.840
5.046187	506.022	0.168	−0.003	4.857
5.518868	464.004	0.288	0.003	4.968
6.005937	427.568	0.383	−0.004	5.044
6.132793	419.061	0.413	0.002	5.067
7.163373	360.929	0.574	−0.005	5.161
8.420614	309.311	0.720	−0.006	5.200
9.858415	266.433	0.829	−0.009	5.170
11.544564	229.749	0.893	−0.013	5.062
12.286467	216.243	0.650	−0.276	4.754
13.240644	202.314	0.927	−0.007	4.921
14.750797	183.187	0.924	−0.012	4.763
14.936318	181.115	0.927	−0.002	4.748
17.783854	154.630	0.886	−0.006	4.426
21.157369	132.510	0.804	0.000	4.033
25.117251	114.135	0.674	−0.004	3.568
29.916611	98.413	0.518	−0.006	3.049
31.671459	93.862	0.467	0.002	2.875
34.914567	86.655	0.373	0.006	2.567
38.991176	79.298	0.261	−0.001	2.210
40.094303	77.570	0.239	0.013	2.125
48.534572	66.927	0.065	0.010	1.522
50.172492	65.275	0.037	0.009	1.419
59.889457	57.342	−0.08	0.022	0.910
63.287796	55.139	−0.111	0.016	0.759
74.286426	49.379	−0.175	−0.000	0.360
81.274301	46.526	−0.180	−0.007	0.175
93.408273	42.564	−0.172	−0.01	−0.078
103.965535	39.851	−0.144	−0.04	−0.238
115.354763	37.464	−0.102	−0.521	−0.364
134.647448	34.303	−0.021	−0.077	−0.507
140.358227	33.521	−0.009	−0.085	−0.550
178.363512	29.550	0.184	−0.002	−0.621
232.476128	25.989	0.434	0.153	−0.567
298.531922	23.22	0.634	−0.005	−0.463

cedure to all Michels et al. [1] experimental points, i.e. to 483 and 417 for hydrogen and deuterium respectively. Although the least squares procedure is commonly used, in fact this method does not assure minimal error in respect to the experimental point. We have chosen the method of finding the minimum function which fulfilled the following relationship:

$$S(a, b, c, d, e) = \sum_{p} \sum_{T} \left| \frac{V(p, T)_{eksp} - V_{a,b,c,d,e}(p, T)}{V(p, T)_{eksp}} \right| \tag{7}$$

In fact, this is an error function at the experimental points and by minimization of this function the variables *a*, *b*, *c*, *d* and *e* can be evaluated. This method always assure finding the minimum, which depends on the starting parameters *a*, *b*, *c*, *d*, *e*. From the many minims, the smallest obtained is considered to be the best solution of the formula (7).

Corresponding equation for the fugacity calculation valid for both hydrogen and deuterium with corresponding parameters is given in form:

$$\ln f = \frac{\{1.5Ap^{2/3} + 3Bp^{1/3} + (D + ET)\ln p - 3Cp^{-1/3}\}}{RT} \tag{8}$$

Comparison with the data calculated from different equations of state is given in the Tables.

As one can see from Tables 1–4, the molar volume at given pressure, both for hydrogen and deuterium, show relatively small errors as compared to the very accurate experimental data of Michels et al. [1]. The biggest disadvantages of using their approximation for extrapolation procedure is the polynomial form which makes such a procedure doubtful due to immediately increasing importance of the contributions from higher power term of equation and lack of temperature dependence as isotherms are given with 25 K steps. The equations given by Mills et al. [4,5] shows large errors in low pressure regions below 100 MPa. Comparison of quality of different equations of state can be shown in term of the average error for approximation expressed in the following form:

$$R = |(V_{\mathrm{exp}} - V)/V_{\mathrm{exp}}| \times 100\% \tag{9}$$

$$\bar{R} = \frac{R_1 + R_2 + \cdots + R_n}{n} \tag{10}$$

where V_{exp} and V denotes volume experimentally determined by [1] and V calculated from different equation of state, respectively. For the Eqs. (3) and (4) this value can be calculated as 6.66 and 3.11% as compared to 0.58 and 0.54% in this work for hydrogen and deuterium, respectively. The best approximation is given in the equation by Hemmes et al. [6], with the average error of 0.14%, but as we mentioned above, it has a rather complicated form, for hydrogen only and when extrapolated to the high pressure region shows minimum of volume at about 60 GPa. It is worth noting that the equation given by Laubeyre et al. [7], despite the fact that it was taken in the region of solid hydrogen, shows relatively small discrepancy with experimental data in gaseous region after subtracting volume change due to solid fluid phase transition.

Table 2
Comparison of extrapolated values of hydrogen volumes as function of pressure obtained from different equation of state. V, V_m, V_g, V_d, V_l correspond to the data by this work, Mills et al. [4], Hemmes et al. [6], Michels et al. [1] and Loubeyre et al. [7] at 298 K, respectively

p (GPa)	V (cm^3/mole)	V_m (cm^3/mole)	V_g (cm^3/mole)	V_d (cm^3/mole)	V_l (cm^3/mole)
1	14.560	14.591	14.499	14.741	
2	11.638	11.598	11.519	11.802	
3	10.270	10.198	10.115	10.423	
4	9.412	9.322	9.240	9.552	
5	8.800	8.698	8.621	8.927	
6	8.131	8.022	7.950	8.242	7.781
7	7.754	7.641	7.573	7.848	7.424
8	7.442	7.325	7.262	7.516	7.123
9	7.176	7.057	6.998	7.229	6.863
10	6.947	6.825	6.769	6.975	6.636
20	5.600	5.473	5.404	5.066	5.262
30	4.928	4.803	4.704		4.553
40	4.496	4.375	4.269		4.091
50	4.185	4.067	3.993		3.756
60	3.945	3.830	3.830		3.496
70	3.752	3.640	3.755		3.287
80	3.592	3.482	3.750		3.113
90	3.455	3.348	3.806		2.966
100	3.337	3.23	3.913		2.838

Table 3
Comparison of the experimental data for deuterium at 298 K of Michels et al. [1] V_{exp} with the data obtained from equation given in this work V, and Mills et al. [5] V_m, respectively

p (MPa)	V_{exp} (cm^3/mole)	100%* $(V_{\mathrm{exp}} - V)/V_{\mathrm{exp}}$	100%* $(V_{\mathrm{exp}} - V_m)/V_{\mathrm{exp}}$
2.133803	1175.768	−1.285	3.228
2.683592	937.813	−1.018	3.7603
3.237739	779.775	−0.768	4.158
3.780131	669.959	−0.559	4.445
4.352719	583.738	−0.364	4.675
4.927130	517.429	−0.187	4.856
5.151666	495.544	−0.121	4.916
5.484621	466.328	−0.049	4.983
6.070482	422.728	0.08	5.076
6.131074	418.714	0.099	5.089
7.312118	353.455	0.301	5.191
8.595298	302.905	0.462	5.220
10.062890	260.916	0.592	5.183
11.783185	224.991	0.673	5.062
12.879522	207.131	0.710	4.970
13.513209	198.125	0.723	4.908
15.242928	177.365	0.739	4.725
15.467767	175.011	0.741	4.702
18.655968	147.728	0.723	4.335
22.206184	126.594	0.663	3.918
26.378647	109.038	0.559	3.433
28.808826	101.162	0.491	3.162
31.440234	94.018	0.425	2.890
35.302946	85.467	0.333	2.518
36.719672	82.785	0.302	2.392
42.199633	74.104	0.189	1.938
43.678573	72.135	0.161	1.825
48.804502	66.241	0.085	1.477
53.525840	61.807	0.021	1.189
61.359684	55.955	−0.050	0.793
65.851521	53.226	−0.076	0.604
78.464357	47.216	−0.119	0.174
81.934534	45.882	−0.123	0.079
99.880104	40.443	−0.097	−0.281
100.097343	40.389	−0.097	−0.285
120.506841	36.141	−0.026	−0.527
128.613646	34.814	0.005	−0.592
169.168774	29.992	0.175	0.758
218.852779	26.381	0.375	0.760
279.124435	23.579	0.544	−0.685

Table 4
Comparison of extrapolated values of deuterium volumes as function of pressure obtained from different equation of state. V, V_m and V_d correspond to the data by this work, Mills et al. [5], Michels et al. [1] at 298 K, respectively

p (GPa)	V (cm^3/mole)	V_m (cm^3)	V_d (cm^3)
1	14.344	14.365	14.466
2	11.470	11.407	11.550
3	10.126	10.027	10.177
4	9.283	9.163	9.307
5	8.681	8.550	8.678
6	8.020	7.881	7.988
7	7.650	7.505	7.585
8	7.342	7.194	7.243
9	7.082	6.931	6.943
10	6.856	6.703	6.673
20	5.529	5.374	
30	4.867	4.715	
40	4.442	4.194	
50	4.135	3.992	
60	3.898	3.759	
70	3.708	3.572	
80	3.550	3.417	
90	3.415	3.285	
100	3.298	3.171	

References

[1] A. Michels, W. De Graaff, T. Wassenaar, J.M.H. Levelt, P. Louwerse, Physica 25 (1959) 25.

[2] D.S. Tsiklis, V.Y. Maslennikova, S.D. Gavrilov, A.N. Egorov, G.V. Timofeeva, Dokl. Akad. Nauk. 220 (1975) 1384.

[3] N.B. Vargaftik, in: Tables on the Thermophysical Properties of Liquids and Gases, Wiley, New York, 1975, p. 7.

[4] R.L. Mills, D.H. Liebenberg, J.C. Bronson, L.C. Schmidt, J. Chem. Phys. 66 (1977) 3076.

[5] R.L. Mills, D.H. Liebenberg, J.C. Bronson, J. Chem. Phys. 68 (1978) 2663.

[6] H. Hemmes, A. Driessen, R. Griessen, J. Phys. C 19 (1986) 3571.

[7] P. Loubeyre, R. LeToullec, D. Hausermann, M. Hanfland, R.J. Hemley, H.K. Mao, L.W. Finger, Nature 383 (1996) 702.