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A GENERALIZED CORRELATION FOR THE SECOND VIRIAL COEFFICIENT BASED UPON THE STOCKMAYER POTENTIAL

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***Abstract*— We have approximated the second virial coefficients obtained from the Stockmayer potential using a two parameter, analytical correlation. The correlation eliminates the need for integration of the potential over nearly the entire range of reduced temperatures. The equation is valid from 0 to 1.5 reduced dipole moment and uses the Boyle temperature as a normalizing variable. Because the equation is a correlation, the parameters do not necessarily have any physical meaning. We have applied the new equation to nonpolar compounds, aromatics, freons, alcohols, ethers, aldehydes, and acids.**

***Keywords*— Second Virial Coefficient, Correlation, Stockmayer Potential, Boyle Temperature.**

I. INTRODUCTION

The precise basis in statistical mechanics of the virial equation is one of its attractions. The virial equation, when truncated after the second virial coefficient, can predict accurate thermodynamic properties in the vapor phase up to about one-half the critical density. Therefore, experiments and correlations have emphasized determination of the second virial coefficient. Correlation use is preferable to experiment if the accuracy in the prediction is close to the experimental error.

Several correlations have appeared in the literature. Among the most popular are those developed by: Pitzer and Curl, (1957); O'Connell and Prausnitz, (1967); Halm and Stiel (1971); Tsonopoulos (1974); and Tanakad and Danner (1977). These correlations, based upon the corresponding states principle, provide generalized expressions for the second virial coefficient. The characteristic parameters for simple molecules in these equations are the acentric factor, the critical pressure and the critical temperature. To predict the second virial coefficient for more complex molecules, the correlations utilize the reduced dipole moment and adjustable parameters. For non-polar and slightly polar substances, prediction of the second virial coefficient is relatively close to experimental values, but the correlations cannot predict strongly polar and associating substances adequately.

Another way to obtain the second virial coefficient is through integration of a pair potential. Hirschfelder *et al.* (1954) give the theoretical expressions for the second and third virial coefficient using different potential functions. The resultant equations can correlate the second virial coefficient fairly well, but they tend to fail at low temperatures.

One of the pair potentials used to represent the second virial coefficient of polar substances is the Stockmayer potential (Hirschfelder *et al.*, 1954). The expression for the second virial coefficient of the Stockmayer fluid is a two characteristic constant equation that requires a numerical integration. Polak and Lu (1972) and Johnson and Eubank (1973) obtained the intermolecular forces constants of alcohols and other polar molecules. They used an iterative least squares method because of the complexity and non-linearity of the expression for the second virial coefficient.

Recently, Tellez-Morales (1998) have developed a simple straight line to correlate the pure and interaction second virial coefficient data and Iglesias-Silva and Hall, (2001) have developed a correlation using the Boyle temperature as a reducing parameter. In this work, we use a new correlation that has the Boyle temperature as a normalizing parameter. This new function can correlate the second virial coefficient from the Stockmayer potential within a maximum error of 3% at low temperatures and within less than 1% at other temperatures. We have generalized the parameters from this correlation in terms of the Stockmayer reduced dipole moment and the Boyle temperature. Also, we use the new equation to represent the second virial coefficient of nonpolars, aromatics, freons, alcohols, ethers, aldehydes, and acids. The force constants used in the new equation agree with the force constants obtained from the Stockmayer expression.

II. DEVELOPMENT

Many correlations for the second virial coefficient are based upon the corresponding states principle. The reduced second virial coefficient is:

$$B^{*}\left(T/T_c\right)=\frac{BP_c}{RT_c}=B^{*}_{np,s}\left(T/T_C\right)+\omega B^{*}_{np,ns}\left(T/T_c\right)+\mu^{*}B^{*}_{p}\left(T/T_c\right)+\cdots \tag{1}$$

where B is the second virial coefficient, T is the absolute temperature, P_c is the critical pressure, T_c is the critical temperature, ω is the acentric factor, and μ is the reduced dipole moment. In Eqn. (1), *np*, *ns*, *s*, and *p* stand for non-polar, non-spherical, spherical and polar, respectively.

A different approach to obtain the second virial coefficient is to use the statistical mechanical definition of the second virial coefficient

$$B = -2\pi N \int_0^\infty \left\{ \exp\left[\frac{u(r)}{kT} \right] \right\} r^2 dr \tag{2}$$

or

$$B = -\frac{N}{4} \int_0^\infty \int_0^{2\pi} \int_0^\pi \int_0^\pi \left\{ \exp\left[\frac{u(r,\theta_1,\theta_2,\phi_2-\phi_1)}{kT} \right] - 1 \right\} \sin\theta_1 d\theta_1 \sin\theta_2 d\theta_2 d(\phi_2-\phi_1) r^2 dr \tag{3}$$

for angle dependent potentials. In the above Eqns. (2) and (3), *u* is the pair potential function, *r* is the intermolecular distance, *k* is the Boltzmann constant. For the Stockmayer potential, *u* is

$$u(r,\theta_1,\theta_2,\phi_2-\phi_1) = 4\varepsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^6 \right] - \frac{\mu^2}{r^3} g(\theta_1,\theta_2,\phi_2-\phi_1) \tag{4}$$

with

$$g(\theta_1,\theta_2,\phi_2-\phi_1) = 2\cos\theta_1\cos\theta_2 - \sin\theta_1\sin\theta_2\cos(\phi_2-\phi_1)$$

Integration over the angles gives

$$B^*(T^*) = \left(\frac{4}{T^*}\right)^{1/4} \left[\Gamma\left(\frac{3}{4}\right) - \frac{1}{4}\sum_{n=1}^{\infty}\sum_{k=0}^{k\le n/2} \frac{2^{n-3k}}{n!} \times G_k \binom{n}{2k} \Gamma\left(\frac{2n-2k-1}{4}\right) \mu^{*4k} T^{*-(n+k)/2} \right] \tag{5}$$

with

$$G_k = \frac{1}{8\pi} \int_0^{2\pi} \int_0^\pi \int_0^\pi \left[g(\theta_1,\theta_2,\phi_2-\phi_1) \right]^{2k} \sin\theta_1 \sin\theta_2 d\theta_1 d\theta_2 d(\phi_2-\phi_1)$$

where T^* is the dimensionless temperature and *m* is the reduced dipole moment defined as $\mu^* = \mu/\sqrt{\varepsilon\sigma^3}$. In this work, we have solved numerically Eqn. (5) using a 1/3-Simpson method with 30 steps for each interval. In the multiple integration, we first apply the Simpson rule in the first dimension with each value of the other dimensions held constant. Then, we apply the method to integrate the second dimension keeping constant the remaining dimensions and so on until having completed all the dimensions.

Several expressions have available to calculate the second virial coefficient. Recently, Tellez-Morales (1998) and Iglesias-Silva and Hall (2001) have suggested simple correlative functions for the second virial coefficient. They use the Boyle and the critical temperatures as reducing variables. We propose a simple function that uses these variables,

$$B^* = \left(\frac{T^*_{Boyle}}{T^*}\right)^m \left[1 - \left(\frac{T^*_{Boyle}}{T^*}\right)^l\right] \exp\left[b_1\left(\frac{T^*_{Boyle}}{T^*}\right)^n\right] \tag{6}$$

where T^*_{Boyle} is the reduced Boyle temperature and *m*, *l*, b_1, and *n* are characteristic parameters.

Table 1. Characteristic parameters used in Eqn. (6).

t^*	T^*_{Boyle}	***m***	***l***	b_1	***n***
0.0	3.4179	0.2092135	0.7989727	0.0200595	1.6389481
0.1	3.4312	0.2094731	0.7997295	0.0214430	1.6408683
0.3	3.5348	0.2110530	0.8063708	0.0323447	1.6472155
0.5	3.7292	0.2138632	0.8168747	0.0508404	1.6228289
0.8	4.1510	0.2195587	0.8328934	0.0839373	1.5707452
1.0	4.4951	0.2234882	0.8413193	0.1147709	1.5228465
1.2	4.8758	0.2277854	0.8471057	0.1386762	1.4900390
1.5	5.4983	0.2342763	0.8489205	0.1691714	1.4514022

Table 2. Average Percentage deviation of Eqn. (6) and Eqn. (6) plus Eqns. (7)-(11).

t^*	ΔB^*, % **Eqn. (6)**	ΔB^*, % **Eqns. (6)-(11)**
0.0	0.54	0.55
0.1	0.53	0.53
0.3	0.45	0.45
0.5	0.51	0.52
0.8	0.77	0.75
1.0	0.68	0.69
1.2	0.85	0.85
1.5	1.30	1.30

III. RESULTS AND DISCUSSION

We have used Eqn. (6) to correlate the reduced second virial coefficient from the Stockmayer potential. We have used the reduced Stockmayer dipole moment, $t^* = 8^{-0.5}(\mu^*)^2$, and solved Eqn. (5) over the interval $0 \le t^* \le 1.5$. We have used a nonlinear least squares method to obtain the parameters of Eqn. (6) using the reduced Stockmayer second virial coefficient. Table 1 contains the characteristic parameters of Eqn. (6). The average percentage error for the second virial coefficient appears in Table 2. We have observed that the reduced Stockmayer Boyle temperature is a function of the reduced dipole moment, t^*.

Figure 1 shows this behavior and can be represented accurately by

$$T^*_{Boyle} = 3.41784169 + 3.12822538 t^{*1.5} - 14.59769654 t^{*1.75} + 24.93465321 t^{*2} - 13.75643403 t^{*2.25} + 1.37224910 t^{*2.75} - 0.00389818 t^{*4.25} \tag{7}$$

Equation 7 has an accuracy of ±0.0001 around the Boyle temperature. Figure 1 shows the behavior of

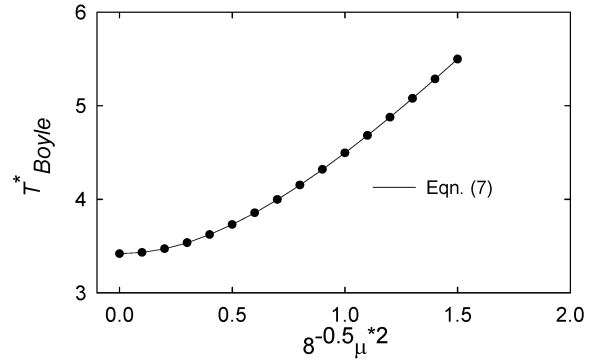

Figure 1. Behavior of the reduced Boyle temperature as a function of reduced dipole moment.

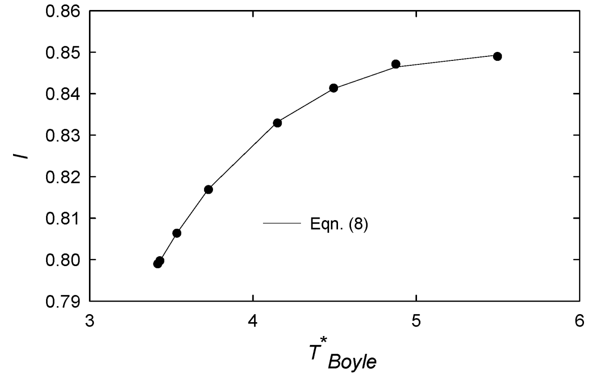

Figure 2. Relation between characteristic parameter l and reduced Boyle Temperature.

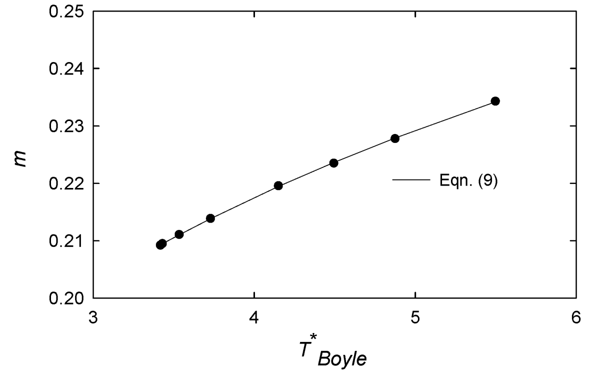

Figure 3. Relation between characteristic parameter m and reduced Boyle temperature.

Equation (7).

The characteristic parameters, m, l, b_1, and n are functions of the reduced Boyle temperature:

$$l = \frac{1.56484}{T^{*0.25}_{Boyle}} - \frac{2.225}{T^{*1.5}_{Boyle}} \tag{8}$$

$$m = 0.144832 + 0.052422 \ln\left(T^*_{Boyle}\right) \tag{9}$$

$$b_1 = 0.55 - \frac{1.2531}{T^{*0.7}_{Boyle}} \tag{10}$$

$$n = 1.08 + \frac{0.525}{T^{*0.25}_{Boyle}} + \frac{10000}{T^{*7}_{Boyle}} - \frac{30960}{T^{*8}_{Boyle}} \tag{11}$$

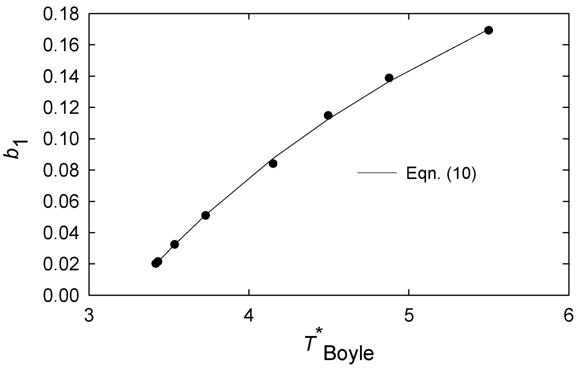

Figure 4. Relation between characteristic parameter b_1 and reduced Boyle temperature.

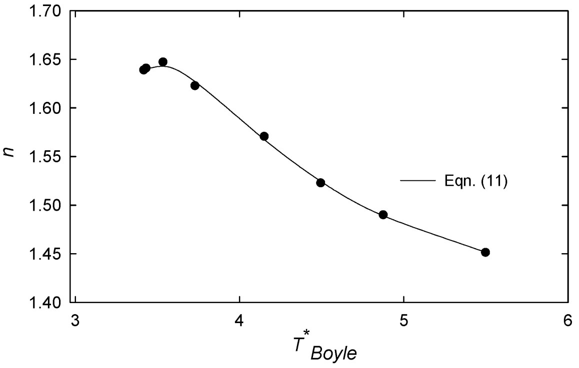

Figure 5. Relation between characteristic parameter n and reduced Boyle temperature.

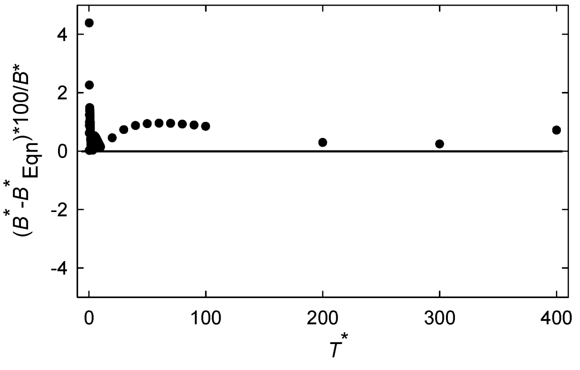

Figure 6. Relative deviation of measured reduced second virial coefficient from Eqn. (6)+Eqns. (7)-(11).

Figures 2-5 show the behavior of these parameters together with Eqns. (8)-(11). Upon imposing Eqns. (7)-(11), the average percentage deviation of these generalized correlations from the calculated reduced Stockmayer second virial coefficient is within 1.3 %. Practically, no degradation of the fit exists when using the generalized correlation to calculate the reduced virial coefficient, as shown in Table 2, therefore the force constants obtained from Eqn. (6) are equivalent to the constants obtained from Eqn. (5). Figure 6 shows the residual second virial coefficient for $t^* = 0$, which is equivalent to the second virial coefficient obtained from the Lennard-Jones potential. To prove the validity of

Eqns. (6)-(11), we have correlated the second virial coefficients of aromatics, freons, ethers, aldehydes, alcohols, and acids.

We have used the Thermodynamics Research Center (TRC) SOURCE Database (1998) as our data source and, we have used a nonlinear least squares method developed by SAS (1991) to fit the curves. The values of the dipole moment come from Poling *et al.* (2001) and TRC Freons Database (1999).

The experimental data have been weighted using the uncertainties supplied by the TRC database. In Table 3, we show the characteristic parameters, σ and ε/k, obtained from the fitting procedure together with the asymptotic standard error associated with them. Also, we present the reduced Stockmayer dipole moment, t^*.

The difference between the values presented in Table 3 and the values presented earlier (Hirschfelder *et al.*, 1954) is that the earlier results appear only at round numbers such as 0.1, 0.2, 0.3, *etc.* while now we can have intermediate values. Table 4 compares the intermolecular force constants obtained by different authors (Hirschfelder *et al.*, 1954 and Polak and Lu, 1971) and the present work. In general, the values are within about 10% of each other except for molecules that can associate.

The larger discrepancy for those molecules is to be expected because the Stockmayer potential does not include associative effects. Intermolecular parameters for t^*=0 from this work are compared to those obtained by Hirschfelder *et al.* (1954). Table 5 shows the absolute average deviation and the average of the absolute deviation divided by the uncertainty using Eqn. (6) and the Tsonopolous equation (Poling *et al.*, 2001). In general, our values of $\Delta B/\sigma$ are more nearly constant and smaller than those from Tsonopolous for each class of compounds although the values are similar for many compounds. Determination of the Boyle Temperature is not accurate when extrapolating the Stockmayer potential. When experimental data near the Boyle temperature exist, we have compared the Boyle temperatures obtained to those reported by Iglesias-Silva and Hall, (2001). Table 6 contains these results. In this work, we have not included a specific term for associating substances and consider only the effect of the dipole moment. We have correlated some substances (such as ethanol, hydrogen cyanide, acetonitrile) outside the range of validity, but we still obtain good agreement with the experimental data. Because of the large number of references, we present only the number of references and the number of points used in the calculation of the force constants.

The references are available through TRC and the authors. Figure 7 shows typical absolute deviations from the new equation for different substances.

Table 3. Characteristic Parameters in Eqns. (6)-(11).

Substances	***t****	σ Å	**Asymptotic Error**	ε/*k* **K**	**Asymptotic Error**
Non-polars					
Methane	0.0000	3.857	0.005	146.671	0.228
Ethane	0.0000	4.879	0.010	203.910	0.627
Ethylene	0.0000	4.781	0.020	184.824	1.128
Propane	0.0000	6.102	0.042	215.780	2.240
Propylene	0.0000	5.661	0.034	225.808	2.215
n-Butane	0.0000	7.459	0.048	212.342	1.893
n-Pentane	0.0000	8.103	0.067	235.921	2.898
Alcohols					
Methanol	1.6007	2.394	0.003	336.883	8.852
Ethanol	4.4498	2.332	0.037	131.079	55.172
n-Propanol	0.5175	2.553	0.014	852.619	9.465
Iso-propanol	0.5636	2.555	0.041	826.869	30.383
n-Butanol	0.8241	2.416	0.108	713.652	157.649
Iso-Butanol	0.4484	2.535	0.138	1012.434	100.288
2-Butanol	0.5361	2.474	0.074	911.089	74.672
n-Hexanol	0.1329	4.027	0.555	955.976	185.991
Freons					
R11	0.0095	6.223	0.376	280.680	26.988
R115	0.0675	2.075	0.016	1146.237	9.504
R12	0.0106	6.689	0.083	200.859	3.259
R123	0.1555	3.286	0.036	852.950	8.653
R124	0.1999	3.105	0.027	722.716	5.364
R125	0.4426	3.087	0.021	466.238	0.818
R13	0.0183	5.583	0.058	184.597	2.567
R134	0.7309	2.273	0.297	504.197	241.116
R134a	0.2966	2.787	0.016	674.178	1.647
R14	0.0000	4.785	0.010	151.403	0.371
R141b	0.3361	3.703	0.028	608.304	2.094
R142b	0.6243	4.031	0.023	354.691	2.331
R143a	0.8825	3.949	0.017	251.279	2.018
R152a	1.0465	4.035	0.011	238.261	1.936
R160	0.6162	3.310	0.090	476.776	24.784
R20	0.0941	3.249	0.168	959.077	52.920
R21	0.0796	5.639	0.162	298.504	14.080
R22	0.3839	3.018	0.028	510.640	1.958
R23	0.8924	3.120	0.036	241.754	5.307
R30	0.3989	3.194	0.006	638.148	0.471
R32	1.1669	3.389	0.015	220.532	4.188
R40	0.2148	5.929	0.035	215.144	1.106
R41	0.9474	3.471	0.025	214.053	2.833
Ethers					
Dimethyl ether	0.2449	3.038	0.278	629.855	38.894
Acetone	1.5957	3.669	0.012	273.140	21.349
Methyl ethyl ether	0.0369	8.476	0.799	163.835	18.281
Diethyl ether	0.1524	3.099	0.075	953.984	16.259
Butyl methyl ether	0.0770	3.536	0.514	1081.046	154.728
Diisopropyl ether	0.0611	4.039	0.179	915.346	46.168
Dipropyl ether	0.0230	7.463	52.787	384.387	4747.284
Ethyl propyl ether	0.0449	5.110	0.204	615.253	36.652

Table 3. (cont)

Substances	***t****	**σ Å**	**Asymptotic Error**	**ε/k K**	**Asymptotic Error**
Acids					
HCl	0.4330	2.665	0.018	377.842	1.746
H_2S	0.1046	4.268	0.039	255.015	34.063
HCN	3.2866	3.894	0.032	118.851	114.058
Gases					
Argon	0.0000	3.471	0.008	118.703	0.453
Hydrogen	0.0000	2.899	0.005	29.790	0.112
Helium	0.0000	2.582	0.013	5.464	0.052
Krypton	0.0000	3.913	0.017	152.226	0.929
Neon	0.0000	2.728	0.008	36.780	0.239
Nitrogen	0.0000	3.772	0.005	95.277	0.146
Oxygen	0.0000	3.537	0.012	116.781	0.562
Xenon	0.0000	4.203	0.021	221.911	1.902
CO	0.0046	3.806	0.009	99.699	0.289
CO_2	0.0000	4.574	0.021	184.603	1.120
NO_2	0.0659	1.472	0.023	486.473	6.908
Nitric oxide	0.0166	2.079	0.033	684.676	13.961
SO_2	0.5866	2.903	0.021	456.629	4.348
Aromatics					
Benzene	0.0000	3.162	0.010	1105.050	5.250
Toluene	0.0096	3.310	0.036	1254.464	16.154
Ethylbenzene	0.0068	3.613	0.073	1270.625	29.107
m-Xylene	0.0077	2.546	0.062	1800.352	34.512
o-Xylene	0.0116	3.385	0.414	1418.291	60.352
p-Xylene	0.0005	3.151	0.033	1502.195	17.313
Others					
Ethyl acetate	0.3163	3.144	0.071	939.995	10.795
C_2H_3N	4.6130	3.946	0.033	110.647	23.830
CH_3Br	0.5370	3.282	0.261	437.072	28.680
Methyl acetate	0.2187	3.347	0.076	902.265	9.779
Ammonia	0.9203	2.724	0.011	309.575	3.618
Water	1.5006	2.551	0.002	332.999	2.689

Table 4. Comparison of intermolecular force constants.

Substances	***t****	**σ / Å This work**	**σ / Å Polak-Lu**	**ε/k / K This work**	**ε/k / K Polak-Lu**
Ethane	0.0000	4.879	3.954	203.91	243.0
Ethylene	0.0000	4.781	4.523	184.82	199.2
Propane	0.0000	6.102	5.637	215.78	242.0
n-Butane	0.0000	7.459	4.971	212.34	297.0
Argon	0.0000	3.472	3.405	118.70	119.8
Hydrogen	0.0000	2.899	2.870	29.79	29.2
Helium	0.0000	2.582	2.630	5.46	6.03
Krypton	0.0000	3.913	3.597	152.23	158.0
Neon	0.0000	2.728	2.749	36.78	35.6
Nitrogen	0.0000	3.772	3.698	95.28	95.05
Oxygen	0.0000	3.537	3.580	116.78	117.5
Xenon	0.0000	4.203	4.100	221.91	221.0
CO_2	0.0000	4.574	4.486	184.60	189.0
R11	0.0095	6.223	4.426	280.68	528.4
Nitric oxide	0.0166	2.079	1.873	684.68	786.2
NO_2	0.0659	1.472	1.428	486.47	517.3
R20	0.0941	3.249	3.390	959.08	922.0
Diethyl ether	0.1524	3.099	2.870	953.98	1041.2
Dimethyl ether	0.2449	3.038	2.868	629.85	667.6
R30	0.3989	3.194	3.150	638.15	716.6
Iso-Butanol	0.4484	2.535	2.575	1012.43	878.7
n-Propanol	0.5175	2.553	2.641	852.62	958.2
2-Butanol	0.5361	2.474	2.521	911.09	1000.3
Iso-propanol	0.5636	2.555	2.422	826.87	694.3
Sulfur dioxide	0.5866	2.903	2.898	456.63	456.8
R160	0.6162	3.31	3.613	476.78	511.6
R142b	0.6243	4.031	3.070	354.69	253.7
n-Butanol	0.8241	2.416	2.649	713.65	1115.3
R143a	0.8825	3.949	3.586	251.28	149.7
R23	0.8924	3.120	3.317	241.75	245.1
R152a	1.0465	4.035	3.452	238.26	180.4
R32	1.1669	3.389	3.657	220.53	292.7
Acetone	1.5957	3.669	3.737	273.14	372.1
Methanol	1.6007	2.394	2.763	336.88	890.2
Ethanol	4.4498	2.332	2.378	131.08	215.5

Table 5. Deviations of experimental second virial coefficients from this work and from Tsonopolous (1974).

Substances	**Data Points**	**ΔB/σ This work**	**ΔB/σ Tsonopoulos**	**ΔB This work cm^3mol^{-1}**	**Number of References**
Non-polars					
Methane	424	3.491	2.060	2.847	56
Ethane	254	2.565	3.012	6.937	30
Ethylene	211	3.248	2.683	5.167	32
Propane	185	2.915	1.915	12.673	23
Propylene	102	2.544	106.141	9.798	12
n-Butane	188	2.781	1.664	24.997	22
n-Pentane	109	2.977	2.255	54.838	15
Alcohols					
Methanol	56	1.969	3.261	73.417	23
Ethanol	46	1.072	1.002	31.422	5
n-Propanol	23	1.058	1.355	93.519	4
Iso-propanol	22	1.288	4.465	31.944	4
n-Butanol	12	1.339	1.140	63.974	3
Iso-Butanol	4	1.250	11.974	17.184	1
2-Butanol	4	1.059	13.804	10.655	1
n-Hexanol	7	0.207	0.280	23.607	1
Freons					
R11	27	0.678	1.919	36.319	4
R115	7	0.019	0.312	0.589	1
R12	79	1.738	1.782	19.781	11
R123	14	2.316	1.678	22.363	2
R124	18	2.301	0.972	6.600	2
R125	59	3.096	1.835	6.066	7
R13	65	1.088	1.254	6.205	8
R134	7	8.174	5.965	36.351	2
R134a	60	4.300	6.518	8.081	7
R14	89	3.178	8.284	3.452	13
R141b	19	1.055	3.116	10.398	2
R142b	20	0.829	1.441	10.056	4
R143a	56	0.881	4.693	6.247	8

Table 5. (cont)

Substances	Data Points	$\Delta B/\sigma$ This work	$\Delta B/\sigma$ Tsonopoulos	ΔB This work cm^3mol^{-1}	Number of References
R152a	65	1.212	6.968	7.565	9
R160	37	2.886	4.761	31.200	5
R20	38	0.842	1.112	48.725	9
R21	13	0.282	2.119	14.725	2
R22	56	1.818	2.021	8.625	10
R23	73	2.287	3.714	6.119	10
R30	36	1.997	27.420	9.941	6
R32	89	2.128	13.993	7.339	10
R40	75	3.597	11.022	15.109	9
R41	38	0.707	5.866	2.191	7
Acids					
HCl	24	0.543	2.629	5.648	3
H_2S	17	1.135	1.268	9.359	2
HCN	9	0.575	0.577	107.717	1
Ethers					
Dimethyl ether	23	2.676	2.619	38.556	5
Acetone	94	1.342	1.591	74.582	16
Methyl ethyl ether	4	1.044	14.525	14.864	1
Diethyl ether	52	1.778	2.559	100.974	11
Butyl methyl ether	3	0.612	----	29.769	1
Diisopropyl ether	7	0.128	0.544	13.477	1
Phenyl methyl ether	12	0.504	----	22.978	2
Dipropyl ether	6	0.852	----	138.054	2
Ethyl propyl ether	4	0.041	1.976	4.085	1
Gases					
Argon	325	3.492	4.098	2.504	40
Hydrogen	160	0.895	5.368	4.448	24
Helium	304	13.954	86.042	12.347	50
Krypton	153	4.437	2.413	6.276	19
Neon	66	0.748	1.718	1.765	10
Nitrogen	231	3.057	3.249	3.410	36
Oxygen	141	1.473	1.787	10.087	13
Xenon	123	3.546	1.727	5.567	15
CO	89	1.841	1.405	2.949	12
CO_2	209	5.047	2.575	7.217	17
NO_2	57	1.679	5.751	4.259	10
Nitric oxide	51	3.877	3.789	10.982	3
SO_2	33	0.381	1.562	10.995	7
Aromatics					
Benzene	234	1.721	1.866	36.187	33
Toluene	69	1.852	3.906	17.787	7
Ethylbenzene	9	0.176	0.408	19.223	1
m-Xylene	5	0.127	1.271	10.403	2
o-Xylene	14	0.547	2.173	42.592	3
p-Xylene	21	1.059	2.781	44.812	4
Others					
Ethyl acetate	24	0.523	2.720	26.321	2
Acetonitrile	94	7.122	43.317	149.266	10
CH_3Br	26	2.971	----	58.175	6
Methyl acetate	38	0.678	3.165	35.813	4
Ammonia	62	1.141	6.771	12.350	7
Water	189	2.825	8.668	27.755	11

Table 6. Comparison of Boyle temperatures obtained in this work with those from Iglesias-Silva and Hall (2001).

Substances	T_{Boyle} / K This work	T_{Boyle} / K Iglesias-Hall
Methane	501.29	508.7
Ethane	696.93	757.1
Ethylene	631.69	681.3
Propane	737.50	891.7
Propylene	771.77	891.4
n-Butane	725.75	1003.5
n-Pentane	806.34	1081.6
Methanol	1926.11	1281.5
Ethanol	1691.72	1086.9
n-Propanol	1125.04	1137.8
R11	959.47	1119.9
R12	686.62	908.6
R13	2375.04	714.5
R134a	1440.45	867.7
R152a	1091.37	891.6
Acetone	1198.35	1151.7
Benzene	3776.88	1347
Toluene	1709.19	1361.6
Water	1831.30	1589

Table 7. Absolute and percentage deviations of experimental second cross virial coefficients from Eqns. (6)-(11).

System	Data Points	ΔB $cm^3 \cdot mol^{-1}$	$\Delta B\%$
Methanol + n-Pentane	2	190.39	19.31
Methanol + Nitrogen	6	3.32	4.56
R11 + R12	1	116.51	26.52
R11 + R13	1	44.80	10.23
$CO + CO_2$	6	3.89	10.57
$CO + H_2$	10	4.98	4.89
Acetone + n-Butane	4	344.90	55.83
Acetone + Diethyl ether	3	159.15	22.36
Diethyl ether + SO_2	4	223.31	23.08
Methyl butyl ether + SO_2	3	36.51	5.48
R22 + R23	1	24.37	9.48
R22 + R12	1	96.88	26.15
R22 + R13	1	29.25	10.81
R23 + R14	4	40.61	43.25
R20 + CO_2	1	89.51	52.96
R20 + Acetone	4	342.07	31.12
R20 + Methyl acetate	4	490.10	34.84
R20 + Diethyl ether	4	292.59	25.70
R20 + Benzene	10	37.19	3.40
CH_3Br + Propane	8	61.53	17.80
CH_3Br + n-Butane	4	104.39	3.03
Methane + Methanol	17	10.28	24.40
Methane + Ethanol	3	19.38	18.78
Methanol + Ethane	5	72.68	29.64
Methanol + Water	10	6.64	2.53

Cross Second Virial Coefficients

Although few experimental data exist for polar systems with which to do a complete evaluation of the equations, we have estimated the cross second virial coefficients of

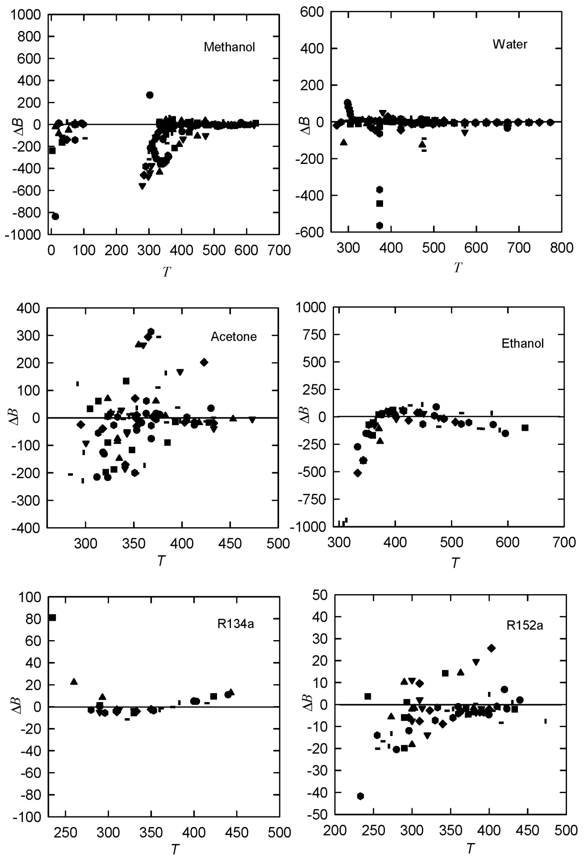

Figure 7. Absolute deviation of measured second virial coefficients from Eqns. (6)-(11) for different substances.

several systems using Eqns. (6)-(11). The combining rules we have used for σ_{12}, ε_{12}, $T^*_{Boyle,12}$ are

$$\sigma_{12} = \frac{1}{2}(\sigma_{11} + \sigma_{22})$$

$$\varepsilon_{12} = \sqrt{\varepsilon_{11}\varepsilon_{22}}$$

and

$$T^*_{Boyle,12} = \frac{2\left(T^*_{Boyle,11} T^*_{Boyle}\right)}{T^*_{Boyle,11} + T^*_{Boyle}}.$$

Table 7 contains the absolute average deviation of the data from the prediction using Eqns (6)-(11). Experimental data come from Warowny and Stecki (1979). Equations (6)-(11) predict the behavior for polar + polar and polar + nonpolar systems reasonably, however it is difficult to assign an accuracy estimate to the prediction because the experimental data themselves are uncertain.

IV. CONCLUSIONS

We have correlated the second virial coefficient from the Stockmayer potential using an analytical expression. The new equation uses the reduced dipole moment and the reduced Boyle temperature as correlating parameters. This generalized correlation allows calculation of the second virial coefficient for polar molecules as well as the Stockmayer potential but without using a numerical integration. The new equation compares favorably with the Tsonopoulos correlation. We show that the reduced Boyle temperature obtained from the Stockmayer second virial coefficient can be accurately correlated using the reduced dipole moment, t^*. Also, we have obtained the force constants for a large number of substances using one of the most complete databases for second virial coefficients. The new parameters agree well with existing values in the literature. We believe this work presents the most recent force constants for the second virial coefficient of the Stockmayer potential.

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