

LIQUID-VAPOUR EQUILIBRIUM AND HEATS OF MIXING IN THE 1-PROPANOL-ACETONITRILE SYSTEM*

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Vapour-liquid equilibrium and heats of mixing were measured in the 1-propanol-acetonitrile system. The vapour-liquid equilibrium data measurements were carried out under isobaric conditions at the pressures of 37.54, 56.44 and 86.05 kPa and isothermally at temperatures of 333.25 and 351.22 K. The heats of mixing were measured at temperatures of 298.15, 308.15 and 318.15 K. The individual vapour-liquid equilibrium data sets were correlated by various two-parameter equations, the data on heats of mixing by a Redlich-Kister polynomial. The extensive data obtained for both excess functions, covering the temperature range of 60 K, were correlated successfully by the Wilson equation with the energy parameters dependent quadratically on temperature.

This work is a continuation of our experimental study of systems formed by n-alcohols with acetonitrile. In one of our previous papers¹ we have reported the data on vapour-liquid equilibrium in the methanol-acetonitrile system at some conditions, and recently we have published² numerous experimental data on vapour-liquid equilibrium and heats of mixing for the ethanol-acetonitrile system as well. To our knowledge, there exist no equilibrium data in the literature, and the heat of mixing data are available³ only at the temperature of 298 K for the 1-propanol-acetonitrile system. Thus, in this work we present the vapour-liquid equilibrium data measured at reduced pressures (3 isobars and 2 isotherms) and the heats of mixing at three temperatures for the 1-propanol-acetonitrile system.

EXPERIMENTAL

Substances Used

1-Propanol, A.R. (Lachema, Brno), was distilled after small addition of sodium on a forty-plate bubble-cup column. After drying up with molecular sieves 4A, the water content found by the Fischer method was lower than 0.01 mass%.

Acetonitrile, A.R. (Avondale Laboratories, Banbury), was distilled on an 1.5 m long column

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filled with stainless steel helices. The product was dried up with molecular sieves 3A. The water content found by the Fischer analysis was lower than 0.01 mass%.

The measured values of density and refractive index of both the substances are compared with the literature ones in Table I.

Measurement of Vapour-Liquid Equilibrium and Heat of Mixing

The vapour-liquid equilibrium was measured using a modified circulation still of the Gillespie type⁴. The auxiliary pneumatic system and its control in isobaric and isothermal regime have been described before¹. The temperature measurement was carried out by a platinum resistance thermometer calibrated *in situ* by several ebulliometric standards. The pressure measurement was performed indirectly by the comparative ebulliometry. To analyze the equilibrium mixtures, we used interferometry¹. The measurement of heats of mixing was carried out in an isothermal calorimeter which has been described⁵ in detail before.

RESULTS

Data Treatment

The vapour-liquid equilibrium was determined isobarically at three pressures (37.54, 56.44 and 86.05 kPa) and isothermally at two temperatures (333.25 and 351.22 K). Activity coefficients γ_i and the excess Gibbs energy G^E were calculated from the experimental T , P , x , y values in terms of the following relations

$$\ln \gamma_i = \ln \frac{y_i P}{x_i P_i^S} + \frac{(B_{ii} - v_i^L)(P - P_i^S)}{RT} + \frac{PD_{ij}(1 - y_i)^2}{RT}, \quad (1)$$

$$D_{ij} = 2B_{ij} - B_{ii} - B_{jj}$$

and

$$G^E = x_1 \ln \gamma_1 + x_2 \ln \gamma_2, \quad (2)$$

where x_i , y_i are the mole fractions of component i in the liquid and vapour phases, respectively, v_i^L is the molar volume of pure liquid component i , P the total pressure and P_i^S the saturated vapour pressure of pure component i at the temperature T . The second virial coefficients B_{ii} , B_{ij} were estimated by means of the correlation by O'Connell and Prausnitz⁶. The saturated vapour pressures were calculated from the Antoine equation whose constants are given in Table I.

The inaccuracies of the measured and further input quantities were estimated as follows: $\sigma(x) = \sigma(y) = 0.0005$, $\sigma(T) = 0.02$ K, $\sigma(P) = 40$ Pa, $\sigma(P_1^S) = 90$ Pa, $\sigma(P_2^S) = 170$ Pa, $\sigma(B) = 300$ cm³ mol⁻¹. According to the error propagation formula, the variances of the calculated activity coefficients were determined⁷ from these inaccuracies. The variances found were used partly in the consistence test, partly

as the weighting factors in an objective function minimized with the aim to find the best values of parameters of correlation equation. The experimental data, the derived values of activity coefficients and their estimated errors are summarized in Table II.

The consistence of measured experimental data was checked by an integral test. For isobaric data subject to no experimental error, should hold

$$D \equiv \int_{x_1^{(1)}}^{x_1^{(n)}} \left(\ln \frac{\gamma_1}{\gamma_2} - \frac{h^E}{RT^2} \frac{\partial T}{\partial x_1} \right) dx_1 + G^E(x_1^{(1)}) - G^E(x_1^{(n)}) = 0, \quad (3)$$

where $x_1^{(1)}$, $x_1^{(n)}$ are the lowest and highest, respectively, experimental values of mole fraction x_1 . For isothermal data, on neglecting the unsubstantial pressure dependence, eq. (3) holds as well, however, naturally, $\partial T / \partial x_1 = 0$. The value of the integral was determined by trapezoidal rule. The calculated values of D for individual sets are given in Table III. Considering that experimental data are always subject to random errors, the value of D is not generally equal zero. The permitted tolerance was determined as a confidence interval by calculating from inaccuracies of input quantities by means of the error propagation formula. Considering that the calculated values of D lie inside their 95% confidence intervals, all the measured data can be considered consistent within the framework of the given errors of input quantities.

TABLE I

Density ρ , refractive index n_D of pure substances at 298.15 K, the temperature dependence of saturated vapour pressures (A , B , C^a) and of molar volumes of liquids (v_A , v_B^b)

Values	1-Propanol	Acetonitrile
ρ , g cm ⁻³ , exptl. lit.	0.7999 0.7998, ref. ¹⁴	0.7766 0.77656, ref. ¹⁵
n_D exptl. lit.	1.3835 1.3834, ref. ¹⁴	1.34150 1.34154, ref. ¹⁵
A	6.95720, ref. ¹⁶	6.46476, ref. ¹⁷
B	1 485.84	1 482.29
C	-70.150	-22.627
v_A , ref. ¹⁴	50.06	31.31
v_B	0.08400	0.07227

$$^a \log P [\text{kPa}] = A - B/(T[\text{K}] + C); \quad ^b v^L [\text{cm}^3/\text{mol}] = v_A + v_B T [\text{K}].$$

TABLE II
Experimental vapour-liquid equilibrium data

x_1	y_1	P , kPa	$\ln \gamma_1$	$\ln \gamma_2$	$\sigma(\ln \gamma_1)$	$\sigma(\ln \gamma_2)$
$P = 37.54$ kPa						
0.0187	0.0227	325.57	1.197	0.002	0.036	0.005
0.0479	0.0524	325.41	1.101	0.007	0.018	0.005
0.0888	0.0892	325.33	1.019	0.014	0.013	0.005
0.1496	0.1340	325.35	0.902	0.032	0.011	0.005
0.2186	0.1680	325.72	0.728	0.064	0.010	0.005
0.2562	0.1884	325.88	0.675	0.083	0.010	0.005
0.3040	0.2094	326.15	0.595	0.114	0.009	0.005
0.3494	0.2252	326.46	0.512	0.150	0.009	0.005
0.4238	0.2521	326.96	0.406	0.219	0.009	0.005
0.4608	0.2664	327.33	0.358	0.253	0.008	0.005
0.4964	0.2849	327.76	0.328	0.281	0.008	0.005
0.5797	0.3153	328.61	0.230	0.389	0.008	0.005
0.6475	0.3484	329.45	0.177	0.486	0.007	0.005
0.7165	0.3905	330.87	0.117	0.589	0.007	0.005
0.7868	0.4446	332.56	0.069	0.724	0.006	0.005
0.8239	0.4833	333.72	0.049	0.804	0.005	0.006
0.8453	0.5226	334.86	0.046	0.817	0.005	0.006
0.8681	0.5659	336.13	0.037	0.840	0.005	0.007
0.9356	0.7233	340.22	0.014	0.976	0.004	0.011
0.9695	0.8555	343.08	0.014	0.986	0.003	0.019
$P = 56.44$ kPa						
0.0376	0.0456	336.76	1.045	0.004	0.022	0.003
0.0621	0.0686	336.55	0.960	0.012	0.017	0.003
0.0790	0.0854	336.52	0.939	0.013	0.015	0.003
0.1349	0.1314	336.47	0.836	0.026	0.012	0.003
0.1917	0.1707	336.58	0.739	0.044	0.011	0.003
0.2651	0.2057	336.84	0.588	0.088	0.010	0.003
0.3133	0.2324	337.13	0.528	0.113	0.009	0.003
0.3403	0.2469	337.26	0.499	0.130	0.009	0.003
0.3650	0.2561	337.37	0.460	0.152	0.009	0.003
0.4069	0.2765	337.82	0.406	0.178	0.008	0.004
0.4767	0.3027	338.35	0.313	0.250	0.008	0.004
0.5314	0.3258	338.82	0.255	0.312	0.007	0.004
0.5437	0.3326	339.09	0.240	0.319	0.007	0.004
0.6064	0.3672	339.85	0.193	0.390	0.006	0.004
0.6495	0.3921	340.54	0.158	0.444	0.005	0.004
0.7343	0.4534	342.31	0.098	0.560	0.005	0.005
0.7931	0.5060	343.85	0.060	0.662	0.005	0.006
0.8433	0.5679	345.43	0.042	0.759	0.004	0.007
0.9159	0.7109	349.40	0.008	0.862	0.003	0.011
0.9489	0.7894	351.17	0.001	0.993	0.003	0.015

TABLE II
 (Continued)

x_1	y_1	T, K	$\ln \gamma_1$	$\ln \gamma_2$	$\sigma(\ln \gamma_1)$	$\sigma(\ln \gamma_2)$
$P = 86.05 \text{ kPa}$						
0.0365	0.0608	349.16	1.217	-0.005	0.024	0.002
0.0749	0.0970	348.92	0.974	0.003	0.019	0.002
0.1025	0.1176	348.82	0.856	0.014	0.017	0.002
0.1210	0.1279	348.74	0.777	0.025	0.016	0.002
0.1261	0.1322	348.75	0.768	0.026	0.016	0.002
0.1647	0.1617	348.70	0.703	0.038	0.015	0.002
0.1936	0.1830	348.74	0.662	0.047	0.014	0.002
0.2418	0.2141	348.87	0.590	0.066	0.013	0.003
0.3017	0.2461	349.08	0.497	0.101	0.012	0.003
0.3477	0.2713	349.37	0.439	0.127	0.011	0.003
0.4153	0.3045	349.87	0.354	0.176	0.010	0.003
0.5941	0.3990	351.82	0.179	0.339	0.008	0.004
0.6746	0.4448	352.89	0.114	0.451	0.007	0.005
0.7395	0.4958	354.19	0.075	0.541	0.006	0.007
0.8147	0.5729	356.14	0.041	0.663	0.004	0.009
0.8318	0.5852	356.57	0.023	0.719	0.004	0.009
0.8568	0.6293	357.57	0.025	0.741	0.004	0.010
0.9120	0.7160	359.80	0.001	0.902	0.003	0.014
0.9525	0.8348	362.52	0.002	0.907	0.002	0.020
0.9625	0.8639	362.95	0.009	0.939	0.002	0.023
x_1	y_1	$P, \text{ kPa}$	$\ln \gamma_1$	$\ln \gamma_2$	$\sigma(\ln \gamma_1)$	$\sigma(\ln \gamma_2)$
$T = 333.25 \text{ K}$						
0.0169	0.0226	49.86	1.189	0.005	0.040	0.004
0.0605	0.0676	50.41	1.019	0.014	0.018	0.004
0.0804	0.0863	50.40	0.978	0.015	0.016	0.004
0.1178	0.1178	50.44	0.906	0.022	0.014	0.004
0.1857	0.1631	50.16	0.769	0.045	0.013	0.004
0.2492	0.1978	49.75	0.659	0.076	0.012	0.004
0.2892	0.2182	49.42	0.601	0.097	0.012	0.004
0.3600	0.2427	48.89	0.477	0.162	0.011	0.004
0.3839	0.2520	48.57	0.443	0.181	0.011	0.004
0.4571	0.2832	47.38	0.360	0.242	0.011	0.004
0.4915	0.2926	36.81	0.308	0.283	0.010	0.004
0.5433	0.3164	45.77	0.263	0.335	0.010	0.004
0.5786	0.3338	44.72	0.231	0.368	0.010	0.004
0.6550	0.3643	43.01	0.155	0.484	0.010	0.004
0.6975	0.3840	41.80	0.116	0.557	0.010	0.005
0.7492	0.4231	39.77	0.092	0.631	0.009	0.005
0.7830	0.4476	38.53	0.072	0.702	0.009	0.005
0.8357	0.4963	36.19	0.048	0.829	0.009	0.006
0.9046	0.6010	31.60	0.025	1.010	0.009	0.008
0.9737	0.8146	24.49	0.002	1.286	0.009	0.020

TABLE II
(Continued)

x_1	y_1	T, K	$\ln \gamma_1$	$\ln \gamma_2$	$\sigma(\ln \gamma_1)$	$\sigma(\ln \gamma_2)$
$T = 351.22 K$						
0.0171	0.0237	91.38	1.007	0.008	0.041	0.002
0.0586	0.0713	92.79	0.889	0.016	0.022	0.002
0.0792	0.0899	93.14	0.822	0.021	0.020	0.002
0.1750	0.1775	93.57	0.709	0.035	0.015	0.002
0.2443	0.2190	93.31	0.581	0.069	0.014	0.002
0.3054	0.2479	92.69	0.473	0.110	0.013	0.003
0.3695	0.2831	91.38	0.400	0.146	0.011	0.003
0.4213	0.3116	90.16	0.350	0.179	0.010	0.003
0.4530	0.3349	89.04	0.337	0.190	0.010	0.003
0.5536	0.3721	86.50	0.212	0.310	0.008	0.004
0.6194	0.4074	84.01	0.160	0.385	0.007	0.005
0.6607	0.4338	82.11	0.135	0.434	0.007	0.005
0.7337	0.4834	78.22	0.090	0.540	0.006	0.006
0.7467	0.4951	77.29	0.084	0.556	0.005	0.006
0.7931	0.5324	74.04	0.054	0.642	0.005	0.007
0.8292	0.5714	71.51	0.045	0.715	0.004	0.008
0.8789	0.6512	65.87	0.036	0.777	0.003	0.010
0.8995	0.6852	63.55	0.028	0.828	0.003	0.011
0.9440	0.7877	57.03	0.012	0.918	0.003	0.014
0.9749	0.8929	51.77	0.010	0.946	0.002	0.024

The measured vapour-liquid equilibrium data were correlated by several two-parameter equations: Margules, van Laar, Wilson⁸, NRTL (ref.⁹), enthalpy Wilson (HMW) (ref.¹⁰), UNIQUAC (ref.¹¹) and LCG (ref.¹²). To evaluate their adjustable parameters, the following objective function was minimized

$$S = \sum_{j=1}^m \sum_{i=1}^2 (\ln \gamma_{ij}^{\text{exp}} - \ln \gamma_{ij}^{\text{calc}})^2 / \sigma^2(\ln \gamma_{ij}^{\text{exp}}), \quad (4)$$

where m is the number of experimental points.

The equations based on the local composition concept describe the experimental data altogether better than the classical ones. The constants and correlation deviations for only two most successful equations, *viz* the Wilson one

$$\ln \gamma_i = -\ln(x_i + A_{ij}x_j) + x_j[A_{ij}/(x_i + A_{ij}x_j) - A_{ji}/(x_j + A_{ji}x_i)] \quad (5)$$

and HMW

$$\ln \gamma_i = - \frac{x_j \ln(A_{ij}A_{ji})}{(x_i + A_{ij}x_j)(x_j + A_{ji}x_i)} \cdot \left[1 + x_i \left(1 - \frac{1}{x_i + A_{ij}x_j} - \frac{A_{ji}}{x_j + A_{ji}x_i} \right) \right], \quad (6)$$

where

$$A_{ij} = (v_j^L/v_i^L) \exp(-a_{ij}/T) \quad (7)$$

with a_{ij} as adjustable parameters, are given in Table IV.

The heats of mixing were measured at temperatures 298.15, 308.15 and 318.15 K in the entire concentration range. The absolute accuracy of the measured values is better than 1%. The heats of mixing are endothermic and reach considerable values at their maxima: 1 852, 1 927 and 1 987 J mol⁻¹ for the temperatures given. The maximum values are approximately 350 J mol⁻¹ higher than those for the ethanol-acetonitrile system.

The values of heats of mixing reported for this system and temperature of 298.15 K by Mato and Coca³ are in very good agreement with our data and the differences correspond to the estimated errors of both the measurements. The concentration dependence of enthalpy of mixing was expressed by the Redlich-Kister polynomial

$$H^E = \frac{h^E}{RT} = x_1 x_2 \sum_{k=0}^p A_k (x_1 - x_2)^k, \quad (8)$$

where A_k are adjustable parameters. The number of these parameters p was controlled by the statistical criterion of significance of difference of two variances (F -test). The same weight was prescribed to all the points. The experimental data, calculated constants of the Redlich-Kister expansion and standard deviation of correlation are given in Table V.

Simultaneous Representation of Vapour-Liquid Equilibrium and Heats of Mixing

The numerous experimental data for both excess functions (168 points) in the temperature range of approximately 60 K were represented simultaneously by the Wilson equation with energy parameters dependent on temperature in terms of the quadratic relation

$$G^E = -x_1 \ln(x_1 + A_{12} x_2) - x_2 \ln(x_2 + A_{21} x_1), \quad (9)$$

$$H^E = \frac{x_1 x_2}{T} \left[\frac{A_{12}(a_1 - c_1 T^2)}{x_1 + A_{12} x_2} + \frac{A_{21}(a_2 - c_2 T^2)}{x_2 + A_{21} x_1} \right], \quad (10)$$

where

$$A_{ij} = (v_j^L/v_i^L) \exp [-(\lambda_{ij} - \lambda_{ii})/RT], \quad (11)$$

$$(\lambda_{ij} - \lambda_{ii})/R = a_i + b_i T + c_i T^2. \quad (12)$$

Six adjustable constants $a_1, b_1, c_1, a_2, b_2, c_2$ were evaluated by a weighted least-

TABLE III

The consistence test of measured vapour-liquid equilibrium data

Set	$D \cdot 10^3$	$2\sigma(D) \cdot 10^3$
37.54 kPa	-0.1	13.0
56.44 kPa	4.0	9.8
86.05 kPa	-8.7	8.8
333.25 K	0.2	13.7
351.22 K	5.3	9.1

TABLE IV

Constants of the Wilson and HMW equations, standard deviations σ_{cor} and variance of fit σ for the representation of single vapour-liquid equilibrium data sets

Set	Equation	a_{12}, K	a_{21}, K	σ_{cor}^a	σ^b
37.54 kPa	Wilson	123.7	345.6	0.024	2.44
	HMW	18.1	251.6	0.022	2.18
56.44 kPa	Wilson	94.1	346.9	0.015	1.96
	HMW	8.6	253.9	0.013	1.78
86.05 kPa	Wilson	99.5	325.3	0.042	2.61
	HMW	11.2	248.2	0.042	2.57
333.25 K	Wilson	91.5	383.9	0.020	1.84
	HMW	9.1	262.1	0.020	1.80
351.22 K	Wilson	79.7	339.9	0.017	2.80
	HMW	4.2	252.8	0.018	2.77

$$^a \sigma_{\text{cor}} = [1/(2m - 2) \sum_{j=1}^2 \sum_{i=1}^m (\ln \gamma_{ij}^{\text{exp}} - \ln \gamma_{ij}^{\text{calc}})^2]^{1/2}; \quad ^b \sigma = [S/(2m - 2)]^{1/2}.$$

-squares method on using the following objective function

$$S = \frac{n_G + n_H}{n_G} \sum_{j=1}^{n_G} \frac{(G_{\text{exp},j}^E - G_{\text{calc},j}^E)^2}{\sigma^2(G_{\text{exp},j}^E)} + \frac{n_G + n_H}{n_H} \sum_{j=1}^{n_H} \frac{(H_{\text{exp},j}^E - H_{\text{calc},j}^E)^2}{\sigma^2(H_{\text{exp},j}^E)}, \quad (13)$$

TABLE V

Experimental data on heats of mixing, constants of the Redlich-Kister expansion and standard deviations of correlation

298.15 K		308.15 K		318.15 K	
x_1	H^E	x_1	H^E	x_1	H^E
0.0454	0.1593	0.0503	0.1709	0.0900	0.2794
0.0799	0.2638	0.0814	0.2638	0.1348	0.3890
0.1342	0.4001	0.1318	0.3899	0.1789	0.4812
0.1760	0.4881	0.1766	0.4851	0.2044	0.5239
0.2424	0.5930	0.2272	0.5722	0.2291	0.5636
0.2965	0.6579	0.2979	0.6608	0.2608	0.6097
0.3408	0.6950	0.3438	0.6982	0.2996	0.6570
0.3723	0.7140	0.3900	0.7267	0.3446	0.6948
0.4351	0.7418	0.4222	0.7435	0.3897	0.7254
0.4700	0.7470	0.4701	0.7521	0.4300	0.7439
0.5011	0.7470	0.4998	0.7521	0.4673	0.7511
0.5359	0.7341	0.5371	0.7451	0.4982	0.7507
0.5373	0.7386	0.5725	0.7302	0.5367	0.7447
0.5783	0.7196	0.5957	0.7158	0.5860	0.7239
0.6127	0.6999	0.6498	0.6782	0.6324	0.6940
0.6505	0.6720	0.6970	0.6330	0.6699	0.6615
0.6973	0.6297	0.7576	0.5534	0.6962	0.6373
0.7388	0.5974	0.8045	0.4816	0.7520	0.5648
0.7587	0.5405	0.8411	0.4129	0.8050	0.4835
0.8046	0.4784	0.8806	0.3310	0.8651	0.3655
0.8448	0.4001	0.9224	0.2295	0.9094	0.2642
0.8807	0.3288	0.9539	0.1444	0.9497	0.1565
0.9173	0.2384				
0.9547	0.1412				
A_0	2.9770		2.9991		2.9983
A_1	-0.2204		-0.1968		-0.1386
A_2	0.5546		0.4959		0.4375
σ^a	0.0052		0.0018		0.0016

$$^a \sigma = \left[\sum_{j=1}^m (H_{\text{exp},j}^E - H_{\text{calc},j}^E)^2 / (m - 3) \right]^{1/2}.$$

where n_G , n_H is the number of experimental values of excess Gibbs energy or excess enthalpy, respectively.

The variances $\sigma^2(G_{\text{exp},j}^E)$ were estimated from the knowledge of variances of activity coefficients $\sigma^2(\ln \gamma_{ij}^{\text{exp}})$ and of composition $\sigma^2(x)$. To estimate the variances $\sigma^2(H_{\text{exp},j}^E)$, the 1% inaccuracy of experimental H^E data, i.e. $\sigma^2(H_{\text{exp},j}^E) = (0.01H_{\text{exp},j}^E)^2$ was considered. To minimize the objective function, we used the Marquardt algorithm¹³. The calculated values of parameters are as follows: $a_1 = 1411.3$ K, $b_1 = -5.6623$, $c_1 = 51.494 \cdot 10^{-4}$ K⁻¹, $a_2 = 708.8$ K, $b_2 = -1.1247$, $c_2 = 4.671 \cdot 10^{-4}$ K⁻¹. The variance of fit is $\sigma = [S/(n_G + n_H - 6)]^{1/2} = 1.79$. The mean deviations of the calculated and experimental values are given in Table VI. The quantities σ and S_v estimate the ratio of correlation deviations and experimental errors for the entire set and single subsets, respectively. It is possible to judge from their values that the Wilson equation with quadratic dependence of the energy parameters on temperature represents our data nearly in the framework of the estimated inaccuracies. Similar results are reached by using the quadratic temperature dependence of parameters also with the HMW equation. The linear dependence of energy parameters on temperature is not sufficient for an adequate description of experimental data on this system for in this case the variance of fit increases several times.

TABLE VI

Summary of results of the simultaneous correlation; mean absolute deviations δ and deviations S_v for single data sets

Quantity	Set	δ	S_v^a
G^E	37.54 kPa	0.004	1.00
G^E	56.44 kPa	0.003	0.86
G^E	86.05 kPa	0.003	1.36
G^E	333.25 K	0.004	1.02
G^E	351.22 K	0.005	2.13
H^E	298.15 K	0.006	1.64
H^E	308.15 K	0.004	0.86
H^E	318.15 K	0.003	0.43

$$^a S_v = [1/m \sum_{j=1}^m (F_{\text{exp},j}^E - F_{\text{calc},j}^E)^2 / \sigma^2(F_{\text{exp},j}^E)]^{1/2}, m \text{ is number of points in the set.}$$

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