Excess Thermodynamic Properties for Hydrogen-Nitrogen Mixtures

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Values of excess thermodynamic properties, including excess enthalpy of mixing, excess Gibbs free energy of mixing, and excess entropy of mixing, were evaluated for the hydrogen-nitrogen binary system over the complete concentration range between 170° and 290° K., and up to 95 atm.

THE PURPOSE of this investigation is to evaluate the excess thermodynamic properties H^E, G^E, and S^E for gaseous mixtures of hydrogen and nitrogen over the complete concentration range. An excess thermodynamic property is defined as the difference between the thermodynamic property of mixing for the system concerned and that for an ideal one at the same temperature, pressure, and composition.

Thermodynamic functions of a 1-to-3 nitrogen-hydrogen mixture have been calculated by Michels, deGroot, and Lunbeck (*5*) between 0° and 300° C. These authors based their calculations on the *P-V-T* data given by Michels and Wassenaar for this mixture (*6*). For other compositions of the binary system, *P-V-T* data are also available in the literature, but limited to temperatures above 0° C. (*7*).

Beenakker *et al.* (*1*) indicated that the excess thermodynamic properties V^E and H^E are much more significant at temperatures below 293° K. This investigation is limited to the low-temperature region.

Numerical values of V^E and H^E for the hydrogen-nitrogen system at temperatures below 293° K. and up to 100 atm. have recently been published by Beenakker and his associates (*4, 8*). In each case, values were reported for three compositions. Using these limited results, consistent H^E, G^E, and S^E values were evaluated for the system over the complete concentration range in this investigation.

CALCULATION OF EXCESS THERMODYNAMIC PROPERTIES

Thermodynamic expressions employed in this investigation are well-known and may be presented briefly here. At constant temperature and composition,

$$dG^E = V^E\,dP \tag{1}$$

where G^E and V^E represent the excess Gibbs free energy and the excess volume of mixing, respectively. They are defined as follows:

$$G^E = \Delta G - \Delta G^{id} \tag{2}$$

and

$$V^E = \Delta V - \Delta V^{id} = \Delta V \tag{3}$$

since $\Delta V^{id} = 0$.

Integration of Equation 1 from the zero-pressure state to that at a finite pressure, P, at constant temperature and composition gives

$$G^E = \int_0^P V^E\,dP \tag{4}$$

as $G^E = 0$ at the zero-pressure state.

When G^E values are calculated by means of Equation 4 at various pressures for fixed temperatures and compositions, the excess entropy of mixing values, S^E, may be obtained at constant pressure and composition by the following equation:

$$S^E = -\,(\partial G^E/\partial T) \tag{5}$$

By definition,

$$H = G + TS \tag{6}$$

Hence,

$$H^E = G^E + TS^E \tag{7}$$

It is, therefore, possible to evaluate G^E, H^E, and S^E values if V^E values are available as a function of temperature and pressure at constant compositions.

Primary Information. Since V^E values are very small compared with pure component and mixture V values, V^E values evaluated from *P-V-T* data generally are of only fair accuracy. The authors found that a difference of 0.25% in Z values could give a 40% difference in V^E values. Zandbergen and Beenakker (*8*) measured the volume change of mixing for the gaseous mixtures of hydrogen and nitrogen, and smoothed V^E values were reported at three temperatures (170.5°, 231.7°, and 292.6° K.) up to 100 atm. for three constant-composition mixtures (25%, 50%, and 70% hydrogen). These values were employed as the primary information for the evaluation.

Procedure. Excess Gibbs free energy values were initially evaluated at the three temperatures at which V^E values were reported by integrating Equation 4 graphically. An attempt to obtain G^E values at other temperatures using interpolated V^E values was made, but the results were rejected. As V^E values were only reported at three temperatures over a range of 122° K., the uncertainty involved in the interpolation procedure is reflected in the G^E values. At low temperature and high pressure conditions, a difference of 0.3% in G^E values could give a 20% difference

Table I. Conditions of Experimental H^E Values Reported in the Literature (*4*)

Temp., ° K.	Compn., % Hydrogen	Pressure Range, Atm.
293	22	53.7–123.7
	47.5	29.0–131.0
	75	44.0–120.1
231	47.5	9.6–123.4
201	22	33.9–116.6
	47.5	10.4–114.2
	75	29.4–116.8
170	47.5	7.8–133.0
147	22	34.6–113.6
	47.5	5.6–134.0
	75	58.6–112.0

in the calculated S^E values and a 15% difference in the calculated H^E values. These differences decrease, however, with an increase of temperature and decrease of pressure. The difficulties encountered in the low temperature and high pressure region led to the application of experimentally determined H^E values to the construction of G^E *vs.* T plots at constant pressure and composition conditions. Knoester, Taconis, and Beenakker (*4*) measured the H^E values for three hydrogen-nitrogen mixtures at the conditions shown in Table I.

Experimental H^E values were graphically smoothed on H^E *vs.* P plots at constant temperature and composition conditions. The differences obtained between the smoothed and experimental values are well within the experimental error reported by the authors (*4*). Interpolated H^E values obtained from these plots, at the pressures at which the G^E values were computed, were then employed to construct H^E *vs.* T plots at constant pressure and composition conditions for the purpose of obtaining interpolated H^E values at the temperatures at which the G^E values were evaluated. These values were then employed to obtain H^E values at the corresponding compositions on H^E/y_1y_2 *vs.* y_1 plots at constant temperature and pressure conditions. No difficulties were encountered in these interpolation steps. The interpolated H^E values were considered "true" values and were combined with the calculated G^E values to obtain the S^E values by means of Equation 7, hence the $(\partial G^E/\partial T)$ values. The constructed G^E *vs.* T curves were used to obtain G^E values at regular temperature intervals. They were further smoothed on G^E *vs.* P plots at constant temperature and composition conditions. The interpolated isothermal G^E curves were slightly adjusted, together with the isobaric G^E curves, until they were consistent with each other and with the $(\partial G^E/\partial T)$ values obtained from the interpolated H^E values. The corresponding S^E values were computed by means of Equation 5, and the H^E values by Equation 7. A similar cross-plotting procedure was employed to obtain consistent values. Following this procedure, consistent values of G^E, S^E, and H^E were obtained at regular intervals of temperature and pressure for the three hydrogen-nitrogen mixtures (25%, 50%, and 70% hydrogen). To extend these values over the complete concentration range, the extrapolation method developed by Deshpande and Lu (*2*) and Jones and Lu (*3*) was employed.

RESULTS

The calculated H^E, G^E, and S^E values for the hydrogen-nitrogen binary system between 170° and 290° K. are presented at 10° intervals and at regular intervals of pressure and composition. Results obtained for the system at 200° K. are given in Table II. The complete table may be obtained from the American Society for Information Science. A typical example is shown in Figure 1, in which calculated H^E, TS^E, and G^E values are plotted over the complete concentration range for the system at 200° K. and 80 atm. The experimental H^E values (*4*) are compared with the interpolated H^E values, using the calculated results listed in these tables. The average deviation is less than 1%. This is the magnitude of error introduced by the cross-

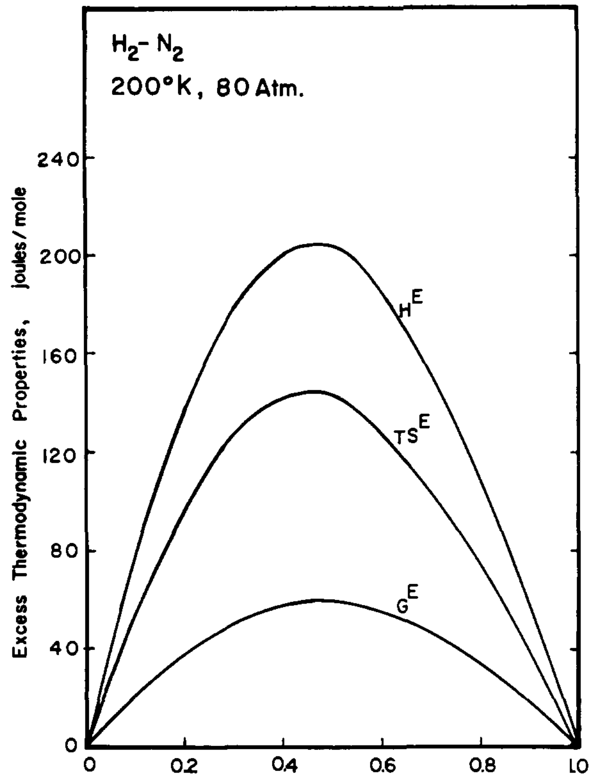

Figure 1. Calculated excess thermodynamic properties at 200° K. and 80 atm.

Table II. Excess Thermodynamic Properties for the Hydrogen-Nitrogen Mixtures at 200° K.

	P., Atm.	Mole Fraction of Hydrogen								
		0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9
H^E	95	99.4	168	218	241	248	224	186	135	76.2
	80	76.8	133	177	200	204	185	153	110	60.0
	60	51.9	92.1	125	142	147	135	111	82.2	42.8
	40	29.7	54.4	73.9	87.7	90.6	84.1	69.7	50.7	26.9
	20	13.5	24.6	33.4	38.7	41.0	38.1	31.0	22.6	12.5
	10	6.05	11.4	15.0	18.2	19.7	18.6	14.9	11.2	6.12
G^E	95	25.2	44.7	60.2	68.9	70.8	67.1	56.3	41.5	22.6
	80	21.2	37.5	50.5	58.0	59.8	56.5	47.5	35.0	19.0
	60	15.7	28.1	37.5	43.3	44.9	42.1	35.6	26.2	14.2
	40	10.2	18.6	24.5	28.5	29.6	27.9	23.7	17.5	9.49
	20	4.96	9.06	12.0	13.9	14.6	13.7	11.6	8.53	4.76
	10	2.35	4.46	5.98	6.97	7.20	6.85	5.91	4.25	2.42
S^E	95	0.371	0.614	0.790	0.859	0.885	0.785	0.648	0.468	0.268
	80	0.278	0.475	0.633	0.708	0.720	0.640	0.527	0.377	0.205
	60	0.181	0.320	0.437	0.491	0.508	0.462	0.379	0.280	0.143
	40	0.0973	0.179	0.247	0.296	0.305	0.281	0.230	0.166	0.0870
	20	0.0428	0.0779	0.107	0.124	0.132	0.122	0.0970	0.0703	0.0385
	10	0.0185	0.0349	0.0451	0.0559	0.0624	0.0588	0.0449	0.0345	0.0185

plotting procedure described above. The comparison made for the y_{H_2} = 0.475 mixture is shown in Figure 2.

Knoester, Taconis, and Beenakker (*4*) reported that, in general, the errors in the H^E measurements were less than 5%. The uncertainty of the calculated G^E and S^E values was estimated by the authors to be of the same magnitude.

Within the range of this investigation, at constant composition conditions, the calculated H^E, G^E, and S^E values increase with increasing pressure, but decrease with an increase in temperature. In all cases, $H^E > TS^E > G^E$, and the quantity TS^E contributes much more than the quantity G^E to the H^E value at a given condition. Hence, gaseous mixtures of hydrogen and nitrogen are neither regular nor athermal solutions.

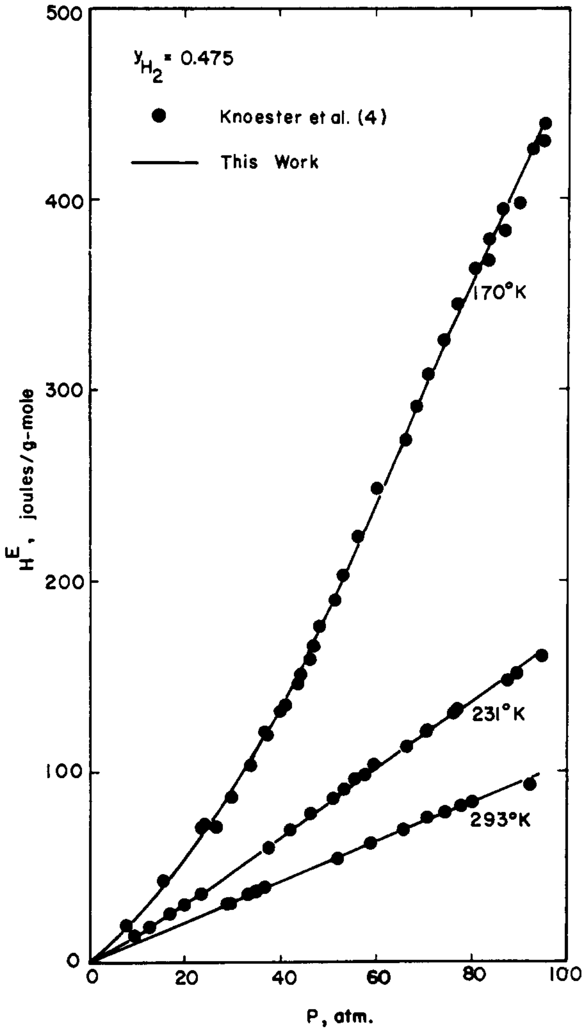

Figure 2. Comparison of the experimental H^E values with the calculated results for y_{H_2} = 0.475 mixture

NOMENCLATURE

G = molal Gibbs free energy, joules/mole
H = molal enthalpy, joules/mole
P = pressure, atm.
S = molal entropy, joules/(mole)(° K.)
T = temperature, ° K.
V = molal volume, ml./mole
y = mole fraction
Z = compressibility factor

Superscripts

id = ideal
E = excess

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