DETERMINATION OF IDEAL GAS THERMODYNAMIC PROPERTY RELATIONS BY MULTIPROPERTY ANALYSIS

Iraj Khajavi Noori and Kenneth E. Starling

School of Chemical Engineering and Materials Science, University of Oklahoma,
Norman, Oklahoma

Multiproperty analysis calculations were performed to correlate simultaneously ideal gas heat capacity, enthalpy, and entropy. The basis for the correlation is a power series in temperature for the heat capacity. It is shown that for any single property simultaneous correlation of three properties gives better results than those based on parameters obtained by correlating the other two. This deviation becomes worse when only one property is used to obtain parameters. Results are given for fifteen compounds of interest in the natural gas industry.

The need for simple yet accurate relations for thermodynamic properties is well known. Although there are compilations of ideal gas properties such as JANAF Thermodynamical Tables (1), API Research Project (2), and the works of Canjar (3) and Din (4), most engineers prefer to use equations which enable them to calculate properties at any given state without having to interpolate or extrapolate between discrete values of tables. For this purpose relations for properties have been developed which give excellent results in prescribed ranges. These relations, although very useful to calculate the properties for which they were developed, lose their significance when they are used to calculate other properties. This is especially true when property relations are differentiated in order to obtain relations for other properties. For example, Ellington and Eakin (5) have shown that an uncertainty of the order of 1% in PVT data causes uncertainty of the order of 10% in the thermodynamic properties obtained by differentiation. For a second differentiation the order of uncertainty rises to 100%.

Owing to these facts, it is very desirable to assume a model for one property and, using the relationship among thermodynamic properties, develop dependent, rather than independent, models for other properties. The remaining task, the most important one, is to determine the parameters of these relations. It can be shown that, when a model for one property is taken as the basis of developing models for other properties, all or most of the parameters of the original model also appear in other models. Therefore, for self-consistent calculations, only one set of parameters is needed for all the properties which are considered.

The object of this work was to find single sets of parameters in self-consistent relations of ideal gas enthalpy, entropy, and heat capacity.

METHODS

The method of multiproperty analysis was used for calculations which were applied to fifteen compounds of interest in the natural gas industry. These compounds are listed in Table 1.

Thermodynamic relations

To calculate the enthalpy, H_t, of any component in the ideal gas state at temperature T, one can write

$$H_T = \int_{T_{HR}}^{T} C_p dT + H_{T_{HR}} + H_f \quad \text{Eq. 1}$$

In this relation C_p is the ideal gas heat capacity. The value of H_T is relative to the enthalpy of elements at 0°R, H_f is the enthalpy of formation of the compound from the elements at 0°R and $H_{T_{HR}}$ is the enthalpy at the reference temperature T_{HR} relative to the enthalpy of the compound at absolute zero of temperature, 0°R.

For entropy we have

$$S_T = \int_{T_{SR}}^{T} \left(C_p/T \right) dT + S_{T_{SR}} \quad \text{Eq. 2}$$

where T_{SR} is the reference temperature and $S_{T_{SR}}$ is the entropy of the compound at the reference temperature relative to the entropy of the compound at absolute zero temperature (assumed to be zero according to the third law of thermodynamics).

Choice of model

One could assume a polynomial expansion in temperature for entropy, for enthalpy, or for heat capacity from which the necessary relations for the other two properties could be developed. These possibilities were compared and the most appropriate model was found to be the one in which we assumed a polynomial for C_p and considered it as the basis for calculating entropy and enthalpy.

$$C_p = a_1 + a_2T + \dots + a_nT^{n-1} \qquad \text{Eq. 3}$$

We observed that, by having only a relation for C_p as a function of temperature, enthalpy and entropy were readily found from equations 1 and 2. Therefore, using the value from equation 3 for C_p in equation 1 for H_T, we have:

$$H_T = a_1\left(T - T_{HR}\right) + (1/2)\, a_2\left(T^2 - T_{HR}{}^2\right) + \dots + (1/n)\, a_n\left(T^n - T_{HR}{}^n\right) + H_f + H_{T_{HR}} \qquad \text{Eq. 4}$$

Similarly, for entropy we obtain:

$$S_T = a_1 \ln\left(T/T_{SR}\right) + a_2\left(T - T_{SR}\right) + \dots + (1/(n-1))\, a_n\left(T^{n-1} - T_{SR}{}^{n-1}\right) + S_{T_{SR}} \qquad \text{Eq. 5}$$

Observing equations 4 and 5, we notice that the reference temperatures T_{HR} and T_{SR} can both be chosen arbitrarily for enthalpy and entropy, respectively. Herein lies the major advantage of using C_p rather than H or S as the basis polynomial. However, no matter which property is chosen as the basis of calculations, we always end up with one set of parameters $a_1, a_2, \dots, a_n$ for all three properties. The use of C_p is merely the most convenient basis.

Multiproperty analysis

To estimate the parameters $a_1, a_2, \dots a_n$ we define an objective function Q by the relation

$$Q = uQ_1 + v\,Q_2 + w\,Q_3 \qquad \text{Eq. 6}$$

where u, v, and w are weighting factors for entropy, heat capacity, and enthalpy, respectively, and Q_1, Q_2, and Q_3 are the sums of squares of errors defined by the relations

$$Q_1 = \sum_{\ell=1}^{NP1}\left[S_{E_\ell} - S_{C_\ell}\right]^2 \qquad \text{Eq. 7}$$

$$Q_2 = \sum_{m=1}^{NP2}\left[C_{p_{E_m}} - C_{p_{C_m}}\right]^2 \qquad \text{Eq. 8}$$

$$Q_3 \sum_{r=1}^{NP3}\left[H_{E_r} - H_{C_r}\right]^2 \qquad \text{Eq. 9}$$

Np1, Np2, and Np3 are the number of data (or tabulated) points for entropy, heat capacity, and enthalpy, respectively; the subscripts E and C indicate the experimental (or tabulated) and calculated values, respectively. The weighting factors u, v, and w were taken to be unity in the present work.

According to the method of least squares, we have

$$\frac{\partial Q}{\partial a_i} = 0, \quad i = 1, 2, \dots, n \qquad \text{Eq. 10}$$

This leads to a set of linear equations in the parameters, known as the normal equations, to be solved for the parameter values. Computations were carried out using the University of Oklahoma IBM 360/50 computer.

For purposes of discussion, the standard error of estimate, S, and average absolute per cent error, a, were calculated, where

$$S = \frac{\sum_{i=1}^{NP}\left(Y_i - f(T_i)\right)^2}{(NP-n)}^{1/2} \qquad \text{Eq. 11}$$

and

$$a = \frac{1}{NP}\sum_{i=1}^{NP}\left|\frac{Y_i - f\,(T_i)}{Y_i}\right| \qquad \text{Eq. 12}$$

In these relations Y_i is the tabulated property value at the temperature T_i and $f(T_i)$ is the polynomial for the property, n is the number of parameters, and NP the number of tabulated points.

Sources of data

The data used in this work were extracted from the following sources.

With the exceptions of four materials (ethylene, nitrogen, carbon dioxide and hydrogen sulfide), the values of enthalpy, heat capacity, and entropy of the remaining compounds were obtained from the API-44 (2). The values of properties for the above four materials were obtained from JANAF Tables (1) because they cover a lower temperature range than that reported in API-44. Table 1 shows the range of temperatures used for enthalpy, heat capacity, and entropy of each compound. Table 2 shows the values of reference temperatures and property values.

TABLE 1. *Temperature ranges of enthalpy, heat capacity, and entropy.*[a]

Compound	Enthalpy	Heat Capacity	Entropy
Methane	160-1660	160-1660	180-1620
Ethane	210-1660	210-1660	180-1620
Propane	210-1660	210-1660	180-1620
n-Butane	360-1660	460-1660	360-1620
i-Butane	360-1660	360-1660	360-1660
n-Pentane	360-1660	460-1660	360-1660
i-Pentane	360-1660	460-1660	360-1660
n-Hexane	460-1660	460-1660	540-1800
n-Heptane	460-1660	460-1660	540-1800
n-Octane	460-1660	460-1660	540-1660
Ethylene	180-1800	180-1800	180-1800
Propylene	460-1860	460-1860	540-1980
Nitrogen	180-1800	180-1800	180-1800
CO_2	180-1800	180-1800	180-1800
H_2S	180-1800	180-1800	180-1800

[a] All temperatures are in degrees Rankine.

The enthalpy data taken from API-44 tables are modified for each compound by addition of the heat of formation of the compound so that all enthalpies are relative to the enthalpies of the constituents at the reference state (zero degree Rankine and 1 psia). The values taken from JANAF are also modified appropriately to maintain consistency among the reference states and units of all data.

The heats of formation of ethylene, nitrogen, carbon dioxide, and hydrogen sulfide were also obtained from JANAF. For isopentane, *n*-heptane, and *n*-octane the values were derived from API-44 Tables. The heats of formation of the remaining compounds were extracted from the compilation of Canjar and Manning (3).

The molecular weights of the compounds are calculated from the following atomic weights (6): hydrogen = 1.008; carbon = 12.011; nitrogen = 14.007; oxygen = 16.000; sulfur = 32.064.

RESULTS AND DISCUSSION

The program written for calculation of parameters has the flexibility of calculating these parameters for any combination of enthalpy, heat capacity, and entropy data, i.e., it is possible to calculate $a_1, \ldots, a$ from the data supplied for only one property, for any of the two properties, or, finally, from all three properties simultaneously. In order to determine the consistency among the data of the different properties used in this study, all these combinations were tested.

TABLE 2. *Constants used in regression analysis.*

Compound	T_{HR} [a]	$h_{T_{HR}}$ [b]	T_{SR} [c]	$s_{T_{SR}}$ [d]	h_f [e]	M.W.[f]
Methane	160.0	79.08	180.0	2.559	-1793.83	16.043
Ethane	210.0	57.09	180.0	1.639	-983.78	30.070
Propane	210.0	41.34	180.0	1.267	-795.29	44.097
n-Butane	360.0	81.59	360.0	1.227	-733.10	58.124
i-Butane	360.0	71.43	360.0	1.167	-783.04	58.124
n-Pentane	360.0	78.56	360.0	1.091	-679.40	72.151
i-Pentane	360.0	72.13	360.0	1.079	-718.68	72.151
n-Hexane	460.0	110.05	540.0	1.139	-645.50	86.178
n-Heptane	460.0	105.52	540.0	1.074	-620.67	100.205
n-Octane	460.0	107.42	540.0	1.023	-601.97	114.232
Ethylene	180.0	51.01	180.0	1.728	931.63	28.054
Propylene	460.0	112.00	540.0	1.645	362.24	42.081
Nitrogen	180.0	44.53	180.0	1.553	0.00	28.014
CO_2	180.0	28.42	180.0	1.093	-3842.53	44.011
H_2S	180.0	41.99	180.0	1.342	-217.55	34.080

[a] T_{HR} = enthalpy reference temperature, °R.

[b] $h_{T_{HR}}$ = compound's absolute enthalpy at T_{HR}, Btu/lb.

[c] T_{SR} = entropy reference temperature, °R.

[d] $s_{T_{SR}}$ = compound's entropy at T_{SR}, Btu/lb.,

[e] h_f = heat of formation, Btu/lb.

[f] M.W. = molecular weight.

Table 3 is a typical example of the results of computations of different combinations of data for *n*-hexane. The first column of this table indicates the combination of the properties used to obtain the parameters. The second column lists the numbers of parameters used in correlation, and other columns give the standard error of estimate and average per cent deviation of enthalpy, heat capacity, and entropy, respectively. Examination of this table reveals that simultaneous correlation of the three properties generally gives a better result for each property than results obtained for the same property when calculated with parameters obtained from correlating the other two. At the same time, correlation of two properties gives better results for those two properties than the results obtained from simultaneous correlation of all three properties. Finally, the parameters from the data of only one property give the best values for that property, and still poorer results for the other two.

These observations indicate that although a nearly perfect fit for a single property might be obtained, it does not imply that other properties can always be predicted accurately on the basis of correlation ob-

TABLE 3. *Comparison of standard error of Estimate and average percent error computed for different combinations of data for n-hexane.*

		Enthalpy		Heat capacity		Entropy	
Data	N	Standard error (Btu/lb)	Average error (%)	Standard error (Btu/lb)	Average error (%)	Standard error (Btu/lb)	Average error (%)
H, C and S	1	40.895	15.70	0.184	25.20	0.033	1.65
	2	4.197	1.16	0.027	3.09	0.002	0.10
	3	0.378	0.06	0.002	0.21	0.001	0.04
	4	0.390	0.05	0.002	0.20	0.001	0.04
	5	0.341	0.06	0.001	0.14	0.001	0.05
H and C	1	40.895	15.70	0.184	25.20	0.033	1.65
	2	4.197	1.16	0.027	3.09	0.002	0.10
	3	0.377	0.06	0.002	0.21	0.001	0.04
	4	0.389	0.05	0.002	0.20	0.001	0.04
	5	0.339	0.06	0.001	0.14	0.001	0.05
S and H	1	40.895	15.74	0.184	25.20	0.033	1.65
	2	4.320	1.13	0.024	3.19	0.003	0.12
	3	0.238	0.04	0.002	0.23	0.001	0.04
	4	0.074	0.02	0.003	0.31	0.001	0.03
	5	0.033	0.01	0.004	0.41	0.001	0.02
C and S	1	53.210	122.78	0.202	25.85	0.039	1.64
	2	6.415	30.37	0.025	3.01	0.009	0.37
	3	0.893	2.86	0.001	0.18	0.000	0.01
	4	0.940	2.92	0.001	0.18	0.000	0.01
	5	0.939	3.18	0.001	0.05	0.000	0.01
H	1	40.894	15.74	0.184	25.20	0.033	1.65
	2	4.325	1.13	0.024	3.19	0.003	0.12
	3	0.233	0.04	0.002	0.23	0.001	0.04
	4	0.080	0.02	0.003	0.30	0.001	0.03
	5	0.038	0.01	0.004	0.36	0.001	0.03
C	1	53.556	124.70	0.203	25.87	0.039	1.65
	2	6.678	31.46	0.025	3.02	0.009	0.39
	3	0.894	2.87	0.001	0.18	0.000	0.01
	4	0.938	2.91	0.001	0.18	0.000	0.01
	5	0.932	3.16	0.001	0.05	0.000	0.01
S	1	44.907	67.95	0.192	25.37	0.033	1.54
	2	4.223	1.38	0.028	3.08	0.002	0.10
	3	0.856	2.87	0.001	0.18	0.000	0.01
	4	0.767	2.22	0.002	0.22	0.000	0.01
	5	0.451	1.33	0.004	0.45	0.000	0.00

tained for that property. Also, it appears that the larger the number of properties included, the better the results for those which were not included originally. Similar conclusions have been reached by Passut and Danner (7) in an independent study reported after completion of the present work.

Examination of Table 3 also reveals that the tabulated values for enthalpy, heat capacity, and, possibly, entropy are not quite consistent. The possibility of inconsistency exists in the data for all 15 compounds considered here, but to various degrees. If the data of different properties of one compound were perfectly consistent and if equations 3, 4, and 5 for C_p, H, and S were correct, essentially the same results would have been obtained no matter what combination of properties was used. None of the 15 compounds considered satisfies this criterion and, as indicated previously, the results obtained from different combinations of data are generally different.

As criteria for the level of accuracy of the calculated values, a maximum standard deviation of 0.3 Btu/lb for enthalpy and 0.003 Btu/lb°R for entropy were considered. Except for *n*-heptane, this level was satisfied for all compounds considered by using polynomials with six or fewer parameters. For nine of these 15 materials the criteria were satisfied with only three parameters. Space does not permit the presentation of all of these results. Table 4 records the values of the parameters in the six-parameter polynomial for all compounds. Table 5 shows the standard error of estimate and average per cent deviations of enthalpies, heat capacities, and entropies of all compounds obtained by using the parameters of Table 4.

TABLE 4. *Parameters in approximating polynomials for enthalpy, entropy, and heat capacity.*

Compound	a_1	a_2	a_3	a_4	a_5	a_6
Methane	0.552005E 00	-0.388922E-03	0.546747E-06	0.522131E-09	-0.677861E-12	0.188727E-15
Ethane	0.354508E 00	-0.660753E-03	0.234779E-05	-0.207878E-08	0.843175E-12	-0.134132E-15
Propane	0.305692E 00	-0.806187E-03	0.320346E-05	-0.333996E-08	0.159272E-11	-0.294042E-15
n-Butane	0.215054E 00	-0.192172E-03	0.174302E-05	-0.174511E-08	0.763104E-12	-0.128167E-15
i-Butane	0.268085E 00	-0.669140E-03	0.300679E-05	-0.316424E-08	0.148839E-11	-0.267666E-15
n-Pentane	0.251921E 00	-0.451137E-03	0.238926E-05	-0.250615E-08	0.118260E-11	-0.215752E-15
i-Pentane	0.152981E 00	-0.902555E-03	0.152256E-05	-0.159462E-08	0.696393E-12	-0.113578E-15
n-Hexane	-0.112451E 00	0.131948E-02	-0.951274E-06	0.551223E-09	-0.182807E-12	0.229476E-16
n-Heptane	-0.925871E 01	0.118539E-02	-0.704731E-06	0.285173E-09	-0.393949E-13	-0.710573E-17
n-Octane	-0.463255E-01	0.941057E-03	-0.123831E-06	-0.331620E-09	0.270474E-12	-0.667791E-16
Ethylene	0.404864E 00	-0.115404E-02	0.343861E-05	-0.334607E-08	0.149325E-11	-0.255603E-15
Proplyene	0.196387E 00	-0.111278E-03	0.134306E-05	-0.131514E-08	0.554482E-12	-0.888333E-16
Nitrogen	0.244689E 00	0.356575E-04	-0.115366E-06	0.152236E-09	-0.758606E-13	0.133867E-16
CO_2	0.142563E 00	0.102378E-04	0.381144E-06	-0.485579E-09	0.249721E-12	-0.472635E-16
H_2S	0.245576E 00	-0.104126E-03	0.262507E-06	-0.207227E-09	0.856292E-13	-0.148408E-16

TABLE 5. *Standard errors of estimates and average percent deviations*

	Enthalpy		Heat capacity		Entropy	
Compound	Standard error	Average error (%)	Standard error	Average error (%)	Standard error	Average error (%)
Methane	0.126	0.01	0.004	0.30	0.000	0.01
Ethane	0.213	0.02	0.003	0.33	0.003	0.08
Propane	0.166	0.03	0.004	0.62	0.003	0.15
n-Butane	0.080	0.07	0.001	0.10	0.002	0.07
i-Butane	0.086	0.02	0.001	0.19	0.001	0.04
n-Pentane	0.088	0.03	0.001	0.13	0.001	0.06
i-Pentane	0.110	0.24	0.001	0.09	0.001	0.02
n-Hexane	0.025	0.06	0.005	0.41	0.001	0.02
n-Heptane	0.034	0.20	0.027	3.05	0.023	0.66
n-Octane	0.029	0.02	0.004	0.41	0.001	0.02
Ethylene	0.065	0.00	0.004	0.37	0.001	0.01
Propylene	0.071	0.01	0.001	0.09	0.001	0.02
Nitrogen	0.022	0.00	0.000	0.01	0.000	0.00
CO_2	0.039	0.00	0.002	0.45	0.000	0.01
H_2S	0.012	0.13	0.001	0.09	0.000	0.00

Analysis of errors in extrapolation of polynomials

It has been shown that the parameters obtained for approximating polynomials give very good results in the range of temperature of the tabulated properties. It was of interest to determine whether these polynomials can be extended beyond their original range of temperature, and, if so, the lowest and highest temperatures between which the extrapolation can be made accurately. Information on the accuracy of extrapolations to low temperatures is particularly important because property tabulations are incomplete in regions of current low-temperature processing of numerous fluids.

To answer these questions, an error analysis was performed for methane. First a temperature range of 460-1660 R was considered and polynomials with six parameters were used to fit the tabulated values for enthalpy, heat capacity, and entropy simultaneously. The polynomials thus obtained fit the data very closely for the temperature range considered. To see how well the polynomials obtained for the three properties can be extrapolated, the polynomials were evaluated for temperatures not within the original range. The results for enthalpy, as an example, are given in Table 6, where the figures indicate that the polynomial for enthalpy can be extrapolated up to 100 Rankine below the lowest temperature originally considered without ignoring the criteria of accuracy set for enthalpy (i.e., 0.3 Btu/lb).

The same procedure was repeated for temperature ranges from 360 to 1660 Rankine and from 260 to 1660 Rankine, respectively. The results of these extrapolations also are recorded in Table 6.

Figure 1 shows a plot of enthalpy deviations obtained from extrapolation of the above three cases, as a function of temperature. We observed that, for the polynomial fits between 460 to 1660 R, 360 to 1660 R, and 260 to 1660 R, the extrapolation can be accurately carried out for 110 R, 75 R, and 40 R below the lowest temperatures considered in each fit, respectively. Extrapolation of these results for the case of 160 to 1660 R (dashed line in Fig. 1), indicated that it is unsatisfactory to extrapolate the polynomial fit obtained for this range for more than about 10 R below the lowest temperature considered, i.e., 160 R. These results showed that the range of extrapolation for the low temperature regions narrows very rapidly as the lower limit of temperature used for polynomial fit decreases. Therefore, for the lower temperature regions it is not possible to give a range of extrapolation applicable to the polynomials of all compounds because the ranges start at different temperatures.

Similar calculation also was performed for the higher temperature range and it was observed that the extrapolation can be carried out accurately up to 100 R beyond the temperature range originally considered.

TABLE 6. *The effect of temperature range upon error terms about extrapolation of polynomials for methane.*

Temperature (R)	H Exptl. (Btu/lb)	H. Calc. (Btu/lb)	Deviation (Btu/lb)	Error (%)
		Temperature range 460 to 1660 R		
409.69	−1590.63	−1590.66	0.03	0.00
359.69	−1615.63	−1615.84	0.21	0.01
309.69	−1640.43	−1641.05	0.62	0.04
259.69	−1665.23	−1666.63	1.40	0.08
209.69	−1690.03	−1692.96	2.93	0.17
159.69	−1714.75	−1720.49	5.64	0.33
		Temperature range 360 to 1660 R		
309.69	−1640.43	−1640.60	0.17	0.01
259.69	−1665.23	1665.79	0.56	0.03
209.69	−1690.03	−1691.54	1.51	0.09
159.69	−1714.75	−1718.21	3.46	0.20
		Temperature range 260 to 1660 R		
209.69	−1690.03	−1690.42	0.39	0.02
159.69	−1714.75	−1716.24	1.49	0.09

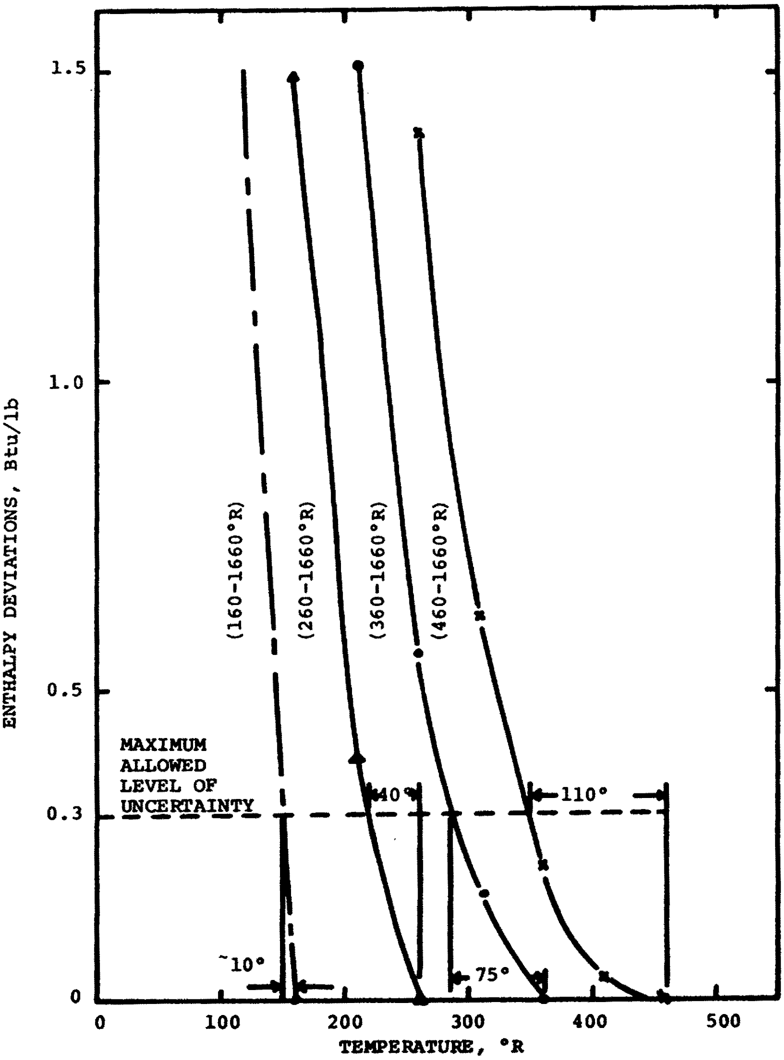

FIGURE 1. Comparison of allowable ranges of extrapolation enthalpy polynomials for methane.

REFERENCES

1. *JANAF Thermodynamical Data*, U.S. Air Force Contract No. AF33(616)-6149, Dow Chemical Co., Midland, Michigan, 1960.
2. R. D. ROSSINI, K. S. PITZER, R. L. ARNETT, R. M. BRAUN, and G. C. PIMENTEL, *Selected Values of Physical and Thermodynamic Properties of Hydrocarbons and Related Compounds*, Extracted from API Res. Proj. 44, Carnegie Press, Pittsburgh, 1953.
3. L. N. CANJAR and F. S. MANNING, *Thermodynamic Properties and Reduced Correlations for Gases*, Gulf Publishing Co., Houston, Texas, 1967.
4. F. DIN, *Thermodynamic Functions of Gases*, Vol. 1, 2, and 3, Butterworths, London 1961.
5. R. T. ELLINGTON and B. E. EAKIN, Chem. Eng. Prog. 59 80-88 (1963).
6. *Physical and Thermodynamic Properties of Elements and Compounds*, Chemetron Corporation, Catalysis Division, New York, 1969.
7. C. A. PASSUT and R. P. DANNER, Ind. Eng. Chem. Process Design Develop. 11: 543-546 (1972).