THERM: Thermodynamic Property Estimation for Gas Phase Radicals and Molecules

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Abstract

We have developed a computer code for an IBM PC/XT/AT or compatible which can be used to estimate, edit, or enter thermodynamic property data for gas phase radicals and molecules using Benson's group additivity method. The computer code is called THERM (THermo Estimation for Radicals and Molecules). All group contributions considered for a species are recorded and thermodynamic properties are generated in old NASA polynomial format for compatibility with the CHEMKIN reaction modeling code. In addition, listings are created in a format more convenient for thermodynamic, kinetic, and equilibrium calculations. Polynomial coefficients are valid from 300–5000 K using extrapolation methods based upon the harmonic oscillator model, an exponential function, or the Wilhoit polynomials. Properties for radical and biradical species are calculated by applying bond dissociation increments to a stable parent molecule to reflect loss of H atom. THERM contains a chemical reaction interpreter to calculate thermodynamic property changes for chemical reactions as functions of temperature. These include equilibrium constant, heat release (required heat, ΔH_r), entropy change (ΔS_r), Gibbs free energy change (ΔG_r), and the ratio of forward to reverse Arrhenius A-factors (for elementary reactions). This interpreter can also process CHEMKIN input files. A recalculation procedure is incorporated for rapid updating of a database of chemical species to reflect changes in estimated bond dissociation energies, heats of formation, or other group values. All input and output files are in ASCII so that they can be easily edited, expanded, or updated.

Introduction

Detailed reaction kinetic models using mechanisms, based upon fundamental thermodynamic and kinetic principles, are currently being developed by researchers attempting to emulate reaction systems in combustion, chemical vapor deposition, rocket propulsion, and other related fields. A major requirement for these simulations is accurate thermodynamic property data (estimated or experimental) for all molecular and radical species considered in a mechanism. In addition, accurate thermodynamic property data over a wide temperature range are needed for chemical reaction equilibria calculations and safety evaluations of chemical incompatibility and explosion hazards.

Benson's group estimation technique is an accurate method for the estimation of ideal gas phase heat capacities, heats of formation, and entropies of molecules. This technique is thoroughly discussed in Benson's text Thermochemical Kinetics [1] as well as other sources [2–4,6]. This method assumes that the properties for a chemical substance are the sum of the contributions from each group or polyvalent atom (central atom) in that

molecule. It is referred to as a second order estimation technique since next-nearest-neighbor corrections, and to some extent, chemical structure are accounted for. Estimation based upon chemical bond contributions alone are known as first order estimation techniques, while those based upon atomic contributions alone are referred to as zero order techniques [7]. The second order estimates are naturally more accurate than lower order techniques, however, more information about the molecule is required. Several other estimation techniques based upon group contribution principles are presented in Reid, Prausnitz, and Sherwood [4]. This method, however, has become the most widely accepted due, in part, to its ease of use and its relative accuracy when compared with other techniques.

Group contributions were derived by Benson and co-workers [2] in addition to various other researchers [6,8–13] by breaking similar molecules with known thermodynamic properties into their constituent groups and then performing multivariable linear regression to find group contributions which gave the best fit to available experimental property data.

To use Benson's method, one must become familiar with the notation used to describe the groups. For example if we consider chlorobenzene (C_6H_5Cl) we say that it has one C_B—(Cl) group and five C_B—(H) groups. C_B—(Cl) refers to a carbon atom in a benzene ring which is attached to a Cl atom, while C_B—(H) refers to a carbon atom in a benzene ring which is attached to an H atom. THERM identifies C_B—(Cl) as CB/CL and C_B—(H) as CB/H. For a second example consider propane (C_3H_8). This molecule contains two C—(H_3)(C) groups for the two terminal methyls, and one C—(H_2)(C_2) for the center CH_2 group. THERM identifies C—(H_3)(C) as C/C/H3, with C—(H_2)(C_2) identified as C/C2/H2. We feel alphabetical order is preferred for simplicity in remembering the order of atoms in the group identifier. In addition to the group identifiers, various corrections for symmetry, optical isomers, ring structure, steric effects must be included where necessary.

Other Computer Implementations of Benson's Method

Benson's method has been programmed by others [14–17]. The most notable implementation of this estimation technique on computer is the code called CHETAH [14,15] which is distributed by ASTM. This program has been in use since 1974. Its primary purpose is to predict chemical reactivity hazards. Many publications are available which demonstrate its usefulness [7].

THERM was not designed to compete with or replace CHETAH. It was written to automate several tasks which are routine and important to high temperature reaction modeling studies. There are several important differences between THERM and CHETAH. THERM estimates properties between 300 and 5000 K while CHETAH estimates are valid from 300–1500 K, a range less suitable for combustion studies. THERM generates thermodynamic property functions in the old NASA format but does not address hazard assessment. Properties for both radicals and molecules can be estimated using THERM, while CHETAH is used for stable molecules only.

Another widely used computer code which utilizes group additivity is the PAC90 and PAC91 programs developed by McBride and Gordon of NASA

Lewis Research Center [17]. PAC91 generates polynomials in the new NASA format which is not currently used by CHEMKIN.

The method THERM uses to calculate properties for radical species is similar for ΔH_f° to that implemented by Muller, Scacchi, and Come [16], but was developed independently.

Source of Group Contribution Data

Group data for molecules containing C, O, N, S, and halogen atoms were obtained from Benson [1–3]; Reid, et al. [4]; Stein and Fahr [11]; Cohen [6]; and Ritter and Bozzelli [12]. Radical group contributions were derived from Benson [1]; McMillen and Golden [18]; Griller [19]; and Lossing [20,21]. Bond dissociation increments [12] were derived from Tsang [22]; Slagle and Gutman [23,24]; and McMillian and Golden [18]. Ring corrections for C, O, N, and S containing rings were obtained by Ritter and Bozzelli [12].

The groups supplied with this code are those of Benson and co-workers [1,3] and those of Stein and Fahr [11]. Additional groups which have been determined (ring corrections, etc.) are consistent with the Benson groups. It is noted that several other researchers [6,13] have derived new group values based upon more recent thermodynamic data, but since these databases are less comprehensive we have chosen to supply the Benson groups. The group datafiles can be edited, however, so that a user can use any group values he so chooses. Group data files, like all of THERM's files are ASCII and can be easily altered using any convenient text editor. A user can easily change group values or add their own groups to the database.

Examples of the THERM Program

In Table I, ΔH_f° for 27 assorted species are compared with literature values obtained from various sources as noted. In most cases, estimates agree within 2.5 kJ/mol. Deviations range from 0.0 kJ/mol for chloroethane (C_2H_5Cl) to 15 kJ/mol for pyrene ($C_{16}H_{10}$). Table I presents deviations both as differences in kJ/mol and percent error. Percent error is given mainly for reference. Differences are generally more meaningful than percent error, since ΔH_f° can have positive, negative, or zero values. Errors in ΔH_f° for a species considered in a chemical reaction translate directly into errors in ΔG_r and equilibrium constants. Consider, for example, i-propyl benzene and azulene. The error in ΔH_f° for i-propyl benzene is -34.3% even though this is only a difference of -1.38 kJ/mol. The -34.3% error translates into only 18% error in an equilibrium constant at 1000 K. The estimate for azulene, on the other hand, is only 1.9% in error. However, the difference is 5.96 kJ/mol which translates into 100% error in an equilibrium constant at 1000 K.

OH   O.

PHENOL   PHENOXY

The structures for phenol and phenoxy radical are shown above. ΔH_f° (298 K) for phenol (C_6H_6O) is estimated as -93.30 kJ/mol; while Burcat

TABLE I. $\Delta H_f^\circ(g)$ [kJ/mol].

Formula	Species	Calc	Exp	Deviation	%error	Ref.
C_5H_6	cyclopentadiene	135.56	133.64	1.92	1.4	31
C_7H_8	toluene	49.41	50.17	−0.75	−1.5	"
C_8H_8	styrene	147.36	147.70	−0.33	−0.2	"
C_8H_{10}	ethyl benzene	29.08	29.92	−0.84	−0.3	"
C_9H_8	indene	169.12	163.51	5.61	3.4	"
C_9H_{10}	indane	61.67	60.33	1.34	2.2	"
C_9H_{12}	n-propyl benzene	8.74	7.91	0.84	10.1	"
C_9H_{12}	i-propyl benzene	2.64	4.02	−1.38	−34.3	"
$C_{10}H_8$	azulene	313.47	307.52	5.94	1.9	"
$C_{10}H_8$	naphthalene	150.62	150.83	−0.21	−0.1	"
$C_{12}H_{10}$	acenaphthane	153.34	156.48	−3.14	−2.0	"
$C_{14}H_{10}$	anthracene	218.40	230.96	−12.55	−5.4	"
$C_{14}H_{10}$	phenanthrene	209.20	207.19	2.01	1.0	"
$C_{16}H_{10}$	fluoranthene	286.14	291.96	−5.82	−2.0	"
$C_{16}H_{10}$	pyrene	230.96	215.85	15.10	7.0	"
$C_{18}H_{12}$	triphenylene	258.57	265.27	−6.69	−2.5	"
C_2H_6O	dimethyl ether	−181.59	−184.05	2.47	1.3	29
C_6H_7N	aniline	87.03	86.86	0.17	0.2	"
C_2H_5Cl	chloroethane	−111.71	−111.71	0.00	0.0	"
C_6H_5Cl	chlorobenzene	53.14	51.84	1.30	2.5	"
C_6H_5F	fluorobenzene	−110.04	−116.57	6.53	5.6	"
C_6H_5I	iodobenzene	163.18	162.55	0.63	0.4	"
C_7H_8	toluene	49.41	50.00	−0.59	−1.2	"
C_6H_6O	phenol	−93.30	−96.36	3.05	3.2	25
C_6H_5O	phenoxy radical	50.63	47.70	2.93	6.1	"
$C_{12}H_{10}$	biphenyl	179.58	182.13	−2.55	1.4	"

[25] gives −96.36 kJ/mol. Seven group contributions are considered for phenol. Phenol is comprised of 5 CB/H groups [CB−(H)], one CB/O group [CB−(O)], and one O/CB/H group [O−(H)(C)]. Groups in brackets refer to names appearing in Benson [1], while those with slashes are the equivalent group name identified by THERM. Figure 1 is a sample of the documentation generated when estimating a species. Elemental formula (C6H5OH), Cp_∞ (limiting high temperature heat capacity), symmetry number and optical isomer corrections (if any) for entropy, and the number of rotors in the molecule (if any) are also recorded. The limiting heat capacity, Cp_∞, is the high temperature limiting value given by the harmonic oscillator approximation.

THERM requires the number of internal rotors in a molecule to be entered. An internal rotation is a nonlinear functional group which can rotate with respect to a stationary part of the molecule. The number of rotors is used by THERM to adjust Cp_∞ by reducing the number of vibrational modes considered when extrapolating Cp to high temperature. No barriers to internal rotation are required. It is assumed that as temperature becomes large, all internal rotors tend to become free rotors [33]. This results in a decrease in Cp_∞ over that for a molecule with the same number of atoms but no internal rotations. The method used to extrapolate the heat capacity to high temperature was developed as part of the THERM package and is discussed in detail elsewhere [32,34,35].

Properties for radicals may be estimated two different ways. One may estimate thermodynamic properties directly with radical group contributions

```
SPECIES
PHENOL
     Thermo estimation for molecule
PHENOL                                                       C6H5OH
UNITS:KJ
GROUPS   3
  Gr # -  GROUP ID  - Quantity
     1 - O/CB/H          - 1
     2 - CB/O            - 1
     3 - CB/H            - 5
     Hf     S    Cp 300   400    500    600    800   1000    1500
   -93.30 314.52 102.09 133.47 160.33 181.29 211.79 232.46    .00
          CPINF =  307.60
     NROTORS:   1
SYMMETRY          2
  CREATION DATE:  1/23/89
  ENDSPECIES

   SPECIES
PHENOXY
Thermo estimation for radical
PHENOXY                                                      C6H5O
RADICAL BASED UPON PARENT  PHENOL
     PARENT FORMULA                      C6H5OH
PARENT SYMMETRY            2
  UNITS:KJ
  GROUPS    4
  Gr # -  GROUP ID  - Quantity
     1 - O/CB/H          - 1
     2 - CB/O            - 1
     3 - CB/H            - 5
     4 - PHENOXY         - 1
     Hf     S    Cp 300   400    500    600    800   1000    1500
    50.63 303.64  96.32 125.02 149.75 169.12 197.40 216.52    .00
          CPINF =  282.66
  SYMMETRY        2
R ln(2) has been added to S to account
        for unpaired electron
  BOND   361.92
  CREATION DATE:  1/23/89
  ENDSPECIES
```

Figure 1. Documentation file entries for Phenol and Phenoxy radical. Each entry begins with the keyword Species and ends with the keyword Endspecies. The lines that follow contain the species name, elemental formula, units, number of different groups considered, group identifications, estimated thermodynamic properties, Cp_∞, number of rotors, symmetry number, and creation date. The units are either KJ which denotes ΔH_f° in kJ/mol with S° and Cp's in J/mol K; or KCAL which denotes ΔH_f° in kcal/mol with S° and Cp's in cal/mol K.

as described in Benson [1]. A second method applies a bond dissociation (BD) increment to stable molecules reflecting loss of an H atom from that species. We prefer this method, especially when estimating resonantly stabilized radicals.

The bond dissociation (BD) groups we have developed incorporate the following: Accurate bond energies (Central Atom-Hydrogen Atom Bonds) for the specific class of compounds; Entropy corrections for electron spin; and Entropy and heat capacity corrections for changes in rotational barrier for the rotors connected to radical centers (Benson [1] tables A.18-A.20).

BD groups are based on specific bond energies, in addition to differences in heat capacities and entropy for specific classes of molecules, where the thermodynamic properties of the radicals and parent molecules are accurately known. The BD Groups have one additional advantage over those of the radical groups developed by Benson [1] in that only one BD Group is needed for a given radical. In the Benson scheme a radical group is needed for each central atom radical, in addition to a group for each central atom group attached to the radical center. This represents a much larger data set for the radical species thermo.

Documentation for phenoxy radical, which was estimated in this way, is shown in Figure 1. Additional notes which are recorded for radicals include bond dissociation energy (298 K) for loss of hydrogen atom from the parent molecule, entropy correction for a free electron, and the name of the parent molecule. $\Delta H_f^\circ(298)$ for phenoxy is estimated as 50.62 kJ/mol while Burcat [25] gives ΔH_f° equal to 47.7 kJ/mol a difference of only 2.9 kJ/mol as shown in Table I.

The units displayed in Table I are kJ/mol for ΔH_f°, however, one can easily switch the units which are displayed. The user can choose between ΔH_f° in kJ/mol with S and Cp in J/mol K, or ΔH_f° in kcal/mol with S and Cp in cal/mol K at any time.

Modified old NASA format polynomial coefficients are generated by THERM for use by such computer codes as CHEMKIN. Polynomial coefficients are valid over the temperature range from 300–5000 K. The major difference in our modified NASA format is that the number of rotors in the species are recorded. The old NASA format includes the species name, creation date/reference, elemental composition, phase, lower and upper temperature limits for the polynomial, and the break point temperature (T_{bk}). Fourteen coefficients follow. The first seven coefficients are used to calculate properties at temperatures above T_{bk}, while the second seven coefficients apply to temperatures below T_{bk} (as described by Kee [30] and Burcat [25]). The break point temperature (T_{bk}) is located at a point of tangency between the two polynomials. T_{bk} is determined by matching Cp, H_f°, and S° to 0.005 %; while dCp/dT, dHf/dT, and dS/dT are matched within an absolute tolerance of 0.005. Solving for a point of tangency between two polynomials differs from the method cited by Kee, et al. [30]. Rather than fixing T_{bk} and then using a linear regression to determine 2 polynomials which are tangent at this fixed temperature, THERMFIT uses a different approach. THERMFIT uses one of the extrapolation methods to generate the required Cp data and then independently determines 2 polynomials from data which is weighted in a region common to both polynomials (overlap region, typically 500 K). The weighting insures that the 2 polynomials will have some point of tangency within this overlap region which is then determined using a line search method. As such T_{bk} changes from species to species. This allows the polynomial fits to be obtained to best match the data without constraining them to be tangent at a predetermined temperature.

Thermo property tables can be generated from the polynomials using the THERMLST procedure. These tables contain species name, $\Delta H_f^\circ(298)$, $S^\circ(298)$, and Cp at 300–1500 K. Creation date, elemental composition, phase (g) and number of rotors are also recorded. An extended table to 5000 K can also be generated. Units for tables can either be in kcal/mol for ΔH_f°

and cal/mol K for $S°$ and Cp or kJ/mol for $\Delta H_f°$ and J/mol K for $S°$ and Cp. An example of this format is presented in Table II. This format provides a convenient list for reviewing or referencing the thermodynamic property data.

In Figure 1, Cp (1500 K) for Phenol is listed as 0.0 since no contribution was available at this temperature for one of the groups. However, the temperature range for Cp data can be extended by THERM to 5000 K by using available low temperature Cp data (300–1000 K). This is done by projecting an asymptote to Cp_∞. To do this we use an harmonic oscillator equation (HOE) derived from statistical mechanics to describe vibrational contributions to Cp [32,35]. The fourth order polynomials can then be determined using linear regression of data estimated with this HOE equation. Alternatively, extrapolations can be performed using either an exponential function or the Wilhoit polynomials [32]. All three of these extrapolation methods are included in the THERM package.

Heat capacity estimates determined in this fashion are compared with literature data in Figure 2 for dimethyl ether, phenol, and biphenyl. It should be emphasized that the solid lines are generated from group additivity values alone, while symbols (literature values) result from rigorous calculations requiring frequency data for all vibrational modes in addition to contributions from all restricted rotors in the particular species. We obtain excellent agreement with typical maximum errors less than 1.5%. Literature data for this comparison are obtained from Stull [29] for dimethyl ether and from Burcat [25] for biphenyl and phenol. Heat capacity estimates for other species agree similarly when compared to available literature data.

One of the powerful features of this computer program is the automatic recalculation procedure. Once one records an estimate with THERM in the format shown in Figure 1, polynomials and tables can be recalculated automatically to reflect changes or improvements made to the group contribution database. This is necessary since new data continue to become available which allow improved estimates of bond dissociation energies, radical increments, and groups which themselves are only estimates. This allows a thermodynamic database to become flexible accepting new data in addition to allowing users to examine the effects of uncertainties in bond energies and group values on conclusions drawn from modeling.

In addition to calculating data from group additivity, data may be entered interactively from literature sources allowing the required polynomials to be generated for literature data as well. Literature data can be entered either from the species estimation procedure (by specifying the number of groups in the species to be zero) or by direct interactive input to the Cp fitting program (THERMFIT). When data are entered to the estimation procedure, a documentation entry is created. Interactive input to THERMFIT is useful if data are at temperatures other than those required by the estimation procedure (ie., 300, 400, 500, 600, 800, 1000, and [1500] K). Automatic recalculation does not effect literature data, or any species where auto-recalculation has been disabled.

THERM contains a chemical reaction interpreter for calculation of thermodynamic property changes for reaction as functions of temperature. One may calculate thermodynamic property changes for a desired reaction or an entire CHEMKIN input file. The thermodynamic properties which are cal-

TABLE II. An example thermodynamic property table created by THERMLST from the NASA format polynomials.

Units: KCAL

| Species	$\Delta H_f°$	S°	CP300	CP400	CP500	CP600	CP800	CP1000	CP1500	Date	Ref.	Elements
CO	−26.40	47.20	6.82	6.98	7.15	7.31	7.60	7.86	8.38		121286	C 1 O 1 0 G 0
CO_2	−94.01	51.00	8.92	9.83	10.61	11.26	12.26	12.95	13.86		121286	C 1 O 2 0 G 0
H_2O	−57.80	45.10	8.23	8.41	8.64	8.91	9.51	10.14	11.50		20387	H 2 O 1 0 G 0
HCO	10.40	53.60	8.44	8.90	9.38	9.87	10.82	11.66	13.03		121286	H 1 C 1 O 1 G 0
HO_2	2.50	54.70	8.36	8.91	9.42	9.88	10.69	11.33	12.37		20387	H 1 O 2 0 G 0
O	59.51	38.40	5.00	5.00	5.00	5.00	5.00	5.00	5.00		120186	O 1 0 0 G 0
H_2O_2	−32.50	55.61	10.39	11.42	12.30	13.07	14.30	15.24	16.75		120186	H 2 O 2 0 G 1
CL	28.90	39.40	5.30	5.30	5.30	5.30	5.30	5.30	5.30		JANAF	CL 1 0 0 G 0
F	18.90	37.90	5.20	5.20	5.20	5.20	5.20	5.20	5.20		JANAF	F 1 0 0 G 0
CLO	24.10	54.10	7.55	7.90	8.15	8.34	8.57	8.69	8.81		JANAF	CL 1 O 1 0 G 0
H	52.10	27.30	4.90	4.90	4.90	4.90	4.90	4.90	4.90			H 1 0 0 G 0
HCL	−22.00	44.60	6.86	6.92	7.00	7.09	7.28	7.48	7.97		JANAF	H 1 CL 1 0 G 0
H_2	.00	31.20	7.01	7.06	7.12	7.19	7.34	7.50	7.88			H 2 0 0 G 0
CCL_3	19.00	70.91	15.45	16.81	17.77	18.40	19.06	19.29	19.60		JANAF	CL 3 C 1 0 G 0
CH_3	34.80	46.30	9.21	9.98	10.74	11.46	12.81	14.00	16.18		J 6/69	C 1 H 3 0 G 0
CH_4	−17.90	44.40	8.56	9.83	11.12	12.39	14.79	16.90	20.49		J 3/61	C 1 H 4 0 G 0
C_2F_6	−321.23	79.41	25.69	29.34	32.19	34.38	37.28	38.93	40.86		JANAF	C 2 F 6 0 G 1
CF_3CN	−118.41	71.31	18.72	21.39	23.48	25.11	27.32	28.62	30.19		JANAF	C 2 N 1 F 3 G 0
C_2CL_4	−2.90	82.01	22.53	24.49	26.01	27.17	28.72	29.61	30.71		JANAF	CL 4 C 2 0 G 0
C_2HCL	51.10	57.81	13.42	14.64	15.67	16.51	17.78	18.62	19.68		JANAF	CL 1 C 2 H 1 G 0
C_2H_4	12.50	52.30	12.52	12.72	14.86	16.76	19.94	22.37	26.10		J 9/65	C 2 H 4 0 G 0
C_2H_6	−20.20	54.81	10.34	15.73	18.64	21.26	25.71	29.21	34.71		L 5/72	C 2 H 6 0 G 1
BIPHEN	42.90	93.91	39.30	52.90	64.11	73.30	86.94	96.13	109.07	3/20/89	THERM	C 12 H 10 0 G 1
C_3H_8	−25.33	64.50	17.88	22.63	27.05	30.93	37.11	41.88	49.36	6/28/90	THERM	C 3 H 8 0 G 2
C_4H_8O	−43.70	72.51	19.17	25.92	31.85	37.02	45.43	51.70	60.92	3/20/89	THERM	C 4 H 8 O 1 G 1
C_2CL_2	41.40	65.41	15.69	16.63	17.38	17.97	18.80	19.32	19.99	3/20/89	THERM	CL 2 C 2 0 G 0
C_2F_4	−155.01	71.81	19.42	21.94	23.93	25.49	27.62	28.87	30.30	3/20/89	THERM	C 2 F 4 0 G 0
C_2H_4O	−12.50	56.11	11.81	15.10	17.95	20.40	24.35	27.28	31.76	3/20/89	THERM	C 2 H 4 O 1 G 0
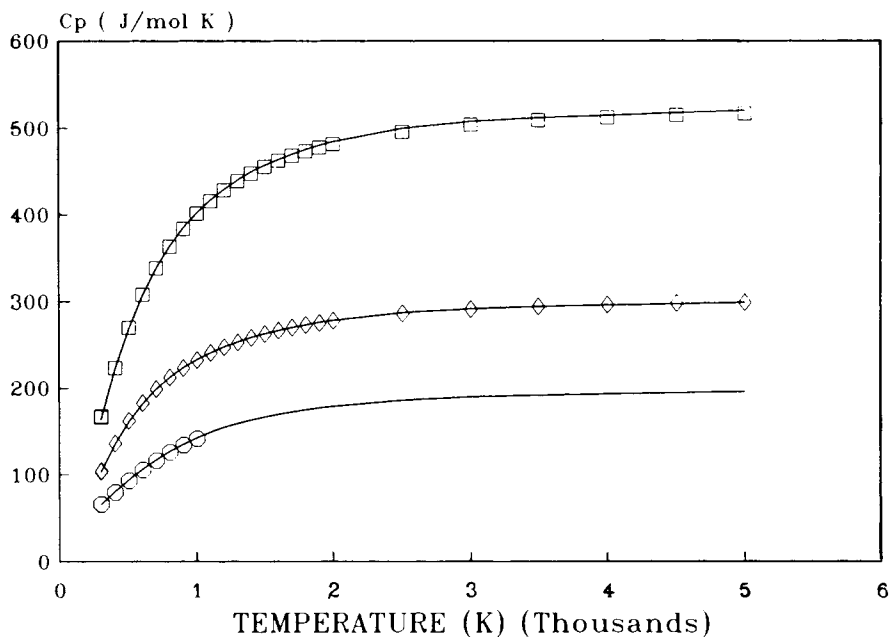
Figure 2. Heat capacity functions: Cp(T). A comparison of THERM estimates with literature data for □-biphenyl, ◇-phenol, and ○-dimethyl ether. Symbols represent literature Cp data, while solid lines represent the Cp(T) functions produced by the THERM computer code.

culated are ΔU_r {ΔE_r}, ΔH_r, ΔS_r, ΔG_r, equilibrium constant (K_c), and A_f/A_r: ratio forward to reverse Arrhenius A factors. All species appearing in a reaction must be defined in the database. Property changes are estimated as a function of temperature over a range specified by the user. This is useful for engineers or kineticists wishing to check thermodynamic and kinetic consistency of reaction mechanisms being developed. An example is shown in Table III for the overall reaction of vinyl chloride with hydrogen. This reaction is shown to be exothermic by about 63 kJ/mol with an equilibrium constant favoring the products ethane and HCl. Shown in this table are the reactants, products, and thermodynamic properties of each at 298 K. A list which contains the ΔH_r, ΔU_r (ΔE_r), ΔS_r, equilibrium constant K_c, and ΔG_r tabulated between 300–2000 K follows.

There are several other features worth noting. THERM contains a significant amount of on-line help. Help may be obtained at most prompts for input simply by entering a question mark (?).

In addition, THERM allows one to edit group data, species name, formula, bond energies, calculated thermodynamic properties, etc. for species either read in from a documentation file or entered from the keyboard. This allows one to easily verify, update, or correct data entered for any species or to generate data for a different species which differs slightly from one which was estimated previously.

A file utility is included which converts documentation and NASA polynomial files from sequential to direct file format. This allows ASCII text editors to be used to alter these files while maintaining the rapid disk access afforded by direct access file formatting.

TABLE III. Thermodynamic property analysis for reaction of vinyl chloride with hydrogen. An example of the output from THERMRXN.

Thermodynamic Analysis for Reaction

Rx	C_2H_3Cl	+	H_2	=	C_2H_4	+	HCl
Hf {kJ/mol}	23.012		0.000		52.30		-92.048
S {J/mol K}	174.473		130.541		218.823		186.606

dHr {kJ/mol} (298 K) = -62.76 dHr avg (298., 1500. K) = -65.76
dU (dE) {kJ/mol} (") = -62.76 dUr avg (298., 1500. K) = -65.76
dSr {J/mol K} (") = 100.42 dSr avg (298., 1500. K) = 94.75
dGr {kJ/mol} (") = -92.70 dGr avg (298., 1500. K) = -150.95
Kc (") = 1.745E + 16 Kc avg (298., 1500. K) = 5.898E + 08

T(K)	dH (kJ/mol)	dU (kJ/mol)	dS (J/mol K)	Kc	dG (kJ/mol)
300.00	-6.278E + 01	-6.278E + 01	1.004E + 02	1.493E + 16	-9.288E + 01
400.00	-6.388E + 01	-6.388E + 01	9.720E + 01	2.630E + 13	-1.028E + 02
500.00	-6.501E + 01	-6.501E + 01	9.466E + 01	5.466E + 11	-1.123E + 02
600.00	-6.609E + 01	-6.609E + 01	9.270E + 01	3.950E + 10	-1.217E + 02
800.00	-6.777E + 01	-6.777E + 01	9.025E + 01	1.381E + 09	-1.400E + 02
1000.00	-6.871E + 01	-6.871E + 01	8.919E + 01	1.773E + 08	-1.579E + 02
1200.00	-6.900E + 01	-6.900E + 01	8.892E + 01	4.455E + 07	-1.757E + 02
1500.00	-6.876E + 01	-6.876E + 01	8.909E + 01	1.119E + 07	-2.024E + 02
2000.00	-6.757E + 01	-6.757E + 01	8.977E + 01	2.846E + 06	-2.471E + 02

Conclusions

We have developed a computer code which can be used to enter, estimate, and edit thermodynamic properties for gas phase molecules and radicals. Some important aspects of this program are heat capacity extrapolation to 5000 K, thermo property polynomial determination, and calculation of thermodynamic property changes for reaction. Prediction/estimates typically compare favorably with available literature data.

Interested parties are encouraged to contact the authors for details on receiving a complementary copy of this program in addition to user documentation. The program is available in an executable format only.

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