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Note

ON COMPUTING REACTION EQUILIBRIUM CONSTANTS

K. NATARAJAN

A.C. College of Technology, Perarignar Anna University of Technology, Madras-600 025 (India)

K.M. KARUPPANNAN and K.A. BHASKARAN

Department of Mechanical Engineering, Indian Institute of Technology, Madras-600 036 (India)

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With the advent of high-speed digital computers and the availability of reliable rate coefficients for a large number of chemical reactions, it has now become possible to analyse theoretically the combustion mechanism of many fuels by simulating the oxidation reactions on a computer. One important pre-requisite for such an analysis is the computation of equilibrium constants based on mole concentrations, K_c, for these reactions. The reaction equilibrium constants based on mole concentrations can be computed by using the equilibrium constants of formation of the species involved and the change in the number of moles of the species as the transformation takes place from reactants to product. The equilibrium constant of formation is based on the equilibrium equation of formation of a species from its elements in their normal states.

The equilibrium constants of formation of the species are available in thermochemical tables, but only at regular temperature intervals. Such tables are most useful for quick hand calculations carried out at tabulated temperatures or with linear interpolation, at intermediate temperatures. The calculations carried out by digital computer generally require continuous representations of the thermodynamic properties as functions of temperature. Such approximations are more efficient, both as regards speed and computer storage, than methods of interpolation between tabulated values [1].

An oxidation mechanism of a fuel may involve a large number of elementary reactions but the chemical species involved will be relatively smaller in number. Hence, for ease of computation it is suggested that the equilibrium constants of formation of the species be expressed as a function of temperature, from which the reaction equilibrium constants can be computed.

REACTION EQUILIBRIUM CONSTANTS

Log K_{pi} values have been published for most of the chemical species in the temperature range 300—6000 K at 100° intervals [2]. They stand for the logarithm of the thermodynamic equilibrium constant for the reaction in which the given species is formed from its elements at the indicated tempera-

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ture. Hence, the equilibrium constant K_{pj} of any reaction j is computed as

$$\log K_{\mathrm{pj}} = \sum_{\mathrm{prod}} \log K_{\mathrm{pi}} - \sum_{\mathrm{reac}} \log K_{\mathrm{pi}} \tag{1}$$

When the log K_{pi} values of the species are not readily available, the reaction equilibrium constants, K_{pj}, can be computed as

$$R \ln K_{\mathrm{pj}} = -\left(\sum_{\mathrm{prod}} H^0_{\mathrm{fi}} - \sum_{\mathrm{reac}} H^0_{\mathrm{fi}}\right)\Big/T - \left(\sum_{\mathrm{prod}} G_{\mathrm{i}} - \sum_{\mathrm{reac}} G_{\mathrm{i}}\right) \tag{2}$$

The equilibrium constants based on mole concentration are then computed using the relationship

$$K_{\mathrm{cj}} = K_{\mathrm{pj}}(R_{\mathrm{p}}T)^{-\Sigma_{i=1}^{N}(\beta_{\mathrm{i}}-\alpha_{\mathrm{i}})} \tag{3}$$

Generally the reaction equilibrium constants, K_{cj}, of chemical reactions are computed at regular temperature intervals and then expressed as a continuous function of temperature by various approximations, such as

$$K_{\mathrm{cj}} = \bar{a}T^{\bar{b}} \exp(\bar{c}/T) \tag{4}$$

$$\ln K_{\mathrm{cj}} = k_1 \ln T + k_2T + k_3T^2 + k_4T^3 + k_5T^4 + k_6T^5 + k_7T^6 + k_8/T + k_9 \tag{5}$$

$$\log K_{\mathrm{cj}} = k_1 \ln T + k_2/T + k_3 + k_4T + k_5T^2 \tag{6}$$

When the above procedure is followed, a definite number of coefficients has to be evaluated for each reaction. Hence for an oxidation mechanism with a large number of elementary reactions, the number of coefficients to be handled becomes large.

For easy computer calculations, a convenient expression for the reaction equilibrium constants can be obtained by fitting an exponential curve of the form $a\ T^{\mathrm{b}}\ \exp(c/T)$ to the equilibrium constants of formation of the species which are available at regular temperature intervals in thermochemical tables. Tables 1 and 2 give the coefficients a, b and c for 51 C—H—O—S—N species for two different temperature ranges, 1000—3000 K and 3000—6000 K. The correlation coefficients in all the cases are above 0.999 and this shows how well the curve fits the data.

The coefficients a, b and c of equilibrium constants of formation are used to compute the reaction equilibrium constants as indicated below.

Considering a chemical reaction of the form

$$\alpha_1\,\mathrm{A} + \alpha_2\,\mathrm{B} = \beta_1\,\mathrm{C} + \beta_2\,\mathrm{D} \tag{7}$$

the equilibrium constants of formation of the species A, B, C and D are expressed as

$$K_{\mathrm{c(A)}} = a_1T^{b_1} \exp(c_1/T) \tag{8}$$

$$K_{\mathrm{c(B)}} = a_2T^{b_2} \exp(c_2/T) \tag{9}$$

$$K_{\mathrm{c(C)}} = a_3T^{b_3} \exp(c_3/T) \tag{10}$$

$$K_{\mathrm{c(D)}} = a_4T^{b_4} \exp(c_4/T) \tag{11}$$

The equilibrium constant K_{cj} of reaction (7) is computed as

$$K_{\mathrm{cj}} = \bar{a}T^{\bar{b}} \exp(\bar{c}/T) \tag{12}$$

TABLE 1

Curve-fitted coefficients for the equilibrium constants of formation of the species for the temperature range 1000—3000 K

$K_{ci} = aT^{b} \exp(c/T)$

$K_{pi} = a'T^{b'} \exp(c/T)$

Species	a	a'	b	b'	c
1 CH_2O	1.038E 02	1.397E-01	1.1751	−0.3249	14 799
2 CHO	8.077E 06	9.843E 04	0.2078	−0.7922	1 236
3 C_2H_4	5.855E 01	1.060E-04	2.9035	−0.0965	−4 475
4 CH_4	1.626E-02	2.414E-06	1.9476	−0.0524	10 982
5 CH_3	7.337E 02	9.870E-01	1.1466	−0.3534	−16 740
6 C_2H_2	4.557E 07	6.768E 03	1.6987	−0.3013	−27 125
7 C_2H	3.878E 12	5.217E 09	0.6220	−0.8780	−57 955
8 CH_2	3.500E 04	4.266E 02	0.7910	−0.2090	−45 963
9 H_2O	1.538E-01	1.698E-02	0.1635	−0.3365	95 744
10 HO_2	6.889E-02	7.604E-03	0.3604	−0.1396	−2 218
11 CO_2	6.377E 02	7.771E 00	0.7601	−0.2399	47 224
12 CO	3.004E 08	3.317E 07	−0.3445	−0.8445	12 598
13 CH	8.941E 07	9.870E 06	0.1573	−0.3427	−71 649
14 OH	2.374E 01	2.374E 01	−0.1760	−0.1760	−4 823
15 O	3.394E 01	3.074E 02	−0.2325	0.2675	−30 160
16 H	2.192E 00	1.986E 01	−0.0093	0.4907	−26 290
17 C	4.051E 09	4.051E 09	−0.3776	−0.3776	−86 753
18 N	1.379E 01	1.249E 02	−0.1278	0.3722	−56 972
19 S	1.397E 01	1.265E 02	−0.2028	0.2972	−25 889
20 CN	1.950E 08	2.152E 07	−0.0981	−0.5981	−52 837
21 CS	1.350E 08	1.490E 07	−0.2126	−0.7126	−20 548
22 NH	8.737E 00	8.737E 00	0.0277	0.0277	−40 706
23 NO	5.222E 00	5.222E 00	−0.0148	−0.0148	−10 906
24 NS	2.653E 00	2.653E 00	0.0832	0.0832	−23 967
25 HS	5.311E 00	5.311E 00	0.0232	0.0232	−9 546
26 SO	2.174E 00	2.174E 00	−0.0215	−0.0215	−6 919
27 O_3	4.490E-04	4.957E-05	0.7195	0.2195	−17 069
28 CS_2	3.126E 02	3.810E 00	0.9337	−0.0663	−1 215
29 NH_2	1.708E-01	1.886E-02	0.3691	−0.1309	−19 633
30 NO_2	2.151E-03	2.374E-04	0.5889	0.0889	−3 784
31 SO_2	2.993E-04	3.303E-05	0.6918	0.1918	43 751
32 N_2O	1.039E-05	1.147E-06	1.1177	0.6177	−9 403
33 H_2S	9.487E-03	1.047E-03	0.6124	0.1124	11 043
34 S_2O	1.680E-03	1.855E-04	0.6152	0.1152	22 400
35 COS	4.575E 02	5.576E 00	0.9378	−0.0622	24 305
36 HNO	1.658E-02	1.830E-03	0.5469	0.0469	−11 547
37 HCN	1.895E 04	2.309E 02	0.7952	−0.2048	−16 207
38 NH_3	1.259E-05	1.534E-07	1.1855	0.1855	6 976
39 NO_3	1.598E-09	1.947E-11	1.8492	0.8492	−7 992
40 SO_3	8.730E-10	1.064E-11	1.6745	0.6745	55 961
41 C_2N_2	4.898E 06	7.274E 02	1.8600	−0.1405	−37 718
42 N_2H_2	1.108E-06	1.351E-08	1.4917	0.4917	−24 225
43 HNO_3	1.183E-12	1.592E-15	2.6468	1.1468	17 501
44 N_2H_4	3.893E-14	5.781E-18	3.4591	1.4591	−8 849
45 N_2O_4	2.751E-19	4.085E-23	4.1099	2.1099	271
46 N_2O_5	2.901E-21	4.756E-26	4.6889	2.1889	−618
47 O_2, H_2, S_2, N_2, C(S)	1.000E 00	1.000E 00	0.0	0.0	0

TABLE 2

Curve-fitted coefficients for the equilibrium constants of formation of the species for the temperature range 3000—6000 K

$K_{ci} = aT^b \exp(c/T)$

$K_{pi} = a'T^{b'} \exp(c/T)$

Species	a	a'	b	b'	c
1 CH_2O	2.248E 03	3.024E 00	0.8411	—0.6589	13 595
2 CHO	2.763E 08	3.367E 06	—0.1819	—1.1819	—11
3 C_2H_4	3.459E 02	6.260E-04	2.7220	—0.2780	—5 434
4 CH_4	2.808E-02	4.170E-06	1.9029	—0.0971	10 432
5 CH_3	7.810E 03	1.051E 01	0.8909	—0.6091	—17 698
6 C_2H_2	1.124E 07	1.669E 09	1.8619	—0.1381	—26 833
7 C_2H	3.827E 11	5.148E 08	0.8853	—0.6147	—57 324
8 CH_2	2.589E 05	3.155E 03	0.5748	—0.4252	—46 774
9 H_2O	8.190E-02	9.041E-03	0.2403	—0.2597	29 629
10 HO_2	2.976E 00	3.285E-01	—0.0550	—0.5550	—3 548
11 CO_2	1.085E 04	1.322E 02	0.4465	—0.5535	46 248
12 CO	3.757E 09	4.148E 08	—0.6248	—1.1248	11 742
13 CH	3.815E 08	4.211E 07	—0.0025	—0.4975	—72 284
14 OH	7.992E 01	7.992E 01	—0.3097	—0.3097	—5 257
15 O	1.914E 02	1.734E 03	—0.4277	0.0723	—30 667
16 H	6.132E 01	5.555E 02	—0.3819	0.1181	—27 347
17 C	7.425E 09	7.425E 09	—0.4473	—0.4473	—86 903
18 N	7.909E 00	7.164E 01	—0.0712	0.4288	—56 665
19 S	4.665E 00	4.226E 01	—0.0814	0.4186	—25 512
20 CN	8.550E 05	9.439E 04	0.5088	0.0088	—51 112
21 CS	6.527E 08	7.205E 07	—0.3880	—0.8880	—21 070
22 NH	1.067E 01	1.067E 01	0.0068	0.0068	—40 805
23 NO	3.134E 01	3.134E 01	—0.2148	—0.2148	—11 484
24 NS	4.068E 00	4.068E 00	0.0351	0.0351	—24 097
25 HS	8.455E 00	8.455E 00	—0.0269	—0.0269	—9 738
26 SO	1.299E 01	1.299E 01	—0.2211	—0.2211	6 345
27 O_3	4.677E-02	5.163E-03	0.2014	—0.2986	—18 578
28 CS_2	1.475E 03	1.798E 01	0.7613	—0.2387	695
29 NH_2	4.688E-01	5.175E-02	0.2624	—0.2376	—20 097
30 NO_2	1.032E-01	1.139E-02	0.1586	—0.3414	—5 070
31 SO_2	2.696E-03	2.977E-04	0.4468	—0.0532	43 035
32 N_2O	8.916E-05	9.842E-06	0.8792	0.3792	—10 130
33 H_2S	7.954E-03	8.780E-04	0.6360	0.1360	11 013
34 S_2O	1.985E-02	2.191E-03	0.3403	—0.1597	21 589
35 COS	1.559E 03	1.899E 01	0.8023	—0.1977	23 879
36 HNO	2.882E-01	3.182E-02	0.2312	—0.2688	—12 536
37 HCN	3.439E 04	4.190E 02	0.7335	—0.2665	—16 510
38 NH_3	3.073E-08	3.745E-10	1.8601	0.8601	8 847
39 NO_3	9.405E-07	1.146E-08	1.1386	0.1386	—10 078
40 SO_3	1.784E-07	2.175E-09	1.0839	0.0839	54 175
41 C_2N_2	7.994E 07	1.187E 04	1.5508	—0.4492	—38 692
42 N_2H_2	1.593E-06	1.941E-08	1.4588	0.4588	—24 515
43 HNO_3	1.428E-10	1.921E-13	2.1178	0.6178	15 819
44 N_2H_4	4.652E-14	6.909E-18	3.4543	1.4543	—9 253
45 N_2O_4	4.685E-16	6.958E-20	3.2841	1.2841	—2 237
46 N_2O_5	6.097E-16	9.996E-21	3.3215	0.8215	—4 588
47 O_2, H_2, S_2, N_2, C(S)	1.000E 00	1.000E 00	0.0	0.0	0

where

$$\bar{a} = a_3^{\beta_1} a_4^{\beta_2} / a_1^{\alpha_1} a_2^{\alpha_2} \tag{13}$$

$$\bar{b} = \beta_1 b_3 + \beta_2 b_4 - \alpha_1 b_1 - \alpha_2 b_2 \tag{14}$$

$$\bar{c} = \beta_1 c_3 + \beta_2 c_4 - \alpha_1 c_1 - \alpha_2 c_2 \tag{15}$$

The coefficients $\bar{a}$, $\bar{b}$ and $\bar{c}$ of the reaction equilibrium constant, K_{cj} (both in the forward and reverse directions) can thus be readily computed for any reaction involving the particular species. The units of $\bar{a}$ are (mole cm^{-3}) raised to the power $\Sigma_{i=1}^{N} (\beta_i - \alpha_i)$, $\bar{b}$ is dimensionless and $\bar{c}$ is in Kelvin.

The equilibrium constants of formation of the species based on partial pressure, K_{pi}, are similarly curve-fitted and their coefficients a', b' and c are also given in Tables 1 and 2. In this case the units of $\bar{a}$ are atm raised to the power $\Sigma_{i=1}^{N} (\beta_i - \alpha_i)$.

The reaction equilibrium constants, K_{cj} and K_{pj}, computed using the coefficients a, b, a', b' and c are found to be in very good agreement with the published thermochemical data.

CONCLUSIONS

The merit of the present method lies in the fact that the equilibrium constants for any number of chemical reactions can easily be deduced with the help of the coefficients of the equilibrium constants of formation of a relatively small number of species. These coefficients are readily useful in the equilibrium composition and flame temperature calculations of fuel-oxidizer mixtures where the equilibrium constants of the dissociation reactions are very much needed. The equilibrium constants of formation of the species given in published thermochemical tables can be readily evaluated with the help of these coefficients with an error <1%. The equilibrium constants of formation of species are as important as the rate coefficients of reactions, and further improvements, including data for larger species not included in the thermochemical tables, are needed to expand detailed combustion kinetic models [3].

NOMENCLATURE

A, B, C, D	chemical species
a, b, c, $\bar{a}$, $\bar{b}$, $\bar{c}$, a', b', k_1, k_2, etc	}constants
G	Gibb's energy function
H_f^0	enthalpy of formation at the reference temperature (298 K)
i	species index
j	reaction index
K_c	equilibrium constant based on concentration (mole cm^{-3})
K_p	equilibrium constant based on partial pressure

N	number of species
R	universal gas constant
R_p	universal gas constant in cc atm/mole K
T	absolute temperature (K)
α	stoichiometric coefficient of reactant
β	stoichiometric coefficient of product.

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