Equilibrium Thermophysical Properties of Alkanes at Very High Temperatures

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In order to perform calculations for thermal plasmas, sparks, and arcs, as in the thermal arc and electrical discharge machining (EDM) processes, thermophysical properties, such as the density, enthalpy, and heat capacity, of the original ambient dielectric liquid are required at very high temperatures and often pressures in the plasma state. A statistical model has been developed to provide these properties. At high temperatures, these hydrocarbons undergo a series of reactions to first dissociate and then to ionize to produce a plasma. The partition functions of each of the species generated are calculated and used to determine the equilibrium mole fractions or particle fractions of each constituent of the resultant plasma. Only the hydrogen-to-carbon ratio matters so mixtures of alkanes can also be used. Specifically, tables of particles fractions, densities, enthalpies, and specific heat capacities are provided for methane and for hexadecane to 60 000 K and 10 kbar.

Introduction

The modeling of thermal plasmas generally assumes local thermodynamic equilibrium (LTE; see Drawin (1971)). Material and energy balances then require the thermophysical properties for the fluid for temperatures up to 60 000 K and pressures to 10 kbar. Methane, ethane, propane, and butane are often used as the arc gas in thermal plasma devices; hydrocarbon oils are commonly used as the dielectric media between electrodes in commercial die-sinking electrical discharge machines (EDM), which are used to cut and shape metals, ceramics, and composites.

More conventional computer programs are available (Frenkel et al., 1994) for calculation of the equilibrium fractions to about 6000 K, where ionization becomes a factor. These programs include a host of chemical species, not considered here, which can be important below 9000 K, principally at pressures above 10 bar. The main goal of this work is to provide equilibrium fractions, densities, enthalpies, and specific heat capacities in the plasma state of (9000−60000) K at pressures to 10 kbar.

Previous plasma-state thermophysical property tables include (1) those in Dresvin et al. (1977) for argon, helium, air, nitrogen, oxygen, hydrogen, and carbon dioxide to 20 000 K at 1 bar, (2) our steam tables (Patel et al., 1990) to 60 000 K and 10 kbar, and (3) those in Boulos et al. (1994) for argon, helium, air, nitrogen, oxygen, and hydrogen to 24 000 K at 1 bar. The only previous work with a hydrocarbon appears to be the graphs of Drawin (1971) for CH_2 to 50 000 K at 1 bar.

Statistical Mechanical Model

An introduction to the use of statistical mechanics to provide chemical equilibria, with both dissociation and ionization, is given by Lee et al. (1973). At these high temperatures, intermolecular forces are negligible; however, Coulombic forces must be considered at extremely high temperatures and pressures, as examined in the Discussion. This leads to a perfect gas mixture assumption where all the particles, including electrons, contribute equally to the system pressure. We use here a partition function approach (Janz, 1958; Reed and Gubbins, 1973; Lide, 1990) that accounts for translational, rotational, vibrational, and electronic contributions to the energy.

Boulos et al. (1994) provide an entire chapter (Chapter 6) devoted to the calculation of thermodynamic properties in the plasma state. Except for numerical procedures, we follow the same general methods except we have not included Coulombic effects. Principally, these procedures are based upon minimization of the total Gibbs energy of a reacting system which leads to the law of mass action, which when written in terms of the equilibrium constant for thermal ionization is termed a Saha equation. These procedures are applicable to the very high temperatures of this work. The lowering of the ionization energy, a limitation of the atomic and ionic partition functions, was found to be negligible in concert with the pressure correction for Coulombic interactions in the Debye−Huckel model (Drawin, 1971). We here assume that the possible species are C_nH_{2n+2}, CH_2, CH_3, C, H_2, H, H^+, C^+, C^{2+}, C^{3+}, C^{4+} and e^-. There are then nine independent equilibrium equations:

$$C_nH_{2n+2} \rightleftharpoons (n-2)CH_2 + 2CH_3; \quad \frac{N_{CH_2}^{n-2}N_{CH_3}^2}{N_{C_nH_{2n+2}}} = \frac{Q_{CH_2}^{n-2}Q_{CH_3}^2}{Q_{C_nH_{2n+2}}}e^{-U_{rxn1}/kT} \quad (1)$$

$$2CH_3 \rightleftharpoons 2C + 3H_2; \quad \frac{N_C^2N_{H_2}^3}{N_{CH_3}^2} = \frac{Q_C^2Q_{H_2}^3}{Q_{CH_3}^2}e^{-U_{rxn2}/kT} \quad (2)$$

$$CH_2 \rightleftharpoons C + H_2; \quad \frac{N_CN_{H_2}}{N_{CH_2}^2} = \frac{U_CQ_{H_2}}{Q_{CH_3}^2}e^{-U_{rxn3}/kT} \quad (3)$$

$$H_2 \rightleftharpoons 2H; \quad \frac{N_H^2}{N_{H_2}} = \frac{U_H^2}{Q_{H_2}}e^{-D_{H_2\rightarrow H}/kT} \quad (4)$$

$$H \rightleftharpoons H^+ + e^-; \quad \frac{N_{H^+}N_{e^-}}{N_H} = \frac{U_{H^+}U_{e^-}}{U_H}e^{-I_{H\rightarrow H^+}/kT} \quad (5)$$

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$$C \rightleftharpoons C^+ + e^-;\quad \frac{N_{C^+}N_{e^-}}{N_C} = \frac{U_{C^+}U_{e^-}}{U_C}e^{-I_{C\to C^+}/kT} \tag{6}$$

$$C^+ \rightleftharpoons C^{2+} + e^-;\quad \frac{N_{C^{2+}}N_{e^-}}{N_{C^+}} = \frac{U_{C^{2+}}U_{e^-}}{U_{C^+}}e^{-I_{C^+\to C^{2+}}/kT} \tag{7}$$

$$C^{2+} \rightleftharpoons C^{3+} + e^-;\quad \frac{N_{C^{3+}}N_{e^-}}{N_{C^{2+}}} = \frac{U_{C^{3+}}U_{e^-}}{U_{C^{2+}}}e^{-I_{C^{2+}\to C^{3+}}/kT} \tag{8}$$

$$C^{3+} \rightleftharpoons C^{4+} + e^-;\quad \frac{N_{C^{4+}}N_{e^-}}{N_{C^{3+}}} = \frac{U_{C^{4+}}U_{e^-}}{U_{C^{3+}}}e^{-I_{C^{3+}\to C^{4+}}/kT} \tag{9}$$

where N_i are the particle concentrations, Q and U denote the molecular and atomic partition functions, respectively, U_{rxn}, D, and I represent the energies of reaction, dissociation energy, and ionization potentials, respectively, and k is the Boltzmann constant. In additon, the following three constraints are imposed:

quasi-neutrality condition:

$$4N_{C^{4+}} + 3N_{C^{3+}} + 2N_{C^{2+}} + N_{C^+} + N_{H^+} = N_{e^-} \tag{10}$$

partial pressure to total pressure relation:

$$P_T = kT(N_{C_nH_{2n+2}} + N_{CH_2} + N_{CH_3} + N_C + N_{H_2} + N_H + N_{H^+} + N_{C^+} + N_{C^{2+}} + N_{C^{3+}} + N_{C^{4+}} + N_{e^-}) \tag{11}$$

atomic balance:

$$n(3N_{CH_3} + 2N_{CH_2} + 2N_{H_2} + N_H + N_{H^+}) = (2n + 2) \times (N_{CH_3} + N_{CH_2} + N_C + N_{C^+} + N_{C^{2+}} + N_{C^{3+}} + N_{C^{4+}}) \tag{12}$$

The above relations result in 12 nonlinear equations for 12 unknown concentrations (N_i), once the carbon number n is specified. These particle concentrations were then replaced by the particle fractions, $y_i = N_i/N_T$. The molecular and atomic partition functions were evaluated for a given temperature and pressure by accounting for the translational, rotational, vibrational, and electronic contributions. A molecule with S atoms requires $3S$ position coordinates and $3S$ momentum coordinates to specify its location in phase space. Of these, three coordinates are required to specify the molecular center of mass, which are the translational degrees of freedom. The remaining would be rotational and vibrational degrees of freedom. Linear molecules, like diatomic molecules, have only two rotational degrees of freedom, whereas nonlinear molecules have three rotational degrees of freedom. The molecular partition function $q \equiv VQ$, with V the molar volume of each species i, can be evaluated as the product of the translational partition function q_t, the rotational partition function q_r, the vibrational partition function q_v, and the electronic partition function q_e using (Reed and Gubbins, 1973)

$$q = q_t q_r q_v q_e \tag{13}$$

$$q_t = \left(\frac{2\pi I_x kT}{h^2}\right)^{3/2} V \tag{14}$$

$$q_r = T/\sigma\theta_R \text{ for linear molecules} \tag{15}$$

$$q_r = \frac{\pi^{1/2}}{\sigma}\left(\frac{8\pi^2 I_x kT}{h^2}\right)^{1/2}\left(\frac{8\pi^2 I_y kT}{h^2}\right)^{1/2}\left(\frac{8\pi^2 I_z kT}{h^2}\right)^{1/2} \text{ for nonlinear molecules} \tag{16}$$

$$q_v = \prod_i [1 - \exp(\theta_{v_i}/T)^{-1}] \tag{17}$$

$$q_e = \Omega_e \tag{18}$$

Here, θ_R is the rotational temperature; I_x, I_y, and I_z are the moments of inertia of the molecules, h is Planck's constant, σ is the symmetry number, θ_{v_i} are the vibrational temperatures, and Ω_e are the electronic ground states. The values of these constants were obtained from several sources (Janz, 1958; McQuarrie, 1976; Lide, 1990). The moments of inertia of the molecules were computed by using the mass of the atoms and the bond lengths. The carbon−carbon bond length is 0.154 nm whereas the C−H bond length is 0.11 nm. The H−H bond length is 0.0746 nm. Dissociation energies were calculated from the bond energies; the C−C bond energy is 9.637×10^{-22} kJ, that for C−H is 5.566×10^{-22} kJ, and that for H−H is 7.173×10^{-22} kJ. The ionization energy of hydrogen is 21.787×10^{-22} kJ. The first, second, third, and fourth ionization energies of carbon are 18.034×10^{-22}, 39.055×10^{-22}, 76.699×10^{-22}, and 103.30×10^{-22} kJ, respectively. The rotational temperature for H_2 is 87.5 K whereas that of CH_2 is 10.51 K, when CH_2 is taken as a linear radical. The vibrational temperature for H_2 is 6335 K whereas those of CH_2 are 4224.4, 4122.3, 2113.6, 2024.4, 1866.1, and 1312.2 K. The vibrational temperatures for CH_3 are 4224.6 (3), 2100.7 (2), 1978.4, 1683.4, and 1189.9 K with the numbers in parentheses denoting degeneracies. These values have been calculated from the vibrational frequencies given by Janz (1958) for CH_2 and CH_3 taken as group contributions; no values could be found for the free radicals themselves.

With this input data, the 12 nonlinear equations were solved by the Newton−Raphson iterative method to provide particle fractions. Equations 1−3 describe the decomposition of the alkane into carbon and diatomic hydrogen. The formation of the CH radical and C^{5+} and C^{6+} ions were initially taken into account along with their equilibrium equations. The calculations showed later that these species are never significant, and hence those equations and species were ignored; other species will be considered in the Discussion.

Once the composition of the resultant plasma is calculated, the mass density ρ can be found from the perfect gas mixture equation. The enthalpies H can be calculated by adding the tranlational, rotational, and vibrational, and electronic contributions of the respective species in addition to the enthalpy of reaction effects due to molecular dissociation and due to ionization. The translational, rotational, and vibrational contributions to the specific heat capacity C_p were calculated analytically from standard statistical mechanics. However, due to mathematical complexity, the chemical contributions were evaluated by numerical differentiation of the corresponding enthalpies. That is

$$C_p = C_{p_t} + C_{p_v} + C_{p_r} + (\partial/\partial T)[H_{diss} + H_{ion}]_p \tag{19}$$

The reference (initial) state for all the enthalpies is 298 K in the perfect gas state.

Results

Tables 1−5 provide the particle fraction and thermophysical properties for methane in the plasma state at 1, 10, 100, 1000, and 10,000 bar, respectively. Tables 6−10 provide the same information for hexadecane ($C_{16}H_{34}$). Figure 1 provides the isobaric heat capacity of methane from 2500 to 60 000 K on the above isobars whereas Figure

Table 1. Particle Fractions and Thermophysical Properties for CH_4 Plasma at 1 bar

	$y_i \times 10^5$														
T/K	CH_4	CH_3	CH_2	C	H_2	H	H^+	C^+	C^{2+}	C^{3+}	C^{4+}	e^-	ρ/(kg/m³)	*H*/(kJ/kg)	C_P/(kJ/kg·K)
1500	99107	594	1	0	298	0	0	0	0	0	0	0	0.1281E+00	0.5510E+04	0.5471E+01
3000	7713	36147	10185	4293	32029	9633	0	0	0	0	0	0	0.3748E−01	0.2256E+05	0.3968E+02
4500	0	5	55	20743	3890	75306	0	0	0	0	0	0	0.8911E−02	0.1259E+06	0.2054E+02
6000	0	0	0	20012	184	79761	1	20	0	0	0	22	0.6436E−02	0.1412E+06	0.7089E+01
9000	0	0	0	18614	7	78500	340	1100	0	0	0	1440	0.4222E−02	0.1668E+06	0.1253E+02
12000	0	0	0	11346	1	64901	5597	6279	0	0	0	11876	0.2831E−02	0.2409E+06	0.4224E+02
15000	0	0	0	3295	0	30591	22963	10092	1	0	0	33058	0.1721E−02	0.4392E+06	0.8440E+02
18000	0	0	0	681	0	7307	35876	10083	32	0	0	46022	0.1156E−02	0.6545E+06	0.4952E+02
21000	0	0	0	167	0	1651	38920	9585	391	0	0	49286	0.9312E−03	0.7572E+06	0.2625E+02
24000	0	0	0	45	0	476	38836	7544	2240	0	0	50860	0.7895E−03	0.8433E+06	0.3369E+02
27000	0	0	0	10	0	172	37678	3897	5554	2	0	52688	0.6757E−03	0.9522E+06	0.3522E+02
30000	0	0	0	2	0	73	36850	1491	7711	27	0	53845	0.5932E−03	0.1042E+07	0.2498E+02
36000	0	0	0	0	0	19	36085	205	7884	937	0	54870	0.4834E−03	0.1188E+07	0.3148E+02
42000	0	0	0	0	0	7	34467	20	3394	5184	20	56908	0.3956E−03	0.1451E+07	0.4635E+02
48000	0	0	0	0	0	3	33436	1	672	7326	360	58201	0.3358E−03	0.1670E+07	0.3095E+02
54000	0	0	0	0	0	2	32650	0	113	5889	2161	59186	0.2915E−03	0.1889E+07	0.4450E+02
60000	0	0	0	0	0	1	31624	0	15	2752	5140	60468	0.2541E−03	0.2168E+07	0.4287E+02

Table 2. Particle Fractions and Thermophysical Properties for CH_4 Plasma at 10 bar

	$y_i \times 10^5$														
T/K	CH_4	CH_3	CH_2	C	H_2	H	H^+	C^+	C^{2+}	C^{3+}	C^{4+}	e^-	ρ/(kg/m³)	*H*/(kJ/kg)	C_P/(kJ/kg·K)
1500	99584	277	0	0	139	0	0	0	0	0	0	0	0.1283E+01	0.5506E+04	0.5433E+01
3000	25321	42660	4621	235	24783	2679	0	0	0	0	0	0	0.4661E+00	0.1681E+05	0.1167E+02
4500	38	1811	2921	21493	19890	53846	0	0	0	0	0	0	0.1125E+00	0.9480E+05	0.7224E+02
6000	0	1	29	20325	1753	77878	0	6	0	0	0	7	0.6542E−01	0.1387E+06	0.1062E+02
9000	0	0	0	19563	72	79436	107	358	0	0	0	465	0.4267E−01	0.1626E+06	0.8505E+01
12000	0	0	0	16607	12	74761	1777	2533	0	0	0	4310	0.3075E−01	0.2003E+06	0.1869E+02
15000	0	0	0	10258	3	58222	9168	6591	0	0	0	15759	0.2165E−01	0.2889E+06	0.4252E+02
18000	0	0	0	4340	0	31891	22600	9279	4	0	0	31887	0.1459E−01	0.4558E+06	0.6508E+02
21000	0	0	0	1500	0	12315	33193	9831	46	0	0	43116	0.1044E−01	0.6400E+06	0.5205E+02
24000	0	0	0	535	0	4313	37505	9616	304	0	0	47729	0.8398E−02	0.7623E+06	0.3197E+02
27000	0	0	0	202	0	1658	38569	8562	1293	0	0	49717	0.7181E−02	0.8497E+06	0.2874E+02
30000	0	0	0	72	0	726	38232	6265	3401	1	0	51303	0.6259E−02	0.9416E+06	0.3229E+02
36000	0	0	0	7	0	193	36888	1856	7318	89	0	53648	0.4965E−02	0.1119E+07	0.2527E+02
42000	0	0	0	1	0	70	36046	426	7425	1177	0	54854	0.4145E−02	0.1277E+07	0.3179E+02
48000	0	0	0	0	0	31	34704	74	4049	4538	23	56581	0.3488E−02	0.1512E+07	0.4176E+02
54000	0	0	0	0	0	16	33673	9	1290	6865	258	57888	0.3007E−02	0.1731E+07	0.3159E+02
60000	0	0	0	0	0	9	33018	1	347	6632	1276	58715	0.2653E−02	0.1922E+07	0.3480E+02

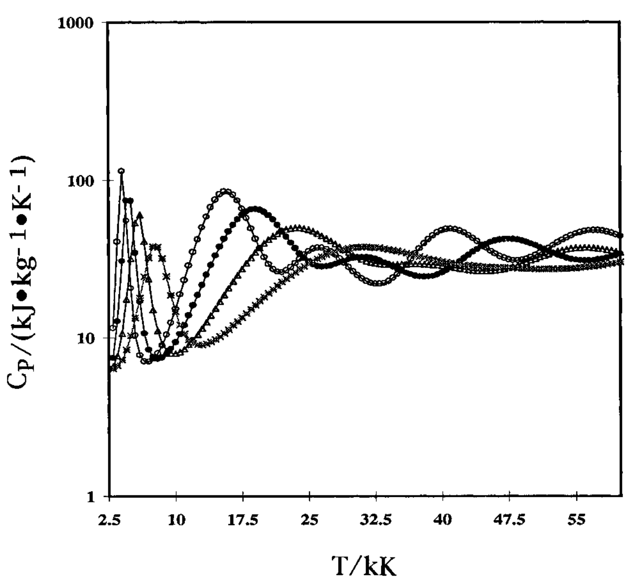

Figure 1. Specific heat capacity of methane as a function of temperature at high temperatures. Symbols: ○ (*P* = 1 bar); ● (*P* = 10 bar); △ (*P* = 100 bar); × (*P* = 1 kbar); + (*P* = 10 kbar).

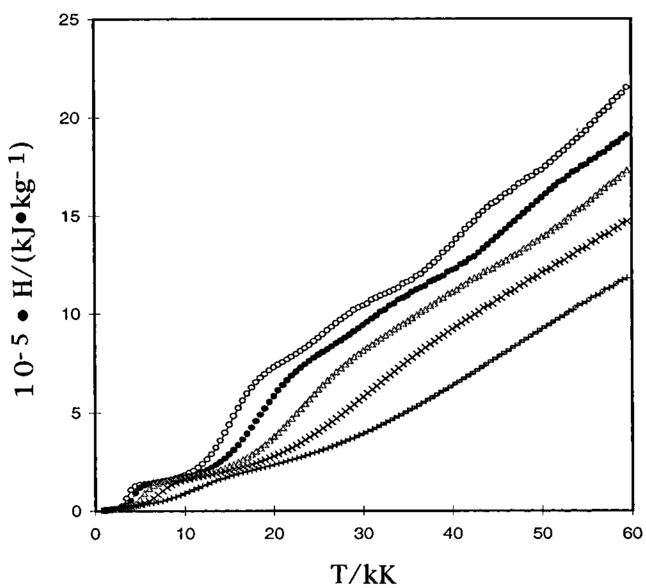

Figure 2. Specific enthalpy of methane as a function of temperature. Symbols: ○ (*P* = 1 bar); ● (*P* = 10 bar); △ (*P* = 100 bar); × (*P* = 1 kbar); + (*P* = 10 kbar).

2 shows the corresponding enthalpy to 60 000 K. Likewise, Figure 3 is the isobaric heat capacity diagram and Figure 4 the enthalpy diagram for hexadecane. On the logarithmic heat capacity scale of Figure 1, differences between the last two isobars, from Tables 4 and 5, are insufficient to make the two lines distinguishable for methane whereas the corresponding isobars for hexadecane in Figure 3 are very different.

Discussion

Before attempting the above model calculations for hydrocarbons, we first performed dissociation/ionization calculations for (1) argon, (2) oxygen, and (3) hydrogen for comparison with the tables of Dresvin (1977) to 20 000 K at 1 bar. Agreement for the particle fractions was within 0.5%. Similar agreement was found for enthalpy, the only energy-related function given by Dresvin. Also, the earlier

Table 3. Particle Fractions and Thermophysical Properties for CH_4 Plasma at 100 bar

	$y_i \times 10^5$														
T/K	CH_4	CH_3	CH_2	C	H_2	H	H^+	C^+	C^{2+}	C^{3+}	C^{4+}	e^-	ρ/(kg/m^3)	H/(kJ/kg)	C_P/(kJ/kg·K)
1500	99807	129	0	0	64	0	0	0	0	0	0	0	0.1284E+02	0.5503E+04	0.5146E+01
3000	49330	31876	1238	10	16847	699	0	0	0	0	0	0	0.5298E+01	0.1562E+05	0.8688E+01
4500	2362	29327	12359	6209	29136	20608	0	0	0	0	0	0	0.2153E+01	0.3914E+05	0.3341E+02
6000	8	828	2016	20848	11964	64332	0	2	0	0	0	2	0.7615E+00	0.1170E+06	0.3849E+02
9000	0	1	18	19986	710	78989	33	115	0	0	0	148	0.4309E+00	0.1603E+06	0.7934E+01
12000	0	0	2	18871	132	78139	560	868	0	0	0	1429	0.3171E+00	0.1865E+06	0.1052E+02
15000	0	0	0	16057	40	72210	3065	2781	0	0	0	5846	0.2421E+00	0.2290E+06	0.1879E+02
18000	0	0	0	11644	13	59150	9157	5439	1	0	0	14597	0.1830E+00	0.3045E+06	0.3224E+02
21000	0	0	0	7089	4	40910	18285	7705	6	0	0	26002	0.1359E+00	0.4229E+06	0.4591E+02
24000	0	0	0	3774	1	23776	27229	8940	37	0	0	36243	0.1024E+00	0.5694E+06	0.4934E+02
27000	0	0	0	1902	0	12357	33281	9344	163	0	0	42952	0.8147E−01	0.7066E+06	0.4100E+02
30000	0	0	0	960	0	6287	36393	9163	547	0	0	46650	0.6857E−01	0.8153E+06	0.3227E+02
36000	0	0	0	237	0	1862	37829	6820	2863	4	0	50385	0.5314E−01	0.9935E+06	0.2927E+02
42000	0	0	0	49	0	696	37124	3310	5997	99	0	52725	0.4340E−01	0.1165E+07	0.2710E+02
48000	0	0	0	9	0	313	36320	1240	7080	828	0	54208	0.3679E−01	0.1327E+07	0.2882E+02
54000	0	0	0	2	0	162	35295	380	5454	3017	12	55680	0.3165E−01	0.1525E+07	0.3668E+02
60000	0	0	0	0	0	92	34239	92	2828	5553	110	57086	0.2758E−01	0.1743E+07	0.3420E+02

Table 4. Particle Fractions and Thermophysical Properties for CH_4 Plasma at 1000 bar

	$y_i \times 10^5$														
T/K	CH_4	CH_3	CH_2	C	H_2	H	H^+	C^+	C^{2+}	C^{3+}	C^{4+}	e^-	ρ/(kg/m^3)	H/(kJ/kg)	C_P/(kJ/kg·K)
1500	99910	60	0	0	30	0	0	0	0	0	0	0	0.1285E+03	0.5502E+04	0.5408E+01
3000	70766	19022	307	0	9736	168	0	0	0	0	0	0	0.5789E+02	0.1504E+05	0.7568E+01
4500	11761	47385	6479	343	27680	6352	0	0	0	0	0	0	0.2826E+02	0.2870E+05	0.1096E+02
6000	1045	24964	13383	6711	24679	29218	0	0	0	0	0	0	0.1481E+02	0.5416E+05	0.2628E+02
9000	1	384	1516	20071	5902	72033	10	37	0	0	0	46	0.4714E+01	0.1464E+06	0.1721E+02
12000	0	10	162	19784	1305	77823	174	284	0	0	0	458	0.3251E+01	0.1797E+06	0.8887E+01
15000	0	1	40	18706	457	76896	979	971	0	0	0	1950	0.2534E+01	0.2082E+06	0.1069E+02
18000	0	0	14	16805	201	72430	3103	2172	0	0	0	5275	0.2034E+01	0.2464E+06	0.1515E+02
21000	0	0	5	14142	95	64334	6980	3731	1	0	0	10712	0.1641E+01	0.3008E+06	0.2140E+02
24000	0	0	2	11092	44	53282	12430	5353	5	0	0	17792	0.3121E+01	0.3756E+06	0.2843E+02
27000	0	0	1	8142	19	40988	18641	6754	20	0	0	25435	0.1065E+01	0.4704E+06	0.3444E+02
30000	0	0	0	5667	8	29490	24540	7778	67	0	0	32451	0.8682E+00	0.5791E+06	0.3738E+02
36000	0	0	0	2507	1	13499	32730	8619	432	0	0	42213	0.6189E+00	0.7967E+06	0.3370E+02
42000	0	0	0	1043	0	6066	36135	7907	1598	3	0	47248	0.4843E+00	0.9823E+06	0.2891E+02
48000	0	0	0	400	0	2947	36903	5886	3630	46	0	50187	0.4002E+00	0.1151E+07	0.2753E+02
54000	0	0	0	140	0	1574	36652	3592	5500	324	0	52218	0.3412E+00	0.1315E+07	0.2752E+02
60000	0	0	0	45	0	915	36028	1858	6066	1264	3	53821	0.2968E+00	0.1844E+07	0.3051E+02

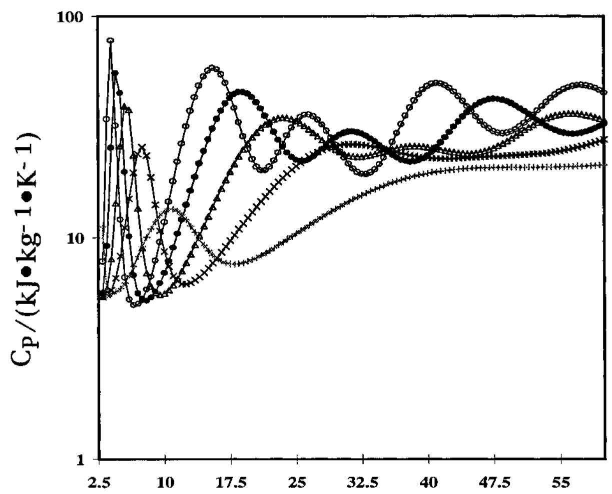

Figure 3. Specific heat capacity of hexadecane as a function of temperature at high temperatures. Symbols: ○ (P = 1 bar); ● (P = 10 bar); △ (P = 100 bar); × (P = 1 kbar); + (P = 10 kbar).

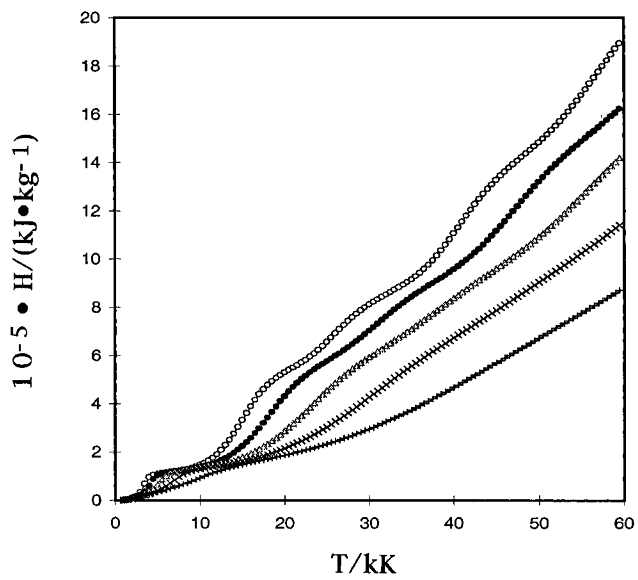

Figure 4. Specific enthalpy of hexadecane as a function of temperature. Symbols: ○ (P = 1 bar); ● (P = 10 bar); △ (P = 100 bar); × (P = 1 kbar); + (P = 10 kbar).

steam results from our group (Patel, et al., 1990) were duplicated.

The perfect gas assumption is invalid, of course, at low temperatures and high pressures. For dissociated molecules, it is possible to estimate a mixture compressibility factor Z_m, using the principle of corresponding states and mixture combining rules. At about 9000 K, where significant ionization begins, any estimate of Z_m would contain a large uncertainty due to the presence of electrons and ions. For this reason we chose to maintain the simplicity of the perfect gas assumption. Because interparticle forces are generally not important at these high temperatures, the results for branched alkanes are nearly the same as for n-alkanes. Indeed, only the hydrogen-to-carbon ratio is of engineering significance at these high temperatures so any hydrocarbon is well predicted as long as that ratio is matched to an alkane. For example, cycloalkanes C_nH_{2n} are roughly approximated by the hexadecane table because there H/C = 17/8 or 2.125, which is approaching 2. In

Table 5. Particle Fractions and Thermophysical Properties for CH_4 Plasma at 10 000 bar

	$y_i \times 10^5$														
T/K	CH_4	CH_3	CH_2	C	H_2	H	H^+	C^+	C^{2+}	C^{3+}	C^{4+}	e^-	ρ/(kg/m^3)	H/(kJ/kg)	C_P/(kJ/kg·K)
1500	99958	28	0	0	14	0	0	0	0	0	0	0	0.1285E+04	0.5502E+04	0.5404E+01
3000	84829	10007	71	0	5055	38	0	0	0	0	0	0	0.6098E+03	0.1475E+05	0.6946E+01
4500	30503	42961	2053	13	22652	1817	0	0	0	0	0	0	0.3235E+03	0.2661E+05	0.8716E+01
6000	6704	47980	7704	347	27510	9755	0	0	0	0	0	0	0.2015E+03	0.4061E+05	0.1012E+02
9000	360	20666	14755	6403	18008	39791	3	6	0	0	0	9	0.9036E+02	0.8071E+05	0.1733E+02
12000	18	4299	8202	14992	8696	63537	51	77	0	0	0	128	0.4432E+02	0.1380E+06	0.1836E+02
15000	1	852	3407	18003	4060	72473	299	303	0	0	0	602	0.2900E+02	0.1838E+06	0.1262E+02
18000	0	231	1609	18295	2119	74324	982	729	0	0	0	1711	0.2234E+02	0.2184E+06	0.1109E+02
21000	0	81	871	17599	1221	72894	2310	1356	0	0	0	3667	0.1827E+02	0.2528E+06	0.1214E+02
24000	0	33	507	16373	744	69257	4393	2149	0	0	0	6543	0.1531E+02	0.2923E+06	0.1432E+02
27000	0	14	302	14806	463	63903	7207	3046	2	0	0	10257	0.1297E+02	0.3393E+06	0.1707E+02
30000	0	6	178	13042	288	57301	10601	3980	8	0	0	14596	0.1106E+02	0.3950E+06	0.2006E+02
36000	0	1	57	9431	107	42518	18156	5712	50	0	0	23968	0.8167E+01	0.5323E+06	0.2546E+02
42000	0	0	16	6322	37	28913	25069	6979	205	0	0	32459	0.6206E+01	0.6953E+06	0.2835E+02
48000	0	0	4	4009	12	18681	30143	7596	604	1	0	38950	0.4906E+01	0.8669E+06	0.2847E+02
54000	0	0	1	2429	4	11910	33265	7482	1375	10	0	43525	0.4033E+01	0.1035E+07	0.2746E+02
60000	0	0	0	1405	1	7700	34889	6675	2508	60	0	46761	0.3421E+01	0.1197E+07	0.2678E+02

Table 6. Particle Fractions and Thermophysical Properties for $C_{16}H_{34}$ Plasma at 1 bar

	$y_i \times 10^5$														
T/K	$C_{16}H_{34}$	CH_3	CH_2	C	H_2	H	H^+	C^+	C^{2+}	C^{3+}	C^{4+}	e^-	ρ/(kg/m^3)	H/(kJ/kg)	C_p/(kJ/kg·K)
1500	96766	1894	595	745	0	0	0	0	0	0	0	0	0.1759E+01	0.3314E+04	0.4884E+01
3000	0	38587	19538	26597	9918	5360	0	0	0	0	0	0	0.4802E−01	0.3671E+05	0.3427E+02
4500	0	5	64	32882	2829	64220	0	0	0	0	0	0	0.1245E−01	0.1049E+06	0.1209E+02
6000	0	0	0	32008	133	67805	1	26	0	0	0	27	0.9078E−02	0.1147E+06	0.4966E+01
9000	0	0	0	29970	5	66582	241	1481	0	0	0	1722	0.5942E−02	0.1336E+06	0.9555E+01
12000	0	0	0	18580	1	57424	4199	9149	0	0	0	13348	0.3929E−02	0.1902E+06	0.3178E+02
15000	0	0	0	5322	0	25916	18704	15674	2	0	0	34382	0.2380E−02	0.3322E+06	0.5816E+02
18000	0	0	0	1090	0	6209	30255	16020	50	0	0	46375	0.1621E−02	0.4774E+06	0.3315E+02
21000	0	0	0	268	0	1403	32954	15280	620	0	0	49475	0.1309E−02	0.5491E+06	0.2012E+02
24000	0	0	0	72	0	404	32567	11943	3501	0	0	51513	0.1099E−02	0.6233E+06	0.3135E+02
27000	0	0	0	16	0	145	31015	6138	8507	3	0	54176	0.9236E−03	0.7274E+06	0.3398E+02
30000	0	0	0	3	0	62	29946	2352	11727	40	0	55871	0.8005E−03	0.8125E+06	0.2288E+02
36000	0	0	0	0	0	16	28995	324	11966	1362	0	57337	0.6449E−03	0.9436E+06	0.2955E+02
42000	0	0	0	0	0	6	27100	33	5191	7504	28	60138	0.5165E−03	0.1205E+07	0.4178E+02
48000	0	0	0	0	0	3	25898	2	1040	10654	493	61911	0.4319E−03	0.1423E+07	0.2953E+02
54000	0	0	0	0	0	1	25038	0	177	8637	2969	63178	0.3711E−03	0.1634E+07	0.4402E+02
60000	0	0	0	0	0	1	23924	0	24	4096	7139	64816	0.3191E−03	0.1916E+07	0.4363E+02

Table 7. Particle Fractions and Thermophysical Properties for $C_{16}H_{34}$ Plasma at 10 bar

	$y_i \times 10^5$														
T/K	$C_{16}H_{34}$	CH_3	CH_2	C	H_2	H	H^+	C^+	C^{2+}	C^{3+}	C^{4+}	e^-	ρ/(kg/m^3)	H/(kJ/kg)	C_P/(kJ/kg·K)
1500	99626	219	69	86	0	0	0	0	0	0	0	0	0.1807E+02	0.3279E+04	0.4213E+01
3000	0	53107	22739	22134	1387	634	0	0	0	0	0	0	0.5553E+00	0.3113E+05	0.9193E+01
4500	0	1782	3407	35232	14155	45424	0	0	0	0	0	0	0.1527E+00	0.8683E+05	0.4498E+02
6000	0	1	33	32384	1271	66294	0	8	0	0	0	9	0.9190E−01	0.1134E+06	0.6778E+01
9000	0	0	0	31359	52	67478	76	480	0	0	0	556	0.6015E−01	0.1301E+06	0.6226E+01
12000	0	0	0	26839	9	63328	1320	3592	0	0	0	4912	0.4312E−01	0.1583E+06	0.1405E+02
15000	0	0	0	16655	2	49237	7164	9889	0	0	0	17054	0.3009E−01	0.2239E+06	0.3100E+02
18000	0	0	0	6990	0	27043	18526	14448	6	0	0	32986	0.2026E−01	0.3426E+06	0.4529E+02
21000	0	0	0	2403	0	10463	27887	15573	72	0	0	43603	0.1461E−01	0.4689E+06	0.3541E+02
24000	0	0	0	856	0	3665	31708	15309	482	0	0	47980	0.1180E−01	0.5535E+06	0.2308E+02
27000	0	0	0	323	0	1409	32488	13593	2035	0	0	50152	0.1005E−01	0.6214E+06	0.2412E+02
30000	0	0	0	116	0	616	31840	9887	5269	2	0	52270	0.8658E−02	0.7030E+06	0.2969E+02
36000	0	0	0	11	0	163	30022	2928	11135	131	0	55611	0.6710E−02	0.8675E+06	0.2296E+02
42000	0	0	0	1	0	59	28966	676	11271	1710	1	57316	0.5531E−02	0.1012E+07	0.2992E+02
48000	0	0	0	0	0	26	27384	119	6181	6567	31	59691	0.4570E−02	0.1241E+07	0.4167E+02
54000	0	0	0	0	0	13	26178	15	1990	9968	352	61484	0.3882E−02	0.1457E+07	0.3047E+02
60000	0	0	0	0	0	8	25442	2	541	9685	1748	62574	0.3395E−02	0.1640E−07	0.3334E+02

addition to methane, tables for hexadecane have been presented to (1) represent a light lube oil, (2) allow the reader to see the influence of the H/C ratio, (3) allow the reader to interpolate linearly between methane [H/C = 4] and hexadecane [2.125] for alkanes of intermediate carbon numbers, and (4) extrapolate slightly for alkanes where n > 16.

Wilhoit (1995) has provided a printout of the Thermocenter of the Russian Academy of Sciences and the Thermodynamics Research Center of Texas A&M University program (Frenkel, et al., 1994) for particle fractions at temperatures from 1500 to 6000 K and pressures to 1 kbar for H/C ratios of 2.125−4. While not including ionization effects, this program is more flexible in the inclusion of additional species, particularly radicals. At 1 bar, these tables and the present tables show close agreement for all temperatures. At 1 kbar, however, considerable differences occur due to the inclusion of C_2H_2, C_3H, and C_2H. While these radicals are not stable at higher temperatures and/or lower pressures, we acknowledge a loss in accuracy in our model results above 10 bar for temperatures below 9000 K. Our tables at higher temperatures are not affected by the presence of these radicals which are prominent only over a narrow range of temperature. State properties are not so affected as long as the initial and final states are absent of these radicals.

With the above exception, we claim an accuracy of about ±5% in the densities and enthalpies plus about ±15% in

Table 8. Particle Fractions and Thermophysical Properties for $C_{16}H_{34}$ Plasma at 100 bar

	$y_i \times 10^5$														
T/K	$C_{16}H_{34}$	CH_3	CH_2	C	H_2	H	H^+	C^+	C^{2+}	C^{3+}	C^{4+}	e^-	ρ/(kg/m^3)	*H*/(kJ/kg)	C_P/(kJ/kg·K)
1500	99957	25	8	10	0	0	0	0	0	0	0	0	0.1813E+03	0.3275E+04	0.4140E+01
3000	0	55163	23105	21522	145	65	0	0	0	0	0	0	0.5656E+01	0.3047E+05	0.5881E+01
4500	0	29266	20161	27061	10904	12608	0	0	0	0	0	0	0.2890E+01	0.4908E+05	0.2602E+02
6000	0	814	2342	33860	8561	54418	0	3	0	0	0	3	0.1049E+01	0.1012E+06	0.2351E+02
9000	0	0	21	31946	513	67165	24	153	0	0	0	177	0.6069E+00	0.1285E+06	0.5532E+01
12000	0	0	2	30288	95	66347	416	1218	0	0	0	1634	0.4465E+00	0.1473E+06	0.7706E+01
15000	0	0	0	25878	29	61225	2361	4073	0	0	0	6434	0.3395E+00	0.1786E+06	0.1378E+02
18000	0	0	0	18787	10	50131	7291	8244	1	0	0	15537	0.2554E+00	0.2335E+06	0.2327E+02
21000	0	0	0	11407	3	34705	14967	11962	9	0	0	26947	0.1893E+00	0.3181E+06	0.3244E+02
24000	0	0	0	6052	1	20193	22710	14080	58	0	0	36909	0.1431E+00	0.4206E+06	0.3427E+02
27000	0	0	0	3046	0	10501	28018	14824	257	0	0	43355	0.1142E+00	0.5158E+06	0.2865E+02
30000	0	0	0	1536	0	5343	30703	14563	863	0	0	046992	0.9615E−01	0.5934E+06	0.2378E+02
36000	0	0	0	380	0	1581	31571	10770	4445	6	0	51247	0.7370E−01	0.7367E+06	0.2537E+02
42000	0	0	0	79	0	588	30426	5214	9156	146	0	54391	0.5910E−01	0.8893E+06	0.2444E+02
48000	0	0	0	15	0	264	29353	1961	10753	1208	1	56446	0.4938E−01	0.1037E+07	0.2658E+02
54000	0	0	0	3	0	135	28104	607	8295	4369	16	58472	0.4185E−01	0.1225E−07	0.3551E+02
60000	0	0	0	0	0	77	26855	149	4332	8042	150	60395	0.3592E−01	0.1437E+07	0.3332E+02

Table 9. Particle Fractions and Thermophysical Properties for $C_{16}H_{34}$ Plasma at 1000 bar

	$y_i \times 10^5$														
T/K	$C_{16}H_{34}$	CH_3	CH_2	C	H_2	H	H^+	C^+	C^{2+}	C^{3+}	C^{4+}	e^-	ρ/(kg/m^3)	*H*/(kJ/kg)	C_P/(kJ/kg·K)
1500	99995	3	1	1	0	0	0	0	0	0	0	0	0.1814E+04	0.3275E+04	0.4131E+01
3000	0	55378	23142	21458	15	6	0	0	0	0	0	0	0.5667E+02	0.3041E+05	0.5536E+01
4500	0	49148	26244	21167	1815	1626	0	0	0	0	0	0	0.3649E+02	0.3997E+05	0.8280E+01
6000	0	24450	20890	26610	9716	18333	0	1	0	0	0	1	0.2039E+02	0.5991E+05	0.1963E+02
9000	0	378	1761	32633	4218	60898	7	49	0	0	0	56	0.6579E+01	0.1207E+06	0.1076E+02
12000	0	10	188	31669	942	66140	129	396	0	0	0	525	0.4572E+01	0.1426E+06	0.6179E+01
15000	0	1	46	29991	330	65316	751	1407	0	0	0	2158	0.3565E+01	0.1628E+06	0.7691E+01
18000	0	0	16	26985	145	61489	2445	3237	0	0	0	5683	0.2857E+01	0.1904E+06	0.1092E+02
21000	0	0	6	22720	69	54606	5616	5682	1	0	0	11300	0.2300E+01	0.2296E+06	0.1535E+02
24000	0	0	2	17812	32	45233	10168	8282	7	0	0	18464	0.1849E+01	0.2829E+06	0.2023E+02
27000	0	0	1	13061	14	34808	15443	10569	30	0	0	26073	0.1490E+01	0.3501E+06	0.2431E+02
30000	0	0	0	9081	6	25053	20512	12263	104	0	0	32982	0.1216E+01	0.4267E+06	0.2628E+02
36000	0	0	0	4014	1	11471	27562	13677	679	0	0	42597	0.8677E+00	0.5807E+06	0.2428E+02
42000	0	0	0	1671	0	5153	30314	12516	2499	5	0	47842	0.6758E+00	0.7198E+06	0.2269E+02
48000	0	0	0	645	0	2499	30620	9275	5596	69	0	51296	0.5522E+00	0.8578E+06	0.2336E+02
54000	0	0	0	227	0	1331	30020	5655	8391	479	0	53896	0.4646E+00	0.1000E+07	0.2438E+02
60000	0	0	0	74	0	770	29128	2938	9211	1843	4	56032	0.3988E+00	0.1156E+07	0.2811E+02

Table 10. Particle Fractions and Thermophysical Properties for $C_{16}H_{34}$ Plasma at 10 000 bar

	$y_i \times 10^5$														
T/K	$C_{16}H_{34}$	CH_3	CH_2	C	H_2	H	H^+	C^+	C^{2+}	C^{3+}	C^{4+}	e^-	ρ/(kg/m^3)	*H*/(kJ/kg)	C_P/(kJ/kg·K)
1500	99999	0	0	0	0	0	0	0	0	0	0	0	0.1814E+05	0.3274E+04	0.4130E+01
3000	0	55400	23146	21452	1	1	0	0	0	0	0	0	0.5668E+03	0.3040E+05	0.5501E+01
4500	0	52398	26988	20251	195	169	0	0	0	0	0	0	0.3765E+03	0.3888E+05	0.5901E+01
6000	0	46328	29186	20211	1787	2486	0	0	0	0	0	0	0.2713E+03	0.4870E+05	0.7443E+01
9000	0	19980	22788	25236	7057	24908	1	14	0	0	0	15	0.1285E+03	0.7882E+05	0.1256E+02
12000	0	4200	10148	29740	5423	50176	33	124	0	0	0	157	0.6265E+02	0.1180E+06	0.1205E+02
15000	0	836	4020	30741	2805	60240	220	459	0	0	0	679	0.4087E+02	0.1480E+06	0.8348E+01
18000	0	227	1876	30098	1502	62573	759	1102	0	0	0	1862	0.3145E+02	0.1713E+06	0.7633E+01
21000	0	79	1012	28593	873	61634	1835	2070	0	0	0	3904	0.2571E+02	0.1953E+06	0.8525E+01
24000	0	32	588	26451	534	58673	3550	3310	1	0	0	6861	0.2153E+02	0.2232E+06	0.1013E+02
27000	0	14	350	23843	333	54197	5896	4731	3	0	0	10634	0.1823E+02	0.2564E+06	0.1208E+02
30000	0	6	206	20957	208	48633	8755	6223	12	0	0	15001	0.1553E+02	0.2958E+06	0.1418E+02
36000	0	1	65	15118	77	36117	15181	9012	78	0	0	24350	0.1147E+02	0.3928E+06	0.1797E+02
42000	0	0	18	10124	27	24569	21086	11062	322	0	0	32793	0.8716E+01	0.5081E+06	0.2015E+02
48000	0	0	5	6419	9	15874	25372	12049	948	2	0	39322	0.6881E+01	0.6313E+06	0.2072E+02
54000	0	0	1	3893	3	10118	27902	11839	2148	15	0	44081	0.5636E+01	0.7559E+06	0.2084E+02
60000	0	0	0	2257	1	6536	29070	10526	3882	91	0	47636	0.4749E+01	0.8822E+06	0.2136E+02

the heat capacities. While a higher temperature provides an approach to the perfect gas assumption, the onset of a high density of charged species brings new possible deviations due to the Coulombic forces of attraction. With the Debye−Huckel model (Drawin, 1971; Boulos et al., 1994), the modification to the perfect gas pressure is

$$p = \frac{NkT}{V_T} - \frac{kT}{24\pi\lambda_D^{\ 3}} \tag{20}$$

with

$$\lambda_D = (\epsilon_0 kTV_T/e^2 \sum_{i=1}^{M} Z_i^{\ 2} N_i)^{1/2} \tag{21}$$

where ϵ_0 is the vacuum permittivity, V_T is the total volume, k is the Boltzmann constant, e the electronic charge, λ_D the Debye length, Z_i the number of ionic charges of species i, and M the total number of charged species. In our calculations, this correction term becomes significant only at the highest pressures and temperatures. For both methane and hexadecane these contributions are nearly the same. The largest deviation is at 10 kbar and 60 000 K, where the correction term is 1004 bar or 10.0%. For 60 000 K, the correction drops to 5.1%, 2.3%, 0.9%, and 0.3% for pressures of 1 kbar, 100 bar, 10 bar, and 1 bar, respectively. For 10 kbar, the correction drops with falling temperature to pass the 5% mark between 27 000 and 30 000 K; it then falls rapidly with loss of ionization to be 0.7% at 18 000 K. For 1 kbar, a correction of near 5% remains down to about 21 000 K, where it drops sharply.

The percent errors in the enthalpy and heat capacity are roughly 2 times and 3 times respectively, those for the pressure or density.

Conclusions

The objective of this study was to provide approximate estimations for the thermophysical properties of plasmas derived from various alkane hydrocarbons. The understanding and modeling of new processes involving plasma technology require closure of mass, momentum, and energy (enthalpy) balances. We believe that a number of previous investigations have reached erroneous conclusions due to gross misestimation of thermophysical properties. For example, heat capacities have been assumed constant over wide ranges of temperature with failure to include enthalpies of dissociation and ionization. With enthalpies low by as much as 100 times, an energy balance would then yield a bulk plasma temperature of 2 million kelvin when it should have been near 20 000 K.

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