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THERMODYNAMICS AND COMBUSTION MODELING

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Modeling fluid phase phenomena blends the conservation equations of continuum mechanics with the property equations of thermodynamics. The thermodynamic contribution becomes especially important when the phenomena involve chemical reactions as they do in combustion systems. The successful study of combustion processes requires (1) the availability of accurate thermodynamic properties for both the reactants and the products of reaction and (2) the computational capabilities to use the properties. A discussion is given of some aspects of the problem of estimating accurate thermodynamic properties both for reactants and products of reaction. Also, some examples of the use of thermodynamic properties for modeling chemically reacting systems are presented. These examples include one-dimensional flow systems and the internal combustion engine.

INTRODUCTION

Modeling fluid phase phenomena always requires a combination of the conservation equations of continuum mechanics with the property functions of thermodynamics. For some applications it is possible to idealize the model so drastically that the continuum equations virtually disappear and the computation becomes wholly thermodynamic. In other situations the thermodynamic properties are so highly idealized that the computation deals solely with the continuum equations. Consequently, thermodynamics and continuum mechanics are often viewed as independent disciplines. However, the complementary nature of the two disciplines is manifested in attempts to generate realistic models of physical systems in which combustion occurs.

The roles of thermodynamics and the conservation equations are easily discerned by examining the relevant equations. The conservation equations (refs. 1 and 2) for mass, species, energy, and momentum are shown in equation (1), where the summation convention is used for an index repeated as a subscript and a superscript:

$$
\begin{aligned}
&\frac{\partial m}{\partial t} + \nabla_k(mv^k) = 0 = \frac{\delta m}{\delta t} + m\nabla_k v^k \\
&\frac{\partial(mn_\lambda)}{\partial t} + \nabla_k(mn_\lambda v^k + d_\lambda^k) = R_\lambda \\
&\frac{\partial(mu)}{\partial t} + \nabla_k(muv^k) = -\nabla_k(q^k + \mu^\lambda d_\lambda^k) + \tau^{kj}\nabla_j v_k - m\frac{\partial\Omega}{\partial t} - v^k f_k = m\frac{\delta u}{\delta t} \qquad (1) \\
&m\frac{\delta v^k}{\delta t} = F^k = -mg^{ki}\nabla_i\Omega + f^k + \nabla_j\tau^{kj} \\
&\tau^{kj} = -pg^{kj} + \Delta\tau^{kj}
\end{aligned}
$$

In these equations, m is the mass density, u the internal energy per unit mass, n_λ the moles per unit mass of species λ, v^k the velocity, q^k the heat flux, μ^λ the chemical potential per mole of species λ, d^k_λ the diffusive flux of species λ, and R_λ the volumetric rate of production of species λ. In the momentum equation, g^{ki} is the metric tensor for three-dimensional space, τ^{kj} is the stress tensor, Ω is the potential energy, and f^k represents all volumetric forces over and above those produced by the stress and the potential energy. The stress tensor is composed of a contribution from the pressure p and the dissipative stresses. The symbol t represents time, ∇_k is the covariant derivative with respect to the spatial coordinates, and $\delta/\delta t = \partial/\partial t + v^k\nabla_k$ is known as the absolute, substantial, or convective derivative. The thermodynamic property functions for pressure, internal energy, and the chemical potentials are shown in equation (2). These properties may be regarded as functions of mass density, temperature T, and moles per unit mass of the species:

$$\begin{aligned} p &= p(m,T,n_\lambda) \\ u &= u(m,T,n_\lambda) \qquad (2) \\ \mu^\lambda &= \mu^\lambda(m,T,n_\tau) \end{aligned}$$

Substitution of the thermodynamic internal energy function into the conservation equation for internal energy converts it into an equation for the temperature, and the resulting equation now contains explicit contributions from changes in composition and mass density. In reacting fluids the temperature largely reflects the energy released or absorbed by chemical reactions. Thus, we see that the thermodynamic property of internal energy determines the temperature and, consequently, the amount of energy released or absorbed. Of course, the temperature, in turn, strongly affects reaction rates and other physical properties of the reacting fluid. The thermodynamic pressure equation (an equation of state) appears in the equation for the conservation of momentum and thus helps to define the local flow field. Clearly, the successful modeling of combustion processes requires two ingredients: (1) accurate thermodynamic properties for both the reactants and the products of reaction and (2) computational capabilities to use the properties in modeling combustion systems.

I shall briefly describe some aspects of our work on the two topics of property estimation and property utilization. First, I shall discuss the estimation of free radical properties in the ideal gas state and the properties of nonideal solutions. Following the discussion of properties, I shall illustrate some of our computational capabilities to use these properties to model the physical systems in which reactions take place.

ESTIMATION OF FREE RADICAL PROPERTIES

Free radicals are highly reactive species which are usually present at low concentrations in chemically reacting systems. These species play an important role in the chemical reaction mechanisms of combustion. They are involved in both the endothermic (heat absorbing) initiation steps of the mechanism and the exothermic (heat releasing) recombination steps. Recently Bauer and Zhang (ref. 3) and others have conjectured that free radicals are also important species in the mechanism of soot formation in hydrocarbon flames. Hence, the thermodynamic properties of free radicals are of considerable interest. Unfortunately, relatively little is known about the thermodynamic properties of radicals over the extended temperature range encountered in combustion systems. Hence, we have found it necessary to estimate the thermodynamic properties of the phenyl, phenoxy, and biphenyl free radicals which are likely to be important species in the combustion of hydrocarbons and in soot formation. Because of their low concentrations and because most combustion processes take place at relatively low pressures and high temperatures, it is usually adequate to estimate free radical properties in the ideal gas state.

Thermodynamic properties for any species in an ideal gas state can be estimated from the canonical partition function using the formulas of statistical thermodynamics. This requires knowledge of the species' molecular structure, its vibrational and rotational energy levels, any barriers to internal rotation, and the standard state heat of formation. The difficulty is that this information is seldom available for free radicals. As a result it becomes necessary to estimate these data from similar, stable species whose molecular properties have been measured. These stable, related species are called the parent species of the radicals. The species benzene, phenol and biphenyl are suitable parent species for the radicals phenyl, phenoxy and o-biphenyl, respectively. The relation between these parent species and the radicals is shown in figure 1. This estimation procedure is based on the work of Forgeteg and Berces (ref. 4). In this method it is usual to assume that the bond lengths and bond angles of the radical are identical to those of the parent. Also the radical's vibrational frequencies are taken to be the same as those of the parent molecule except that three frequencies are eliminated for each atom which appears in the parent molecule but not in the radical. In some cases, where additional information about the radical is available, the assumed structure and vibrational frequencies can be adjusted to take into account this extra information.

One of the difficulties with this method of estimation is the selection of the appropriate frequencies for elimination. The reason for this is that a molecule's frequencies correspond to vibrations of the molecule as a whole rather than vibrations of a particular bond. Naturally this introduces some uncertainty into the resulting properties. To ascertain the degree of uncertainty one might try eliminating different frequencies or, perhaps, perform the estimation with a different parent species.

Comparisons of the results of our estimation of phenyl and phenoxy properties (ref. 5) with estimates made by Benson, et al. (refs. 6 and 7) are shown in tables I and II for entropy and heat capacity. Our estimation of the phenyl properties from benzene and phenol agree surprisingly well with each other and with the room temperature values estimated by Benson. Our estimates of the phenoxy properties estimated from phenol also agree very well with Benson's estimates which, for this species, were available over an extended temperature range.

NONIDEAL SOLUTION MODELS

The properties of fuels and oxidizers must be accurately known if combustion processes are to be modeled properly. Since reactants, especially fuels, are often multicomponent, nonideal, liquid solutions, it is desirable to have accurate mathematical representations of the composition dependence of their thermodynamic properties. Such representations (solution models) can be used to analyze, interpolate and extrapolate thermodynamic measurements of nonideal solutions. Solution models can also be used for the calculation of equilibria. The utility of a solution model is directly proportional to its ability to handle both a wide range of nonideal behaviors and a great diversity of multicomponent systems.

Many solution models have been proposed, but most of them have a limited capacity to treat nonideality. Some of them either are only able to deal with relatively small deviations from ideality or cannot handle the complete composition range. Others are limited to binary or ternary solutions. Still others exhibit undesirable mathematical behavior. Many contain nonlinear parameters which greatly complicate the analysis of experimental measurements. I have proposed a solution model (ref. 8) which overcomes most of these difficulties. The model is applicable to solutions containing an arbitrary number of constituents. It can treat highly nonideal solutions, electrolyte and nonelectrolyte, over the complete composition range. It has a relatively simple mathematical form, and all parameters appear linearly in the model. Finally, it contains both ideal and regular solutions as special cases. The model's expression for the Gibbs free energy is given in equation (3) where G is the Gibbs free energy, x_i is the mole fraction of species i, $\varphi^{(\ell)}$ represents the elementary symmetric functions, and $\mu_{jk}^{(\ell)}$, and $\varepsilon_{jk}^{(\ell)}$ are functions of temperature and pressure.

$$G = \sum_{\ell=1}^{N} \varphi^{(\ell)}(x_i;N) \sum_{j=1}^{N} \sum_{k=1}^{N} \left(\mu_{jk}^{(\ell)} + \varepsilon_{jk}^{(\ell)} \ln x_j \right) x_j x_k$$

$$= \sum_{\ell=1}^{N} \varphi^{(\ell)}(x_i;N) G^{(\ell)}(x_i) \qquad (3)$$

I shall illustrate the flexibility and the capabilities of the model by demonstrating how it handles three very different, highly nonideal solutions (ref. 9).

The first solution is the ethanol-heptane binary system, for which there are three sets of excess enthalpy measurements at 30 °C. The solution is endothermic, and measurements extend into the very dilute solution range. The representation of the measurements by the solution model is shown in figure 2. Clearly the model reproduces the data very well over the complete composition range, including the steep gradient that occurs in the dilute ethanol region. The second solution is the chloroform-ethanol binary solution at 50 °C, whose excess enthalpy exhibits exothermic behavior over a part of the composition range and endothermic behavior over the rest of the range. The representation of the data is shown in figure 3, and again the data are well represented by the model. These two solutions display very different behavior yet both can be accommodated easily by the same solution model.

The first two examples were nonelectrolyte solutions. The last example is an electrolyte solution of sodium chloride in water. Measurements for this system extend from the very dilute solutions to saturated solutions and cover a temperature range of almost 200 °C. A comparison between the measurements and the model are shown in figures 4 to 7, where the composition is given as molality (g mol of solute/kg solvent). Figures 4 to 6 show the integral heats of solution while the excess heat capacity is shown in figure 7. Once again the model gives more than an adequate representation of the experimental measurements.

CHEMICAL REACTION EQUILIBRIA

Sometimes the behavior of chemically reacting systems can be predicted quite well on the basis of chemical equilibrium. Over the years we have developed a capability to perform computations reliably for several applications involving chemical reactions (refs. 10 to 16). The calculations are based on free energy minimization and assume that the gaseous phase behaves ideally, that the condensed phases are pure liquids and solids, and that the volume of the condensed phases is negligible. The computations can evaluate composition and, also, thermodynamic and transport properties for complex chemical systems involving up to 20 chemical elements and 600 reaction products.

Composition and properties can be calculated for a thermodynamic state defined by pressure and one of the three variables: temperature, enthalpy, or entropy. Alternatively, the thermodynamic state can be specified by assigning the volume and one of the three variables temperature, internal energy, or entropy. In addition to the calculation of compositions and properties for an assigned thermodynamic state, we can also compute the results for three different one-dimensional flow processes neglecting heat transfer effects: (1) rocket nozzle expansions, (2) incident and reflected shocks, and (3) Chapman-Jouguet detonations. The rocket nozzle and shock calculations can be performed for either equilibrium or frozen compositions. Table III is an example of the calculation of the composition and of the thermodynamic and transport properties for a simple system composed of hydrogen and oxygen at assigned pressures and temperatures. Table IV illustrates the results for the calculation of a one-dimensional shock in a hydrogen-oxygen mixture diluted with argon.

MODELING THE SPARK-IGNITED INTERNAL COMBUSTION ENGINE

The spark-ignited internal combustion engine is an example of a chemically reacting system for which purely thermodynamic predictions are inadequate. A realistic model must take into account not only thermodynamic properties but also heat transfer rates, finite rate chemistry (chemical kinetics), and intake and exhaust flow rates. These effects lead to a complex model and difficult calculations.

A schematic representation of the operation of the spark-ignited internal combustion engine is shown in figure 8. Each cycle of the operation can be described qualitatively by dividing the cycle into four parts, each part spanning π radians (180°) of crankangle. Each part corresponds approximately to one of four processes taking place in the engine. The parts are given names which are reasonably descriptive of the four processes: (1) the intake stroke, (2) the compression stroke, (3) the power stroke and (4) the exhaust stroke. A fuel-air mixture enters the cylinder during the intake stroke and is compressed by the piston during the compression stroke. The compressed working fluid is ignited and expanded during the power stroke and is expelled from the cylinder during the exhaust stroke. Because matter enters and leaves the cylinder, the internal combustion engine is an open system. Furthermore, the burned gases are not completely expelled from the cylinder, and thus the residual gases provide a "memory" of each cycle for the subsequent cycle. Each cycle occurs rapidly with a cycle repetition rate which ranges from about 25 to 250 msec. This cycle repetition rate is comparable to the time scale for the complex chemistry which takes place during combustion, and thus the rates of chemical reactions become important. The engine has a movable boundary (the piston) and a complex geometry. Finally, the operation of the engine is nonrepeatable, and the engine experiences "cycle-to-cycle" variations. These features of the internal combustion engine make its modeling difficult indeed. Additionally, often there is insufficient information to describe completely the details of the engine operation even if it were mathematically and numerically possible.

I have chosen to develop (ref. 17) a hierarchy of models of differing complexity in order to accommodate the varying amounts of information available in particular cases. The models range from a simple model requiring only thermodynamic properties (modeling level 1) to a complex model demanding full combustion kinetics, transport properties and poppet valve flow characteristics (modeling level 5). The members of the hierarchy are classified according to their treatment of several important features of the internal combustion engine as shown in table V. The description of the operation of the internal combustion engine as being divided into four parts is adequate for a qualitative description. It is, however, inadequate to describe the operation of a real engine corresponding to modeling at levels 4 and 5. The timing for the initiation and cessation of important events in a more realistic cycle is sketched in figure 9. This figure, often referred to as an indicator diagram, is a plot of working fluid pressure as a function of cylinder volume for one complete cycle spanning 4π radians (720°) of crankangle. It should be noted that between stations 7 and 2 the intake and the exhaust valves are simultaneously open; this corresponds to what is called the valve-overlap portion of the cycle.

I shall use the fuel-rich combustion of gaseous propane with air as an example of modeling the internal combustion engine at level 5. The air is humidified (75 percent relative humidity), and recirculated exhaust gas is 10 percent of the charge. The calculation was a multicycle calculation, but only cycle 11 is shown. The modeling parameters and a summary of results for cycle 11 are given in table VI. The combustion of propane was given a full kinetic treatment using a mechanism of 121 reactions. Figures 10 to 15 are plots of some of the calculated quantities. Straight line segments are apparent on some of these plots. These are not indicative of the accuracy of the calculations but rather reflect both the number of points saved for plotting and the scale of the plots. Figure 10 shows the indicator diagram for cycle 11. Figure 11 shows the fraction of working fluid which has been converted to burned, but still reacting, gas during the combustion phase of the cycle. The burned and unburned gas temperatures are shown in figure 12 (both temperatures were calculated during the combustion phase of the cycle). The quenching effect of the endothermic initiation reactions is clearly visible. The carbon monoxide concentration in mole percent is shown in figure 13. Here we can easily see the freezing of carbon monoxide early in the power stroke. A similar plot for nitric oxide, as parts per million in mole fraction, also shows freezing in figure 14. Finally, in figure 15 is a history of the mass content of the cylinder during cycle 11.

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TABLE I. - COMPARISON OF PROPERTIES FOR PHENYL RADICAL[a]

Property	Benson (ref. 6)	Estimated from benzene	Estimated from phenol
S^{o}_{300}	69.4	69.03	69.30
C^{o}_{p} 300	18.8	18.96	19.51
C^{o}_{p} 500	----	31.03	31.70
C^{o}_{p} 1000	----	46.59	46.93
C^{o}_{p} 3000	----	59.04	59.09

[a] All values as eu (cal/g-mol K).

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TABLE II. - COMPARISON OF PROPERTIES FOR PHENOXY RADICAL[a]

Property	Benson (ref. 6)	From phenol
S^{o}_{300}	73.7	73.70
C^{o}_{p} 300	22.5	22.64
C^{o}_{p} 400	29.8	29.82
C^{o}_{p} 500	35.8	35.80
C^{o}_{p} 600	40.6	40.57
C^{o}_{p} 800	47.5	47.48
C^{o}_{p} 1000	52.3	52.17

[a] All values as eu (cal/g-mol K).

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TABLE III.

THERMODYNAMIC EQUILIBRIUM PROPERTIES AT ASSIGNED TEMPERATURE AND PRESSURE

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CASE NO.     6668
                                                                              WT FRACTION     ENERGY     STATE     TEMP
           CHEMICAL FORMULA                                                   (SEE NOTE)    KJ/KG-MOL              DEG K
FUEL     H  2.00000                                                             1.000000     -9012.332     L       20.27
OXIDANT O   2.00000                                                             1.000000    -12978.762     L       90.18

                O/F=  7.9370      PERCENT FUEL=  11.1894      EQUIVALENCE RATIO= 1.0000      PHI= 1.0000

THERMODYNAMIC PROPERTIES

P, MPA            0.10132  0.10132  0.10132  0.10132  0.10132  0.10132  0.10132  0.10132  0.10132  0.10132  0.10132
T, DEG K           5500.0   5000.0   4500.0   4000.0   3500.0   3000.0   2500.0   2000.0   1500.0   1000.0    500.0
RHO, KG/CU M     1.3416-2 1.4967-2 1.7468-2 2.3376-2 3.8936-2 6.2488-2 8.5005-2 1.0938-1 1.4635-1 2.1955-1 4.3909-1
H, KJ/KG          55513.9  52669.0  47251.0  33833.1  12360.5 -1457.79 -6953.36 -9278.31 -10745.6 -11979.6 -13038.5
U, KJ/KG          47961.3  45899.1  41450.5  29498.5  9758.19 -3079.30 -8145.34 -10204.6 -11438.0 -12441.1 -13269.2
G, KJ/KG        -123677.1-107511.2 -91736.2 -76960.8 -64513.3 -54702.2 -46385.9 -38774.8 -31609.1 -24892.6 -18767.8
S, KJ/(KG)(K)     32.5802  32.0360  30.8861  27.6985  21.9640  17.7481  15.7730  14.7483  13.9090  12.9130  11.4586

M, MOL WT           6.055    6.141    6.450    7.672   11.182   15.383   17.438   17.951   18.013   18.015   18.015
(DLV/DLP)T       -1.00811 -1.02147 -1.06320 -1.15917 -1.16898 -1.06245 -1.01196 -1.00121 -1.00004 -1.00000 -1.00000
(DLV/DLT)P         1.0831   1.2419   1.7935   3.2778   3.8474   2.2710   1.2997   1.0382   1.0015   1.0000   1.0000
CP, KJ/(KG)(K)     4.6981   7.2046  16.3371  38.8059  39.0979  17.2068   6.6083   3.3997   2.6424   2.2907   1.9548
GAMMA (S)          1.5032   1.3668   1.2355   1.1639   1.1268   1.1106   1.1235   1.1705   1.2124   1.2523   1.3091
SON VEL,M/SEC      3369.4   3041.9   2677.0   2246.2   1712.4   1341.9   1157.2   1041.3    916.2    760.2    549.6

TRANSPORT PROPERTIES (GASES ONLY)
  CONDUCTIVITY IN UNITS OF MILLIWATTS/(CM)(K)

VISC,MILLIPOISE   1.3674   1.2723   1.1761   1.0869   1.0207  0.94586  0.83841  0.70639  0.55364  0.37747  0.17324

  WITH EQUILIBRIUM REACTIONS

CP, KJ/(KG)(K)    4.6844   7.2044  16.3359  38.8069  39.1072  17.2071   6.6077   3.3935   2.6423   2.2907   1.9548
CONDUCTIVITY     12.6667  16.4726  31.4208  70.9281  79.3619  34.1601   9.6648   3.2468   1.7354   0.9740   0.3603
PRANDTL NUMBER    0.5057   0.5564   0.6115   0.5947   0.5030   0.4764   0.5732   0.7383   0.8430   0.8878   0.9398

  WITH FROZEN REACTIONS

CP, KJ/(KG)(K)    3.5289   3.5100   3.4743   3.3857   3.2373   3.1124   2.9951   2.8393   2.6140   2.2907   1.9548
CONDUCTIVITY     10.3699   9.6043   8.7109   7.4819   5.8067   4.3630   3.3449   2.4942   1.7049   0.9740   0.3603
PRANDTL NUMBER    0.4653   0.4650   0.4691   0.4918   0.5691   0.6747   0.7507   0.8041   0.8488   0.8878   0.9398


MOLE FRACTIONS

H                 0.66077  0.65095  0.61751  0.50212  0.25268  0.05763  0.00517  0.00012  0.00000  0.00000  0.00000
HO2               0.00000  0.00000  0.00000  0.00003  0.00008  0.00005  0.00001  0.00000  0.00000  0.00000  0.00000
H2                0.00387  0.01037  0.03230  0.10047  0.18534  0.13479  0.04283  0.00581  0.00020  0.00000  0.00000
H2O               0.00002  0.00018  0.00213  0.02961  0.23353  0.64341  0.91089  0.98950  0.99968  1.00000  1.00000
O                 0.33098  0.32663  0.31048  0.24985  0.11877  0.02421  0.00182  0.00003  0.00000  0.00000  0.00000
OH                0.00363  0.00967  0.02972  0.08948  0.15096  0.09367  0.02331  0.00214  0.00004  0.00000  0.00000
O2                0.00073  0.00219  0.00786  0.02845  0.05865  0.04624  0.01596  0.00238  0.00009  0.00000  0.00000

ADDITIONAL PRODUCTS WHICH WERE CONSIDERED BUT WHOSE MOLE FRACTIONS WERE LESS THAN  0.50000E-05 FOR ALL ASSIGNED CONDITIONS

 H2O2              O3                   H2O(S)               H2O(L)
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TABLE IV.

SHOCK WAVE PARAMETERS ASSUMING
EQUILIBRIUM COMPOSITION FOR INCIDENT SHOCKED CONDITIONS

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CASE NO.    1207
                                                                          MOLES        ENERGY    STATE    TEMP
          CHEMICAL FORMULA                                                             CAL/MOL            DEG K
FUEL     H  2.00000                                                       0.050000      13.324     G     300.00
FUEL     O  2.00000                                                       0.050000      12.952     G     300.00
FUEL     AR 1.00000                                                       0.900000       9.191     G     300.00

               O/F=  0.0000 PERCENT FUEL= 100.0000    EQUIVALENCE RATIO= 0.5000     PHI= 0.0000
INITIAL GAS (1)
MACH NO.            3.3528    3.5052    3.6576    3.8100    3.9624    4.1148    4.2672    4.4196    4.5720    4.7244
U1, M/SEC          1100.00   1150.00   1200.00   1250.00   1300.00   1350.00   1400.00   1450.00   1500.00   1550.00
P, ATM             0.01316   0.02632   0.02632   0.02632   0.02632   0.02632   0.02632   0.02632   0.02632   0.02632
T, DEG K             300.0     300.0     300.0     300.0     300.0     300.0     300.0     300.0     300.0     300.0
RHO, G/CC        2.0126-5 4.0252-5 4.0252-5 4.0252-5 4.0252-5 4.0252-5 4.0252-5 4.0252-5 4.0252-5 4.0252-5
H, CAL/G           0.25457   0.25457   0.25457   0.25457   0.25457   0.25457   0.25457   0.25457   0.25457   0.25457
U, CAL/G           -15.578   -15.578   -15.578   -15.578   -15.578   -15.578   -15.578   -15.578   -15.578   -15.578
G, CAL/G           -371.94   -360.97   -360.97   -360.97   -360.97   -360.97   -360.97   -360.97   -360.97   -360.97
S, CAL/(G)(K)       1.2407    1.2041    1.2041    1.2041    1.2041    1.2041    1.2041    1.2041    1.2041    1.2041

M, MOL WT           37.654    37.654    37.654    37.654    37.654    37.654    37.654    37.654    37.654    37.654
CP, CAL/(G)(K)      0.1372    0.1372    0.1372    0.1372    0.1372    0.1372    0.1372    0.1372    0.1372    0.1372
GAMMA (S)           1.6249    1.6249    1.6249    1.6249    1.6249    1.6249    1.6249    1.6249    1.6249    1.6249
SON VEL,M/SEC        328.1     328.1     328.1     328.1     328.1     328.1     328.1     328.1     328.1     328.1


SHOCKED GAS (2)--INCIDENT--EQUILIBRIUM
U2, M/SEC           666.94    602.16    576.32    560.44    549.22    540.35    532.52    524.96    517.29    509.40
P, ATM             0.10778   0.27659   0.32363   0.36873   0.41405   0.46053   0.50878   0.55917   0.61191   0.66707
T, DEG K            1528.1    1693.3    1817.1    1932.4    2044.1    2153.0    2258.8    2360.3    2456.7    2547.3
RHO, G/CC        3.3195-5 7.6873-5 8.3812-5 8.9778-5 9.5277-5 1.0057-4 1.0582-4 1.1118-4 1.1672-4 1.2248-4
H, CAL/G            91.697    114.97    132.65    149.45    166.17    183.16    200.60    218.59    237.18    256.35
U, CAL/G            13.067    27.830    39.138    49.982    60.929    72.259    84.165    96.788    110.22    124.45
G, CAL/G          -1940.61  -2079.42  -2225.77  -2363.02  -2496.51  -2627.06  -2753.88  -2875.57  -2990.89  -3098.89
S, CAL/(G)(K)       1.3300    1.2959    1.2979    1.3002    1.3026    1.3052    1.3080    1.3109    1.3140    1.3172

M, MOL WT           38.619    38.617    38.614    38.608    38.597    38.579    38.551    38.510    38.452    38.378
(DLV/DLP)T        -1.00001  -1.00002  -1.00005  -1.00011  -1.00021  -1.00041  -1.00073  -1.00123  -1.00193  -1.00286
(DLV/DLT)P          1.0003    1.0008    1.0019    1.0038    1.0070    1.0125    1.0209    1.0330    1.0492    1.0695
CP, CAL/(G)(K)      0.1403    0.1420    0.1443    0.1478    0.1532    0.1613    0.1728    0.1883    0.2078    0.2308
GAMMA (S)           1.5795    1.5700    1.5576    1.5403    1.5165    1.4859    1.4497    1.4110    1.3734    1.3400
SON VEL,M/SEC        720.9     756.6     780.6     800.6     817.2     830.3     840.4     848.0     854.1     859.9

TRANSPORT PROPERTIES (GASES ONLY)
  CONDUCTIVITY IN UNITS OF MILLICALORIES/(CM)(K)(SEC)

VISC,MILLIPOISE 0.72845   0.77927   0.81611   0.84959   0.88129   0.91160   0.94048   0.96775   0.99326    1.0169

  WITH EQUILIBRIUM REACTIONS

CP, CAL/(G)(K)    0.1396    0.1415    0.1431    0.1478    0.1522    0.1613    0.1728    0.1882    0.2078    0.2308
CONDUCTIVITY      0.1536    0.1678    0.1786    0.1992    0.2158    0.2576    0.3087    0.3799    0.4721    0.5823
PRANDTL NUMBER    0.6619    0.6573    0.6539    0.6304    0.6215    0.5706    0.5264    0.4796    0.4371    0.4031

  WITH FROZEN REACTIONS

CP, CAL/(G)(K)    0.1396    0.1401    0.1405    0.1408    0.1411    0.1413    0.1416    0.1418    0.1420    0.1422
CONDUCTIVITY      0.1536    0.1658    0.1747    0.1829    0.1907    0.1984    0.2058    0.2131    0.2201    0.2270
PRANDTL NUMBER    0.6619    0.6587    0.6563    0.6540    0.6519    0.6495    0.6469    0.6440    0.6406    0.6368

P2/P1              8.191    10.511    12.298    14.012    15.734    17.500    19.334    21.248    23.253    25.349
T2/T1              5.094     5.644     6.057     6.441     6.814     7.177     7.529     7.868     8.189     8.491
M2/M1             1.0256    1.0256    1.0255    1.0253    1.0250    1.0246    1.0238    1.0227    1.0212    1.0192
RHO2/RHO1         1.6493    1.9098    2.0822    2.2304    2.3670    2.4984    2.6290    2.7621    2.8997    3.0428
V2(U1-U2)M/SEC    433.06    547.84    623.68    689.56    750.78    809.65    867.48    925.04    982.71   1040.60


MOLE FRACTIONS

AR               9.2306-1 9.2302-1 9.2294-1 9.2279-1 9.2254-1 9.2211-1 9.2144-1 9.2045-1 9.1909-1 9.1732-1
H                1.2073-7 8.7884-7 4.2747-6 1.5554-5 4.7175-5 1.2409-4 2.8829-4 5.9812-4 1.1195-3 1.9103-3
HO2              4.6101-8 1.5001-7 2.8252-7 4.7303-7 7.3544-7 1.0786-6 1.5029-6 1.9983-6 2.5453-6 3.1190-6
H2               2.6458-6 1.1305-5 3.5151-5 8.8613-5 1.9569-4 3.8922-4 7.0587-4 1.1754-3 1.8088-3 2.5906-3
H2O              5.1241-2 5.1163-2 5.1019-2 5.0770-2 5.0361-2 4.9725-2 4.8791-2 4.7502-2 4.5833-2 4.3804-2
H2O2             6.699-10 2.448 -9 4.449 -9 7.237 -9 1.097 -8 1.574 -8 2.147 -8 2.796 -8 3.485 -8 4.173 -8
O                2.8572-6 1.2578-5 3.9852-5 1.0208-4 2.2885-4 4.6242-4 8.5400-4 1.4542-3 2.3021-3 3.4157-3
OH               7.5326-5 2.0713-4 4.3641-4 8.0004-4 1.3432-3 2.1036-3 3.0994-3 4.3177-3 5.7144-3 7.2211-3
O2               2.5622-2 2.5587-2 2.5527-2 2.5430-2 2.5285-2 2.5082-2 2.4818-2 2.4497-2 2.4133-2 2.3738-2

ADDITIONAL PRODUCTS WHICH WERE CONSIDERED BUT WHOSE MOLE FRACTIONS WERE LESS THAN  0.50000E-08 FOR ALL
  ASSIGNED CONDITIONS

 O3                    H2O(S)              H2O(L)
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TABLE V. - MODELING LEVELS

Feature	Modeling level				
	5	4	3	2	1
Flow	Poppet valve formulas		Zero-pressure-drop flow; flow reversal only at $\theta = 0$ or $\theta = 3\pi$, where discontinuities are possible		
Flame	Kinetic	Equilibrium			
Flame propagation	Mass burning formulas				Instantaneous
Burned-gas chemistry	Finite rate			Equilibrium	
Heat transfer	Nonzero				Zero

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TABLE VI.

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INTERNAL COMBUSTION ENGINE MODEL ZMOTTO                                    CYCLE  11    LEVEL 5    CASE NO.       111
    REF:  ZELEZNIK, FRANK J.; AND MCBRIDE, BONNIE J.:  MODELING THE INTERNAL COMBUSTION ENGINE. NASA RP-1094, 1985.

COMPRESSION RATIO =  10.5      RPM = 3500.0      EGR = 0.100      T(EGR) =  900.6 K      SPARK ADVANCE =  20.00 DEG
FUEL PRESSURE = 1.00000 ATM      MANIFOLD PRESSURE = 0.42760 ATM      EXHAUST PRESSURE = 1.00000 ATM
FLOWS ARE ISENTROPIC
BORE = 10.922 CM      STROKE = 10.312 CM      ROD = 17.145 CM      CHAMBER AREA =129.030 SQ CM      WALL TEMP =  360.0 K
TOTAL VOLUME = 1067.83 CC      DISPLACEMENT VOLUME =  966.13 CC

IVOPEN = 699.00 DEG      IVSHUT = 265.00 DEG                                 EVOPEN = 465.00 DEG      EVSHUT =  45.00 DEG

HEAT TRANSFER PARAMETERS   C1 =      0.000000   C2 = 0.387200E 00   C3 =      0.000000     A =  0.4000     B =  0.8000

    KINETIC FLAME    FINITE BURNING INTERVAL = 88.7 DEG    WIEBE    COMBUSTION    TAU =0.8930E-04 SEC    BETA =   3.200
                                                                         WT FRACTION    ENERGY   STATE    TEMP
                                                                                        CAL/MOL           DEG K
          CHEMICAL FORMULA
FUEL      C  3.00000   H  8.00000                                          1.000000    -24821.770  G      298.15
AIR       N  1.56168   O  0.41959   AR 0.00936   C  0.00032               *1.000000     -1386.340  G      298.15
                     * AIR INCLUDES   0.02348 MOLE FRACTION WATER        RELATIVE HUMIDITY= 0.7500

                    A/F= 12.5823   PERCENT FUEL=   7.3625   EQUIVALENCE RATIO= 1.2500   PHI=   1.2647

                                        PERFORMANCE PARAMETERS FOR ONE CYLINDER

     MASS PER CYCLE (G)                   MEAN INLET MASS FLOW RATE (G/SEC)       MEAN EXHAUST MASS FLOW RATE (G/SEC)

    TOTAL         0.49685                       CHARGE       12.6027                   EXHAUST       13.2527
    FUEL          0.02860                       FUEL          0.8351                   CO            0.71753
    AIR           0.35987                       AIR          10.5073                   NOX           0.00013
                                                NET          12.6376                   NET           13.2526

   ENERGY PER CYCLE (JOULES)                 AVERAGE ENERGY RATE - POWER (KW)               CYCLE EFFICIENCIES

  INDICATED WORK          404.672          INDICATED POWER          11.803           NET WORK       0.243361
  INDICATED PUMP WORK     -86.886          INDICATED PUMP POWER     -2.534           HEAT LOSS      0.269577
  HEAT LOSS               352.020          HEAT LOSS RATE           10.267           EXHAUST        0.435675
  CHEM. ENERGY           1305.823          EXHAUST POWER            16.593

                                                   MISCELLANEOUS

                              INDICATED MEAN EFFECTIVE PRESSURE (ATM)             4.1338
                              PUMP MEAN EFFECTIVE PRESSURE (ATM)                 -0.8876
                              MEAN TORQUE (NEWTON-METERS)                        25.2886

COMPOSITE EXHAUST GAS MOLE FRACTIONS AT  900.63 K  AND  1.0000 ATM     MOLECULAR WEIGHT =  26.947
      AR         0.007952      CH4        0.000914      CO        0.052088     CO2       0.077497       C2H2       0.002239
      C2H4       0.000131      H2         0.026569      H2O       0.169476     NO        0.000009       N2         0.663041
      O2         0.000070

FRESH CHARGE MOLE FRACTIONS AT  292.50 K  AND  0.4276 ATM      MOLECULAR WEIGHT =  29.192
      AR         0.000861      CH4        0.000099      CO        0.005643     CO2       0.008395       C2H2       0.000243
      C2H4       0.000014      H2         0.002878      H2O       0.018359     N2        0.071827       O2         0.000008
      C3H8       0.043867      AIR        0.847803

NOTE:  INLET AND EXHAUST VALUES CALCULATED WHEN THE VALVES CLOSE.

COMPUTER CYCLE TIME=  48.858 SEC
```

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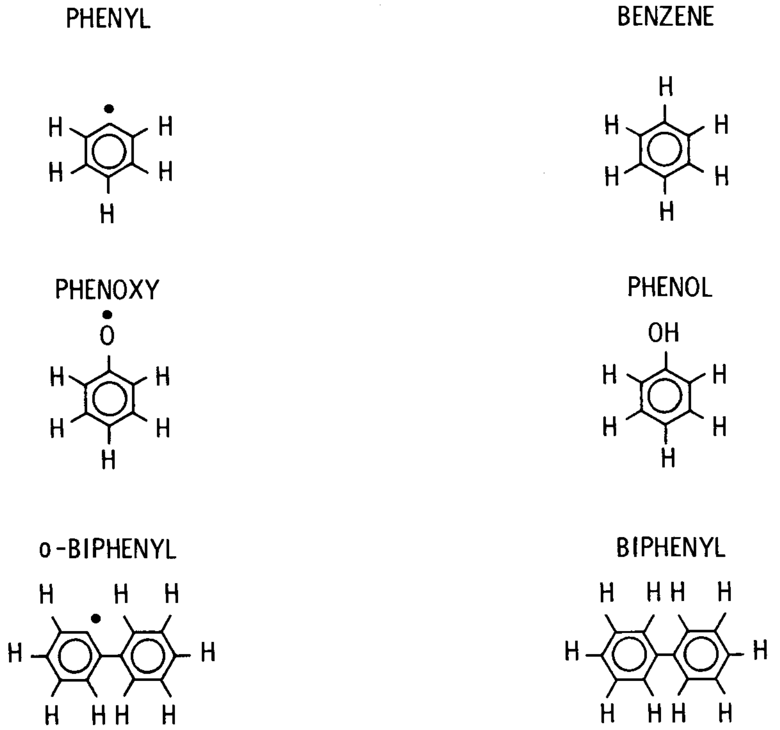


Figure 1. - Radicals and parent species.

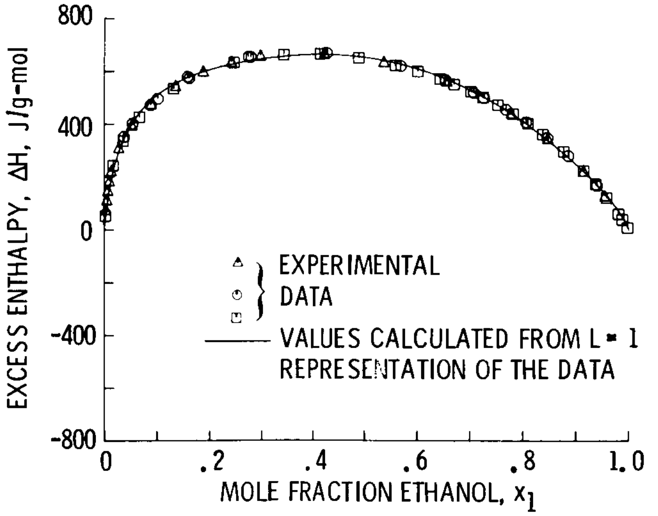


Figure 2. - Excess enthalpy of ethanol (1) - heptane (2) binary system at 30 °C.

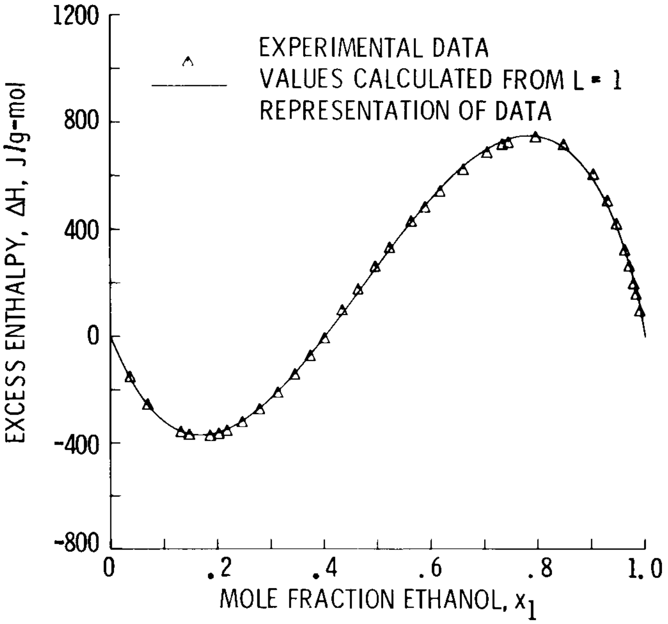


Figure 3. - Excess enthalpy of chloroform (1) - ethanol (2) binary system at 50 °C.

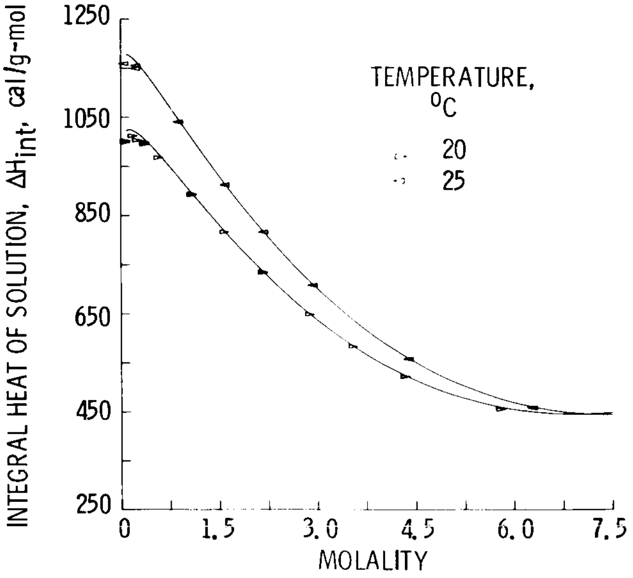


Figure 4. - Integral heat of solution of sodium chloride in water.

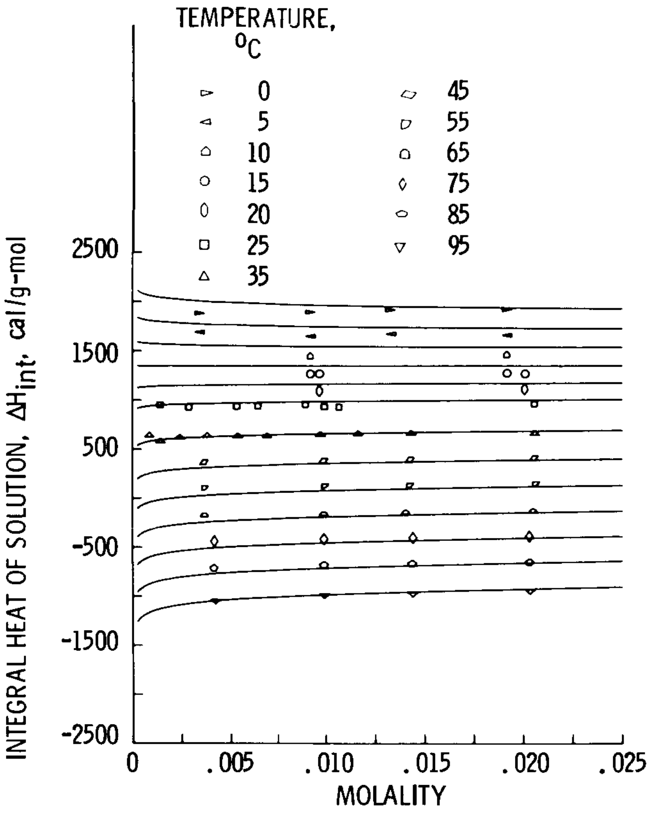


Figure 5. - Integral heat of solution of sodium chloride in water.

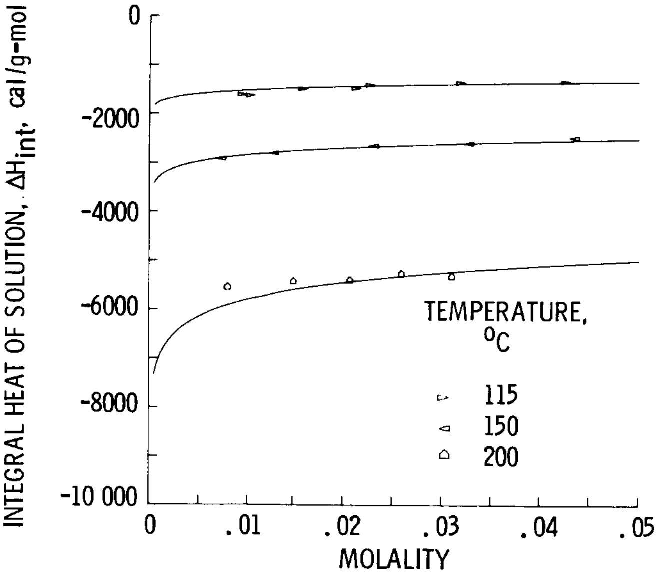


Figure 6. - Integral heat of solution of sodium chloride in water.

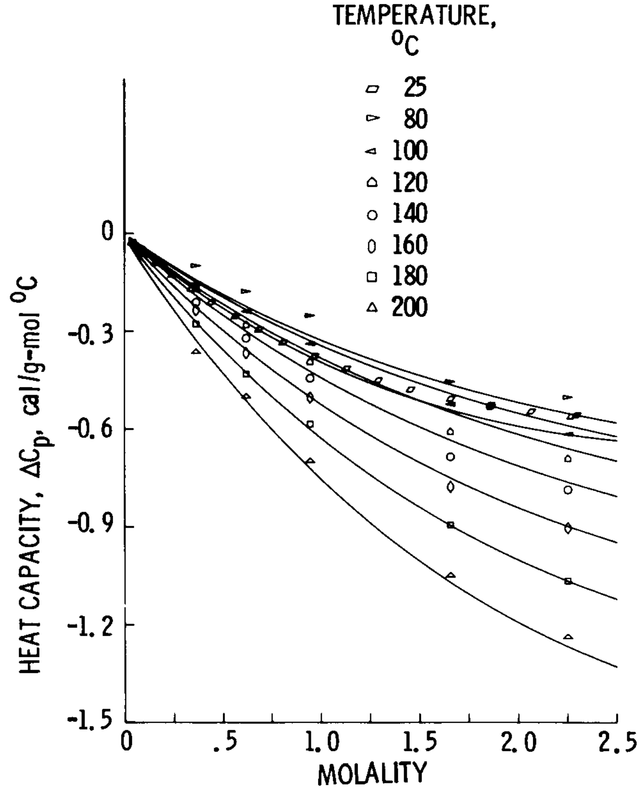
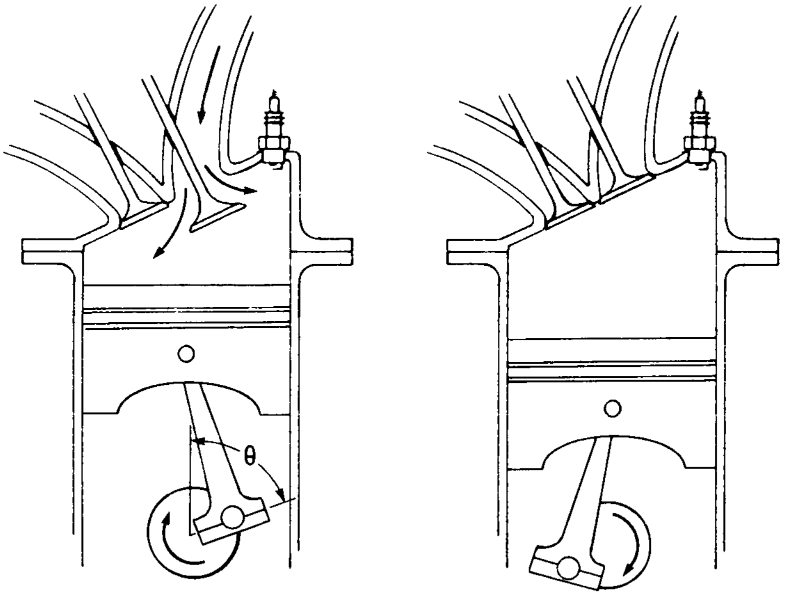
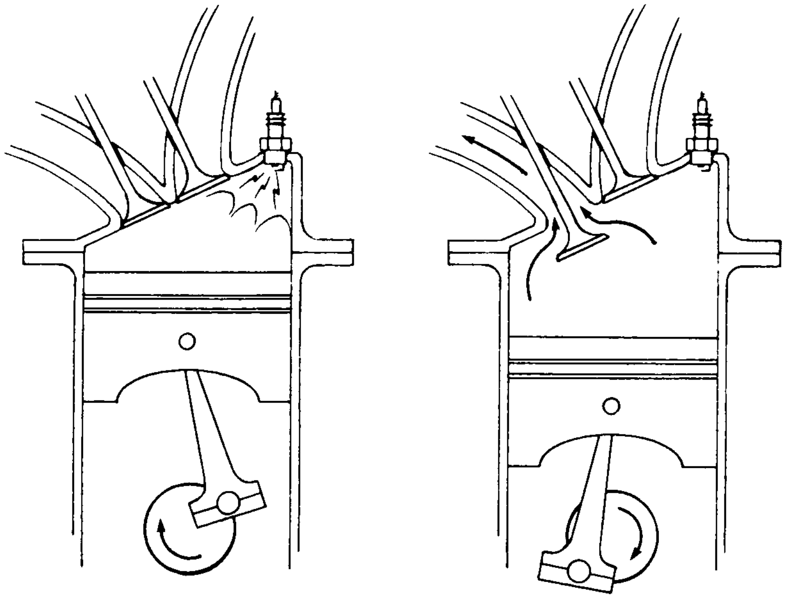


Figure 7. - Excess heat capacity of aqueous sodium chloride solutions.



INTAKE STROKE, $0 \leq \theta \leq \pi$ COMPRESSION STROKE, $\pi \leq \theta \leq 2\pi$



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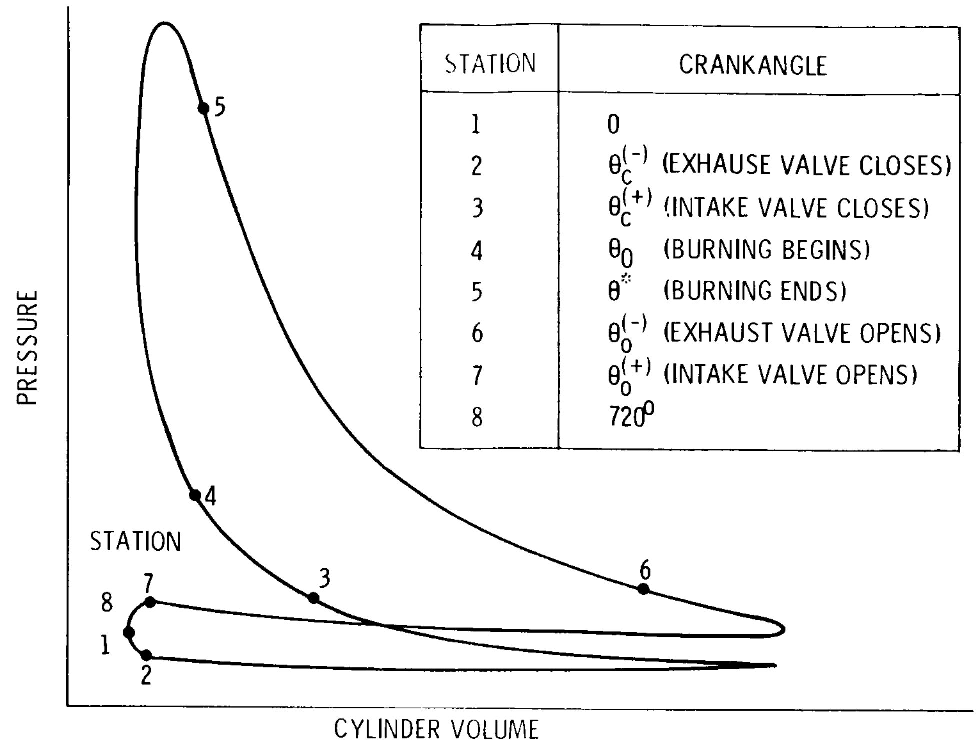
POWER STROKE, $2\pi \leq \theta \leq 3\pi$ EXHAUST STROKE, $3\pi \leq \theta \leq 4\pi$

Figure 8. - Four-stroke operation of spark-ignited internal combustion engine.



STATION	CRANKANGLE
1	0
2	$\theta_c^{(-)}$ (EXHAUSE VALVE CLOSES)
3	$\theta_c^{(+)}$ (INTAKE VALVE CLOSES)
4	θ_0 (BURNING BEGINS)
5	θ^* (BURNING ENDS)
6	$\theta_0^{(-)}$ (EXHAUST VALVE OPENS)
7	$\theta_0^{(+)}$ (INTAKE VALVE OPENS)
8	720^0

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Figure 9. - Stations for modeling levels 4 and 5.

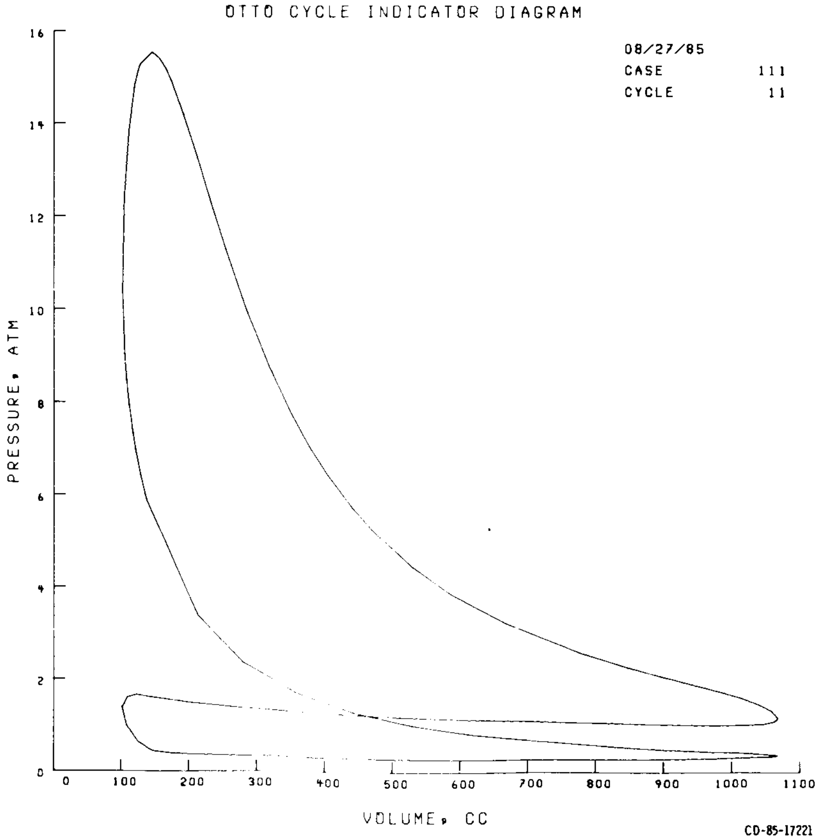

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Figure 10.

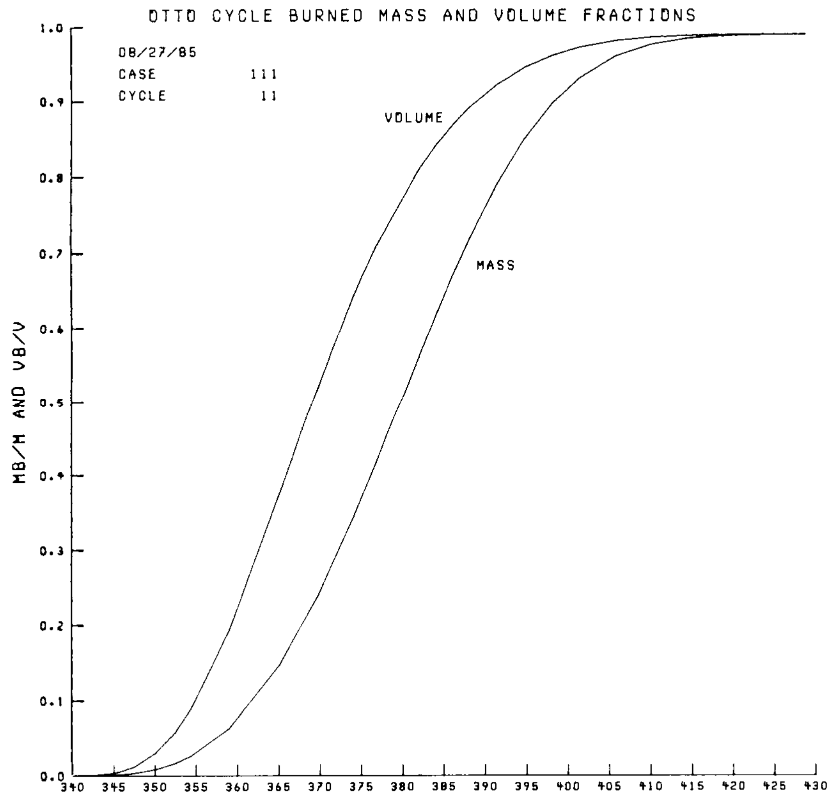

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Figure 11.

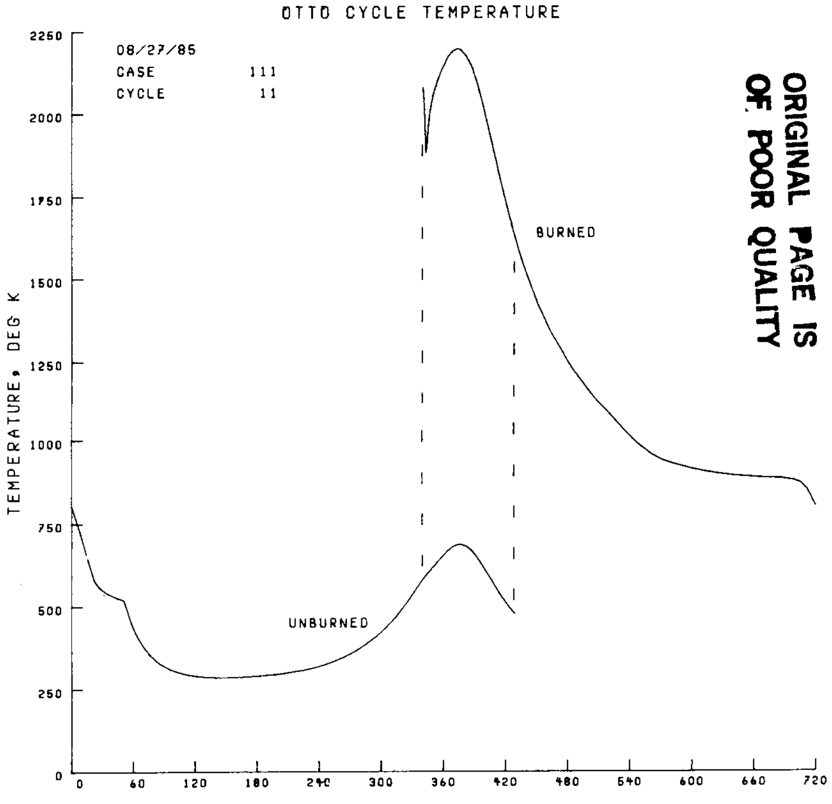

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Figure 12.

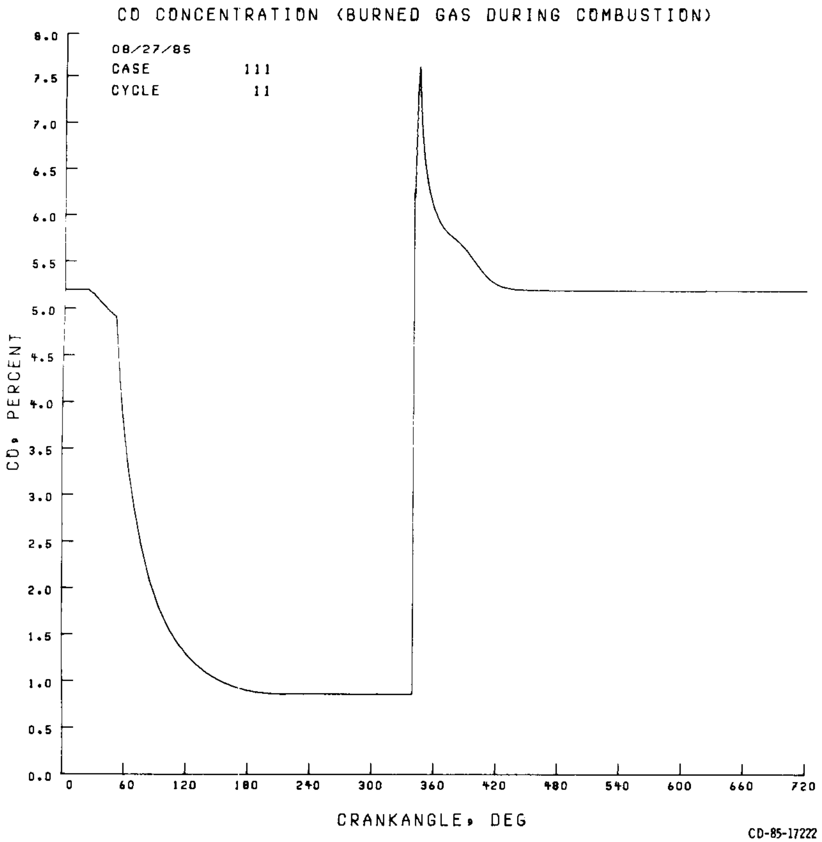

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Figure 13.

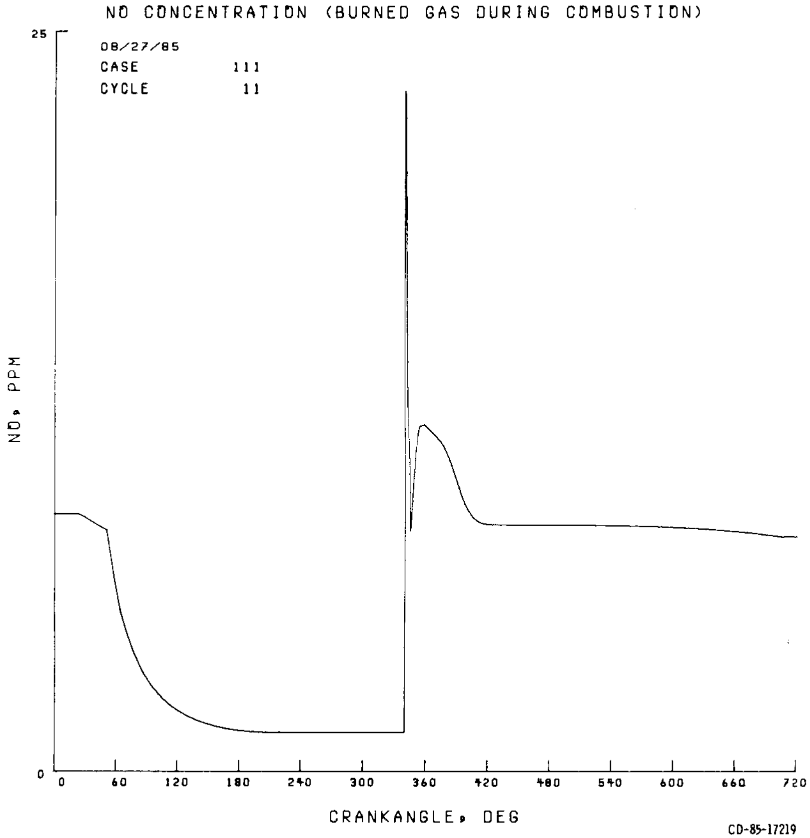

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Figure 14.

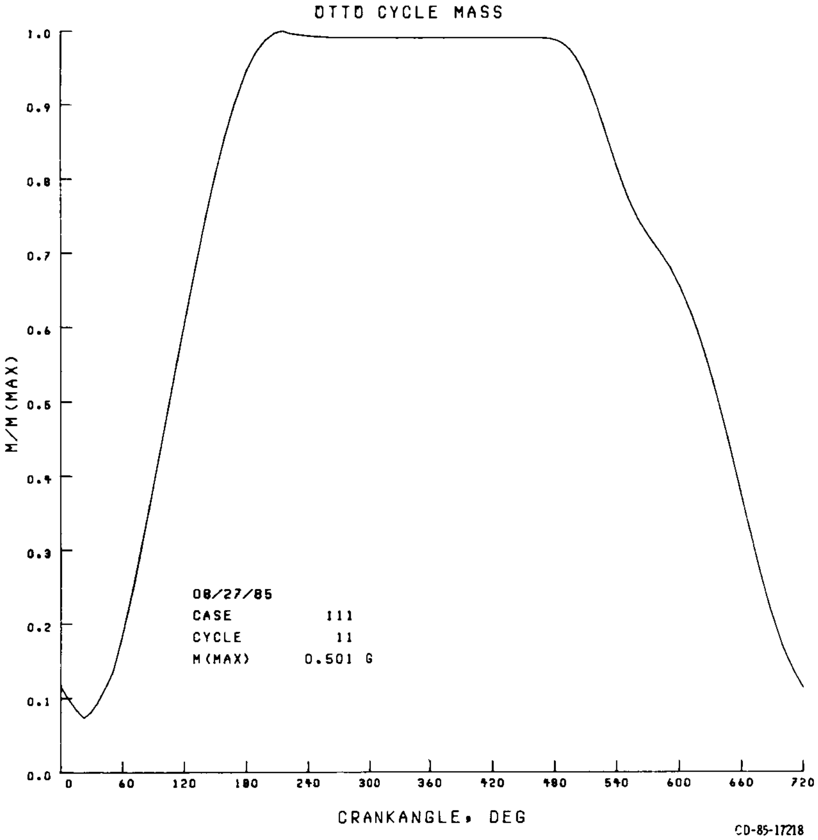

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Figure 15.