

AME599 Combustion Chemistry and Physics

Lecture 1

0.1 Introduction

Combustion has been essential to our existence since the beginning as we know it. For example, the invention of steam and internal combustion engines gives rise to the possibility of industrial revolution. Today, fossil fuel combustion remains to be a part of our daily life and nation's economy. Take one of the most important aspects of our living—food, as an example. The production of food consumes about 17% of total fossil fuel in the US.¹ On average, the production of each calorie of food energy requires 3 calories of fossil energy (to power farming machinery, to process and refrigerate food, to transport food, to produce food packaging materials, and to synthesize fertilizers and pesticides²). Another example that directly relates fossil-fuel combustion to our daily life is the use of heating, air conditioning and ventilation (HVAC) systems. The energy for heating or running our air conditioning systems comes largely through electricity. In 2004, about 70% of electricity in the US is generated from fossil fuel combustion. Computer and information technology, now a major part of our life, relies on the availability of electricity or fossil fuel combustion. Transportation and aviation, by and large, rely on internal combustion engines to convert the chemical energy into power and work.

Currently fossil fuels (oil, coal, and natural gas) are responsible for approximately 86% of the total U.S. energy consumption.^{3,4} According to the Department of Energy, in 2004, the U.S. consumed approximately 1100 million tons of coal, 22,300 billion cubic feet of natural gas, and 20 billion barrels of oil.⁴ Table 1.1 lists breakdown of energy usage by source.

Table 1.1 2004 U.S. energy consumption estimates by source and end-use⁴

Source	Percentage of total	End-use sector	Percentage of total
Petroleum	40	Residential	21
Coal	22	Commercial	18
Natural gas	24	Industrial	33
Nuclear	8	Transportation	28
Hydro power	2		
Others	4		

¹ Horrigan, Leo, Robert S. Lawrence, and Polly Walker. ["How Sustainable Agriculture Can Address the Environmental and Human Health Harms of Industrial Agriculture."](#) Environmental Health Perspectives Vol 110, 5 May 2002.

² For example, the production and transport of 1 lb of nitrogen for nitrogen fertilizer releases an average of 3.7 lbs of CO₂ (Soil Conservation Council of Canada . ["Global Warming and Agriculture: Fossil Fuel"](#) Factsheet volume 1, #3. January 2001.)

³ Union of Concerned Scientists (UCS) ["Clean Energy: Backgrounder: the sources of energy"](#) UCS February, 2003.

⁴ *Annual Energy Review* , US Department of Energy.
http://www.eia.doe.gov/emcu/aer/ep/ep_frame.html

Other sources of energy include nuclear electric power (8%), hydroelectric power (2%). Renewable energy (~4%), including mainly electricity generated from burning wood and waste, geothermal, wind, photovoltaic and solar thermal energy, accounts for the rest of total energy consumption.

To illustrate the importance of energy production and consumption in the US economy, let us look at crude oil consumption, utilization, and imports. In 2004, the US consumes on average about 20 million barrels of oil per day, among which about 11 million barrels are imported. At the current crude oil price (~\$65/barrel), we are spending about 1.3 billion dollars per day or about 474 billion dollars per year on crude oil⁵ (about 4% of the GDP). About a half of the oil is used to produce gasoline. Currently, the US consumes 320,500,000 gallon of gasoline per day.⁶ At the current national average of \$2.55/gallon, the daily gasoline expense is estimated to be 820 million dollars. In March 2004, the total trade deficit was about \$46 billion for the month, and oil imports accounted for \$13.2 billion or a quarter of the total trade deficit for the month.

0.2 Problems Associated with Fossil Fuel Combustion

There are several problems associated with fossil fuel combustion. Combustion of fossil fuels is responsible for a large range of air pollution problems, including acid rain and photochemical smog. The emission of CO₂, as an inevitable outcome of fossil fuel combustion, is thought to be leading to global warming. Indeed the level of CO₂ in the atmosphere has risen about 25% since the beginning of industrial revolution.

The enormous rate of energy consumption is undesirable since oil is a scarce natural resource which will eventually be exhausted. The US Department of Energy estimates that the known world oil reserve is at 1.28 trillion barrels.⁷ The daily demand is 82.5 million barrels, which is to rise to 84.2 and 86 million barrels per day in 2005 and 2006. Using the 2006 consumption rate (i.e., assume 0% economical growth), the world reserve can only run for about 30 years. Clearly, the US and world economy will be significantly impacted long before the oil resources is depleted, because of rising oil prices.

It is for these reasons that combustion remains to be both the solution and problem of economical development. The recent push on alternative and renewable energy will provide some relieve to the problems but by and large increasing combustion efficiency and lowering pollutant emission will continue to drive the future of our economy.

0.3 Combustion – A Tradition of Innovation

Advances in combustion science and technology over the last quarter of century are enormous, but these advances are perhaps overshadowed recently by other more visible

⁵ <http://www.gravmag.com/oil.html#highcost>.

⁶ <http://www.eia.doe.gov/neic/a-z/petroleuma-z.htm>.

⁷ <http://www.eia.doe.gov/emeu/international/petroleu.html>.

advances, including computer and information technology. We now mention very little the success of nation's space technology, where the foundation of this technology is based on combustion. Meanwhile, combustion engine efficiency has risen dramatically over the last twenty years, and emission levels have decreased by more than an order of magnitude. The increase of fuel economy would have a notable impact on our fuel consumption if it wasn't because of consumers' desire for bigger and heavier cars, SUVs, and trucks.

To continue the tradition of scientific and technological innovations, one is to realize that the subsequent combustion improvements will require a detailed knowledge of combustion processes. Improvements will come often by large scale computer simulations that consider both fluid transport and mixing, and chemical reactions that lead to fuel oxidation as well as pollutant formation. Over the last decade, most automobile and engine companies have relied heavily on computer simulation to design engines and optimize its performance, and to reduce the cost associated with engine design.

A basic understanding of the chemistry and physics of combustion is critical to these design tools as it defines the underlying physical processes and provides necessary model parameters. Because of the underlying complexity of combustion processes (e.g., highly non-linear response to changes in boundary conditions), these parameters will have to be determined from a fundamental approach as empirical approaches usually do not work for highly nonlinear processes.

This course is designed to provide the students with a basic knowledge and application of thermodynamics, chemical kinetics, and transport theories as applied to combustion design and analysis. Details of the course topics are described in the section that follows.

0.4 Course Description

This course introduces

- the fundamental and application of combustion chemistry;
- transport processes and properties in chemically reacting flows;
- topics of combustion chemistry include:
 - the explosion limits of hydrogen and hydrocarbons,
 - cool flames,
 - reaction mechanisms of hydrocarbon fuel combustion and pollutant formation,
 - surface chemistry and catalytic combustion,
 - theories and methods of thermochemical kinetics
 - Benson's group additivity method
 - the basics of quantum chemistry calculation
 - transition state theory
 - Rice-Ramsperger-Kassel-Markus theory, and solution of the master equation of collision energy transfer.
 - transport theory and properties
 - the Chapman-Enskog theory and its applications
 - particle transport in reacting flows.

- concepts and application of detailed kinetic modeling of laminar reacting flows

Course objectives include

- (1) To develop a basic understanding of the fundamental chemistry related to various combustion phenomena;
- (2) To understand the role of transport processes in laminar combustion;
- (3) To develop the basic skills to analyze a simple combustion problem.

Reference Materials

- ***Lecture notes***
- S. W. Benson *Thermochemical Kinetics*, Second Edition, Wiley, New York, 1976.
- C. F. Curtiss and R. B. Bird *Molecular Theory of Gases and Liquids*, Wiley, New York, Wiley; 2nd corrected printing, 1964.
- Glassman *Combustion*, Academic Press, San Diego, California, 1996.
- Technical Papers and Review Articles

1. THERMOCHEMISTRY

Thermodynamics is the foundation of a large range of physical science problems. It provides us with a basic understanding about the driving force of a physical process and the limits of such a process. The development of thermodynamic theory was intimately related to combustion. In particular, the second law of thermodynamics was conceived largely to prove that a perpetual motion machine cannot exist.

1.1 Thermodynamic First Law

The first law of thermodynamics states that the energy is conserved when this energy is transformed from one form to another. In the context of combustion analysis, we state that for a control mass (or the working fluid),

$$Q - W = \Delta U \quad (1.1)$$

where Q (kJ or kcal) is the heat transferred from the working fluid to the surrounding, W (kJ or kcal) is the work done by the working fluid to the surrounding, and U (kJ or kcal) is the internal energy of the working fluid.

It is important to mention that energy transformation always involves a process that has a initial state (1) and a final state (2). $\Delta U = U_2 - U_1$ is therefore the change of internal energy of the working fluid from the initial state to the final state. Thermodynamic analysis follow the convention that if the working fluid gives off heat to the surrounding, $Q < 0$, and if the working fluid receives heat from the surrounding, Q is positive. For example, in a simple cooling process, a fluid loses its internal energy to the surrounding (i.e., lowering its temperature) and thus $\Delta U < 0$. Assuming that no work is done ($W = 0$), then $Q < 0$. Likewise, if the working fluid does net work to the surrounding, W is positive, and if the surrounding does net work to the working fluid, $W < 0$ (e.g., for adiabatic compression ($Q = 0$), the work done by the surrounding to the working fluid serves to raise the internal energy of the working fluid, since $-W = \Delta U > 0$).

The symbol U designates the internal energy of a given mass of a substance. Internal energy is a measure of the total energy of the control mass. For example, excluding nuclear energy the internal energy of air is a sum of the kinetic energy of each atom. Therefore, the internal energy can be made a material property if it is defined as the internal energy per mass, an *intensive* property, denoted here as u (kJ/kg) or \bar{u} (kJ/kmol). In this course, we shall follow the notation that *intensive properties* are expressed in lower cases.

Assuming that we are running a thermodynamic process that the only work done during the process is that associated with boundary work under a constant pressure $P_1 = P_2 = P$ (e.g., a piston work), the work done may be calculated from

$$W = \int_1^2 P dV = P(V_2 - V_1) \quad . \quad (1.2)$$

Putting Eq. (1.2) into Eq. (1.1), we have

$$Q = (U_2 + P_2 V_2) - (U_1 + P_1 V_1) \quad , \quad (1.3)$$

where V is the volume of the working fluid. In this case, the heat transferred during the process corresponds to a net change of the controlled mass in the quantity $U + PV$ between the initial and final states. We find it convenient to define a new thermodynamic property, the enthalpy

$$H = U + PV \quad , \quad (1.4a)$$

$$h = u + Pv \quad , \quad (1.4b)$$

$$\bar{h} = \bar{u} + P\bar{v} \quad . \quad (1.4c)$$

Here v and \bar{v} are the specific volumes, having the units (m^3/kg) and (m^3/kmol) respectively. Clearly, these specific volumes are related to the mass density ρ and molar density (or concentration) c , respectively, i.e., $v = 1/\rho$ and $\bar{v} = 1/c$.

In general, the internal energy u and enthalpy h depend on only two independent properties that specifying the thermodynamic state, e.g., (T, P) , (T, v) , or (P, v) . For a low-density gas like air or combustion gases, T , P , and v are related by the ideal gas law or the equation of state,

$$Pv = R'T \quad , \quad (1.5a)$$

$$P\bar{v} = R_u T \quad , \quad (1.5b)$$

where R_u is the universal gas constant (8.314 kJ/kmol-K), R' is the specific gas constant and equal to R_u/MW , and MW is the molecular weight of the substance.

For a low-density gas, the internal energy is primarily a function of T , i.e., $\bar{u} \cong \bar{u}(T)$. This relationship may be expressed by defining a constant-volume specific heat \bar{c}_v (kJ/kmol-K)

$$\bar{c}_v = \left(\frac{\partial \bar{u}}{\partial T} \right)_v \quad . \quad (1.6)$$

For an ideal gas we have $d\bar{u} = \bar{c}_v dT$. Likewise, the relationship between enthalpy and temperature may be established by defining a constant-pressure specific heat \bar{c}_p (kJ/kmol-K)

$$\bar{c}_p = \left(\frac{\partial \bar{h}}{\partial T} \right)_p \quad , \quad (1.7)$$

and $d\bar{h} = \bar{c}_p dT$. In other words, the two specific heats defined above characterize the heat required to raise the temperature of a substance by 1 K. Since for an ideal gas $d\bar{h} = d\bar{u} + d(p\bar{v}) = d\bar{u} + R_u dT$ and $\bar{u} \cong \bar{u}(T)$, we see that \bar{h} and \bar{c}_p are also function of temperature only. The relation between $d\bar{h}$ and $d\bar{u}$ also yields $\bar{c}_p = \bar{c}_v + R_u$.

Here it is important to note that the enthalpy discussed thus far involves only the heating or cooling a substance. This type of enthalpy is known as the *sensible* enthalpy or *sensible* heat. Later, we will introduce two other types of enthalpy, one of which is critical to combustion problems.

The first law of thermodynamics is quite insufficient to describe energy conversion. Equation (1.1) states that it is possible to cool a substance of a given mass spontaneously (i.e., lowering its internal energy U), and transfer this energy to the surrounding. In other words, within the first law of thermodynamics, it is possible to transform heat from a low-temperature body to a high temperature body. We know that this cannot be true. The second law of thermodynamics, to be discussed below, will address this problem.

1.2 Thermodynamic Second Law and Entropy

In contrast to the first law of thermodynamics, the second law is more difficult to understand. The Kelvin-Planck statement of this law is *It is impossible to construct a device that will operate in a cycle and produce no effect other than the raising of a weight and the exchange of heat with a single reservoir*. In other words, it is impossible to construct a heat engine that (a) receives heat continuously from a heat reservoir, (b) turns the heat transferred entirely to work, (c) without having to leave any marks on the surrounding. Without diverging into a lengthy discussion of the second law of thermodynamics, let us define entropy S (kJ/K) as

$$S = \left(\frac{\delta Q}{T} \right)_{\text{int rev}} . \quad (1.8)$$

where $(\delta Q)_{\text{int rev}}$ is the heat a control mass received during an infinitesimal, internally reversible process. Based on an analysis of thermodynamic cycles, it may be shown that for a spontaneous process to occur, the entropy of the control mass must be equal to or greater than zero,

$$\Delta S = S_2 - S_1 \geq 0. \quad (1.9)$$

Neither the Kelvin-Planck statement nor Eq. (1.8) really tells us what entropy is. An understanding of entropy will have to come sometime later when we introduce statistical thermodynamics. Here let us place some discussion about entropy in a non-rigorous fashion. Entropy is a measure of *molecular randomness*. This randomness may be measured by the predictability of the positions of atoms in a substance. A crystal material would have a small entropy because atoms are more or less “locked” into the crystal lattice. In fact, the third law of thermodynamics states that the entropy of a pure crystalline substance at absolute

zero temperature is zero. In other words, the atoms in a pure crystal are “frozen” (no oscillation) at 0 K. Therefore, their spatial position is completely predictive. In contrast, a gas would have a large entropy because molecules that make up the gas constantly move about in the space, resulting in small predictability regarding their positions. Moreover, an increase in temperature of the gas leads an increase in the speed of molecular motion and smaller predictability of the molecular positions. In other words, entropy increases with an increase in temperature. In contrast, an increase in pressure leads to closer spacing among molecules. As a result, the molecules become more confined spatially and the entropy is smaller at higher pressures. The dissociation of a chemical substance into gaseous fragments always leads to an increase in entropy since it is harder to predict the spatial positions of the fragments than the molecules of their parent substance.

The inequality expressed by Eq. (1.9) basically says that for a spontaneous process to occur, the entropy of the control volume must increase, i.e., natural processes favor more randomness than orderness. Conceptually this makes sense since our experience tells us that a building can spontaneously collapse into a pile of rubble, but a pile of rubble would not spontaneously transform into a building (not without our intervention). Two different gases, say, N_2 and O_2 , would always mix and they never spontaneously separate spatially, leading to better predictability of their positions.

The concept of entropy is also deeply rooted in our life. Take the life of a workaholic as an example, the first law of thermodynamics states that it is possible for him/her to receive heat Q in the form of food and hopefully without gaining weight ($\Delta U = 0$), to transform this heat entirely to work W . The second law says that he/she really cannot do this. That is, my office always gets messier over time and I will need to clean it (i.e., not all the heat goes to useful work) as time goes by.

Because entropy is a measure of randomness, which in turn, is determined by T and P , it is also a material property. It follows that we can define and denote the entropy of a substance by s (kJ/kg-K) or \bar{s} (kJ/kmol-K). Although we do not know for the time being how to directly measure entropy, we may develop some relationships that can help us to determine the entropy value. Here we apply the first law to a constant T and P , internally reversible process (e.g., compress a volume immersed in a temperature bath by a piston very slowly),

$$\delta Q_{\text{int rev}} - \delta W_{\text{int rev}} = dU, \quad (1.10)$$

but since $\delta Q_{\text{int rev}} = TdS$ and $\delta W_{\text{int rev}} = PdV$, we have

$$TdS = dU + PdV \quad (1.11)$$

or

$$d\bar{s} = \frac{d\bar{u}}{T} + \frac{Pd\bar{v}}{T} = \bar{c}_v \frac{dT}{T} + \frac{Pd\bar{v}}{T} . \quad (1.12)$$

Replacing \bar{u} by $\bar{h} - T\bar{s}$ and rearranging, we obtain

$$d\bar{s} = \frac{d\bar{h}}{T} - \frac{\bar{v}dP}{T} = \bar{c}_p \frac{dT}{T} - \frac{\bar{v}dP}{T} . \quad (1.13)$$

Applying the ideal gas law, we may rewrite equations (12) and (13) as

$$d\bar{s} = \bar{c}_v \frac{dT}{T} + R_u \frac{d\bar{v}}{\bar{v}} , \quad (1.14)$$

$$d\bar{s} = \bar{c}_p \frac{dT}{T} - R_u \frac{dP}{P} . \quad (1.15)$$

One may integrate the above equations to show that

$$\Delta\bar{s} = \bar{s}_2 - \bar{s}_1 = \int_1^2 \bar{c}_p \frac{dT}{T} + R_u \ln \frac{\bar{v}_2}{\bar{v}_1} , \quad (1.16)$$

$$\Delta\bar{s} = \bar{s}_2 - \bar{s}_1 = \int_1^2 \bar{c}_p \frac{dT}{T} - R_u \ln \frac{P_2}{P_1} . \quad (1.17)$$

Equation (1.17) states that if \bar{c}_p is a constant, an increase of temperature by ΔT from T causes the entropy to increase by $\bar{c}_p \ln(1 + \Delta T/T)$ and an increase of pressure by ΔP from P leads to the entropy to decrease by $R_u \ln(1 + \Delta P/P)$. Given the third law of thermodynamics, which establish the absolute zero for entropy, the entropy of an ideal gas at a given thermodynamic state (i.e., known T and P) can be easily determined if \bar{c}_p is known.

Equation (1.17) also states that unlike enthalpy and internal energy, the entropy of an ideal gas is a function of both temperature and pressure. In application, we define the *standard* entropy \bar{s}° as

$$\Delta\bar{s}^\circ = \bar{s}_2^\circ - \bar{s}_1^\circ = \int_1^2 \bar{c}_p \frac{dT}{T} = \left[\int_0^{T_2} \bar{c}_p \frac{dT}{T} - R_u \ln(P^\circ) \right] - \left[\int_0^{T_1} \bar{c}_p \frac{dT}{T} - R_u \ln(P^\circ) \right] , \quad (1.18)$$

or

$$\bar{s}^\circ = \int_0^T \bar{c}_p \frac{dT}{T} - R_u \ln(P^\circ) , \quad (1.19a)$$

where P° is the standard pressure of 1 atm. Hence,

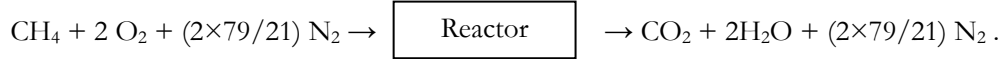
$$\Delta\bar{s}^\circ = \int_0^T \bar{c}_p \frac{dT}{T} , \quad (1.19b)$$

By tabulating this standard entropy, we may easily determine the entropy change of an ideal gas under an arbitrary condition by

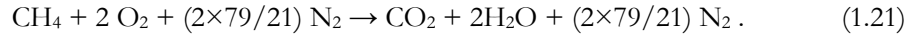
$$\bar{s}(T, P) = \bar{s}^\circ(T) - R_u \ln \frac{P}{P^\circ} . \quad (1.20)$$

1.3 Chemical Reactions

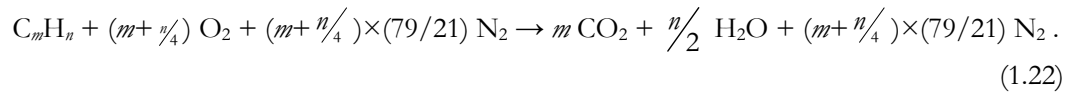
Before we apply the above thermodynamic principles to combustion analysis, we need to take a moment to review a few aspects of chemical reactions. From a process point of view, a chemical reaction may be viewed as the conversion of reactants that enter into a reactor (the initial state) to products that leaves the reactor (the final state). For example, methane (CH_4) flows into a reactor with air (21% O_2 and 79% N_2). Suppose the molar ratio of oxygen to methane is 2-to-1. We may write that to burn 1 mole of methane,



Here the products include 1 mole CO_2 , 2 moles of H_2O and $(2 \times 79/21)$ moles of N_2 . Of course, in writing the above process reaction, we may neglect the box and simply write



The above reaction is known as the *complete combustion* reaction as all the carbon in the fuel is oxidized to CO_2 and all the hydrogen is converted to H_2O . These compounds are called the complete combustion products. If there is no excess oxygen (i.e., all oxygen is consumed in the oxidation process), the characteristic fuel-to-oxygen molar ratio is known as the stoichiometric ratio (equal to $1/2$ for methane). The stoichiometric ratio for an arbitrary fuel C_mH_n may be readily determined by writing out the complete, stoichiometric reaction,



which gives the stoichiometric ratio equal to $1/(m + n/4)$.

In a practical combustion process, however, the fuel-to-oxygen molar ratio needs not to be the stoichiometric ratio. For example, a gasoline engine often runs slightly above the stoichiometric ratio at the cold start, for reasons to be discussed later. To characterize fuel-to-oxygen ratio in a practical combustion process, we introduce the equivalence ratio, defined as the molar ratio of fuel-to-oxygen for an actual combustion process by that of stoichiometric combustion:

$$\phi = \frac{(\text{moles of fuel/moles of oxygen})_{\text{act.}}}{(\text{moles of fuel/moles of oxygen})_{\text{stoi}}} . \quad (1.23)$$

Of course, it may be shown that the equivalence ratio may be calculated using the molar ratio of fuel-to-air or the mass ratio of fuel-to-oxygen or fuel-to-air.

By examining the equivalence ratio, we can quickly tell the nature of the fuel/air mixture. That is, if $\phi = 1$, we have stoichiometric reaction; if $\phi < 1$ we have excess oxygen that is not completely used in a reaction process and the combustion is called fuel-lean combustion; if $\phi > 1$ we have excess fuel and the combustion is called fuel-rich combustion.

$$\phi = \begin{cases} < 1 & \text{fuel lean} \\ 1 & \text{stoichiometric} \\ > 1 & \text{fuel rich} \end{cases}$$

Under the fuel rich combustion, the combustion reaction inherently yields incomplete combustion products, like CO, H₂ etc.

1.4 Enthalpy of Formation, Enthalpy of Combustion

As we discussed in section 1.1, there are 3 types of enthalpy. The first type is associated with heating or cooling of a substance. The second type is latent enthalpy (or heat). This is the enthalpy associated with the phase change of a substance. For example, the latent heat of evaporation of H₂O, \bar{h}_{lg} , is

$$\bar{h}_{lg} = \bar{h}_g - \bar{h}_l, \quad (1.24)$$

where \bar{h}_g and \bar{h}_l are the enthalpy of water in its vapor and liquid states, respectively. What is perhaps more important to combustion analysis is the reaction enthalpy. For example, reaction (21) releases an amount of heat due to chemical bond rearrangements. Combining Eqs (1.3) and (1.4a), we have

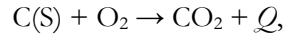
$$\mathcal{Q} = H_2 - H_1.$$

Since state 1 corresponds to the reactants, and state 2 corresponds the products, the above equation states that (a) in a non-adiabatic reactor, the heat released from the reactor is equal to the total enthalpy of the combustion products subtracted by the total enthalpy of the reactant, and (b) since for a combustion process $\mathcal{Q} < 0$, $H_2 < H_1$, i.e., the total enthalpy of the products is lower than that of the reactants.

The nature of reaction enthalpy is very different from the sensible enthalpy, as the former is due to re-arranging chemical bonds and the latter is simply due to heat and cooling without changing the chemical nature of the substance. To calculate the exact amount of reaction enthalpy and therefore the amount of heat release, we need to first understand the concept and application of enthalpy of formation.

The enthalpy of formation \bar{h}_f° at a given temperature is defined as the heat released from producing 1 mole of a substance from its elements at that temperature. These elements are, for example, graphite [denoted by C(S) hereafter], molecular hydrogen H₂, molecular oxygen (O₂), molecular nitrogen (N₂), and molecular chlorine (Cl₂). By this definition, the enthalpy of formation is zero for the reference elements.

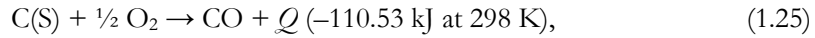
The enthalpy of formation of CO₂, say at 298 K, may be conceptually measured by reacting 1 mole of graphite and 1 mole of O₂ at 298 K, producing 1 mole of CO₂ at the same temperature:



where Q is the heat released from the above process ($Q = -393.522$ kJ). Using Eq. (1.24), we have

$$\begin{aligned} Q = -393.522 \text{ (kJ)} &= H_2 - H_1 = 1 \times \bar{h}_{f,298\text{K}}(\text{CO}_2) - 1 \times [\bar{h}_{f,298\text{K}}(\text{C(S)}) + \bar{h}_{f,298\text{K}}(\text{O}_2)] \\ &= \bar{h}_{f,298\text{K}}(\text{CO}_2) \end{aligned}$$

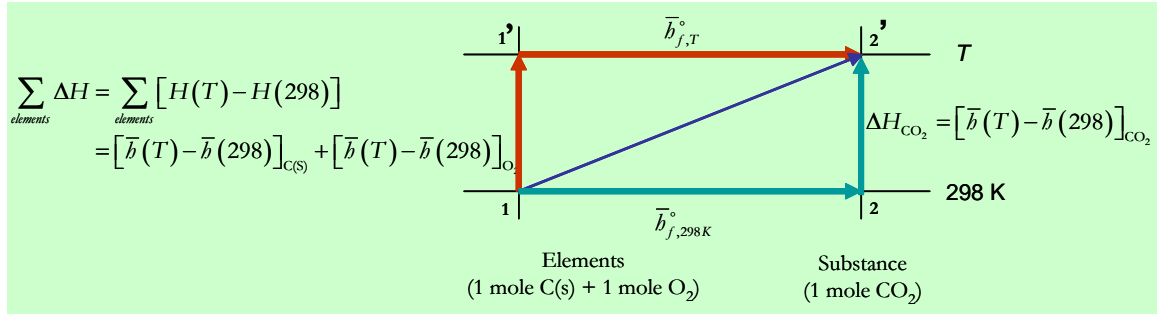
The enthalpy of formation of CO₂ is therefore $\bar{h}_f^\circ = -393.522$ kJ/mol at 298 K. Likewise the enthalpy of formation of CO is determined by measuring the heat release from



and $\bar{h}_f^\circ(\text{CO}) = -110.53$ kJ/mol at 298 K.

The conceptual definition uses the same temperature for the reactor, reactants, and products, and this condition is known as the standard condition. *For this reason, we use a superscript "o", i.e., \bar{h}_f° , to designate this standard condition* and the corresponding enthalpy of formation is termed as the *standard enthalpy of formation*.

Obviously if reaction (25) is carried out at a different temperature under the standard condition, we do not necessarily get the same heat release. In other words, the enthalpy of formation is dependent on temperature, yet this temperature dependence is related to sensible heat. To illustrate the relationship of enthalpy of formation of a substance at two different temperatures, we sketch the following diagram :



Recognizing that enthalpy is a state function, i.e., for an ideal gas the enthalpy of a substance is fully defined if the temperature is known, and the change of enthalpy for a process is independent of the path, we may write

$$\begin{aligned} H_{2'} - H_1 &= H_{2'} - H_2 + (H_2 - H_1) = [\bar{h}(T) - \bar{h}(298)]_{CO_2} + \bar{h}_{f,298}^{\circ}(CO_2) \\ &= H_{2'} - H_{1'} + (H_{1'} - H_1) = \bar{h}_{f,T}^{\circ}(CO_2) + [\bar{h}(T) - \bar{h}(298)]_{C(s)} + [\bar{h}(T) - \bar{h}(298)]_{O_2} \end{aligned}$$

It follows that

$$\begin{aligned} \bar{h}_{f,T}^{\circ}(CO_2) &= \bar{h}_{f,298}^{\circ}(CO_2) + [\bar{h}(T) - \bar{h}(298)]_{CO_2} \\ &\quad - \left\{ [\bar{h}(T) - \bar{h}(298)]_{C(s)} + [\bar{h}(T) - \bar{h}(298)]_{O_2} \right\} \end{aligned}$$

which may be generalized to

$$\bar{h}_{f,T}^{\circ} = \bar{h}_{f,298}^{\circ} + [\bar{h}(T) - \bar{h}(298)]_{\text{substance}} - \sum_{\text{elements}} \nu_i [\bar{h}(T) - \bar{h}(298)]_i, \quad (1.25a)$$

where ν_i is the stoichiometric coefficients of the i^{th} elements in the reaction that forms the substance. Therefore if the specific heat or sensible enthalpy of a substance is known, we only need to know the value of enthalpy of formation at a particular temperature, and in general this temperature is equal to 298 K .

In combustion analysis, we often group the first and second term of Eq. (1.25a) by defining a *total enthalpy* as

$$\bar{h}_T^{\circ} \equiv \bar{h}_{f,298}^{\circ} + [\bar{h}(T) - \bar{h}(298)]_{\text{substance}}, \quad (1.25b)$$

and

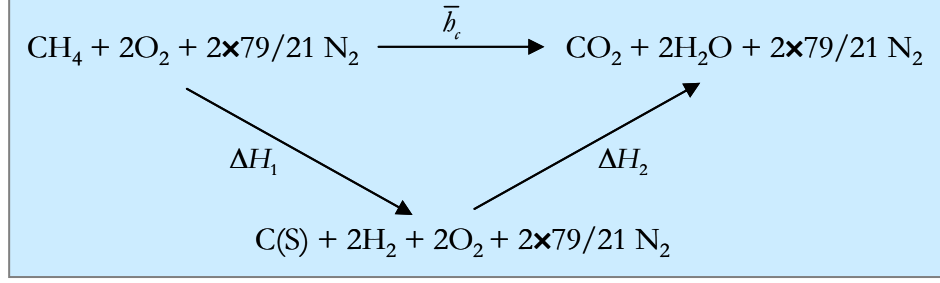
$$\bar{h}_{f,T}^{\circ} = \bar{h}_T^{\circ} - \sum_{\text{elements}} \nu_i [\bar{h}(T) - \bar{h}(298)]_i. \quad (1.25c)$$

Table 1.2 lists the enthalpy of formation of some important species for combustion analysis.

Table 1.2 Standard enthalpy of formation of key combustion species in the vapor state

Species	Name	$\bar{h}_{f,298}^{\circ}$ (kJ/mol)
H ₂ O	Water	-241.8
CO	Carbon monoxide	-110.5
CO ₂	Carbon dioxide	-393.5
CH ₄	Methane	-74.9
C ₂ H ₆	Ethane	-84.8
C ₃ H ₈	Propane	-104.7
C ₄ H ₁₀	Butane	-125.6
C ₈ H ₁₈	Octane	-208.4
C ₂ H ₄	Ethylene	52.5
C ₂ H ₂	Acetylene	226.7
CH ₃ OH	Methanol	-201.0
C ₆ H ₆	Benzene	82.9
H•	Hydrogen atom	218.0
O•	Oxygen atom	248.2
OH•	Hydroxyl radical	39.0

The *standard enthalpy of combustion* \bar{h}_c (kJ/mol-fuel) is defined as the heat released from the complete combustion of 1 mole of fuel at 298 K. Consider the complete combustion of methane (Eq. 1.21). We will again utilize the path independent property to illustrate that \bar{h}_c may be determined by the sum of enthalpy of formation of the products (multiplied by the molar ratio of the product-to-fuel) subtracted by the sum of enthalpy of formation of the reactants:



$$\bar{h}_c(\text{kJ/kmol-fuel}) = \Delta H_1 + \Delta H_2 = -1 \times \bar{h}_{f,298}^\circ(\text{CH}_4) + 1 \times \bar{h}_{f,298}^\circ(\text{CO}_2) + 2 \times \bar{h}_{f,298}^\circ(\text{H}_2\text{O}).$$

For an arbitrary fuel (C_mH_n) undergoing combustion (1.22), we determine its enthalpy of combustion as

$$\bar{h}_c(\text{kJ/kmol-fuel}) = m \times \bar{h}_{f,298}^\circ(\text{CO}_2) + \frac{n}{4} \times \bar{h}_{f,298}^\circ(\text{H}_2\text{O}) - \bar{h}_{f,298}^\circ(C_mH_n).$$

In addition, for an arbitrary reaction given by



where A_i and A_i' are the i^{th} reactants and products, respectively, and ν_i are termed as the stoichiometric coefficients, we determine the enthalpy of reaction at an arbitrary temperature T by

$$\begin{aligned} \Delta H_{r,T}^\circ &= \sum_{\text{prod.}} \nu_i' \bar{h}_T(A_i') - \sum_{\text{react.}} \nu_i \bar{h}_T(A_i) \\ &= \sum_{\text{prod.}} \nu_i' \bar{h}_{f,298}^\circ(A_i') - \sum_{\text{react.}} \nu_i \bar{h}_{f,298}^\circ(A_i) + \left\{ \sum_{\text{prod.}} \nu_i' [\bar{h}(T) - \bar{h}(298)]_{i'} - \sum_{\text{react.}} \nu_i [\bar{h}(T) - \bar{h}(298)]_i \right\} \\ &= \Delta H_{r,298}^\circ + \left\{ \sum_{\text{prod.}} \nu_i' [\bar{h}(T) - \bar{h}(298)]_{i'} - \sum_{\text{react.}} \nu_i [\bar{h}(T) - \bar{h}(298)]_i \right\} \end{aligned}$$

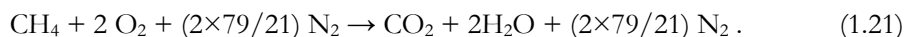
Since the total numbers of the elements in the reactants and products are identical, the sensible enthalpy terms for the elements in Eq. (1.25c) are canceled out. If $\Delta H_{r,T}^\circ$ is positive, the reaction absorbs heat. This type of reactions is known to be *endothermic*.

If $\Delta H_{r,T}^\circ < 0$, the reaction releases heat as it proceeds to completion. This type of reactions is known to be *exothermic*. Conversely, If $\Delta H_{r,T}^\circ > 0$, the reaction requires heat to achieve completion. This type of reactions is known to be *endothermic*.

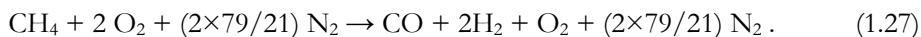
1.5 Chemical Equilibrium

The complete combustion reactions given by Eqs. (1.21) and (1.22) essentially correspond to maximum heat release. That is, if products other than CO_2 and H_2O are formed, the enthalpy of reaction will be decidedly lower. In practical combustion processes, a combustion reaction can never reach completion. Rather the products of combustion will acquire the state of *chemical equilibrium*. Although often than not the products will be dominated by the complete combustion products, incomplete combustion products (CO , H_2 , soot, NO etc) are inherent to a combustion process.

Our experience tells us that a process or reaction would be spontaneous if it releases heat. For example, the combustion of methane spontaneously produces CO_2 and H_2O ($\Delta H_{r,298}^\circ < 0$), but a mixture of CO_2 and H_2O would not spontaneously react and produce methane and O_2 . On the other hand, the entropy of 1 mole of CO_2 is decidedly smaller than the entropy for a mixture made of 1 mole of CO and 0.5 mole of O_2 . Likewise the entropy of 1 mole of H_2O is smaller than the entropy for a mixture made of 1 mole of H_2 and 0.5 mole of O_2 . Therefore it may be said that reaction (1.21)

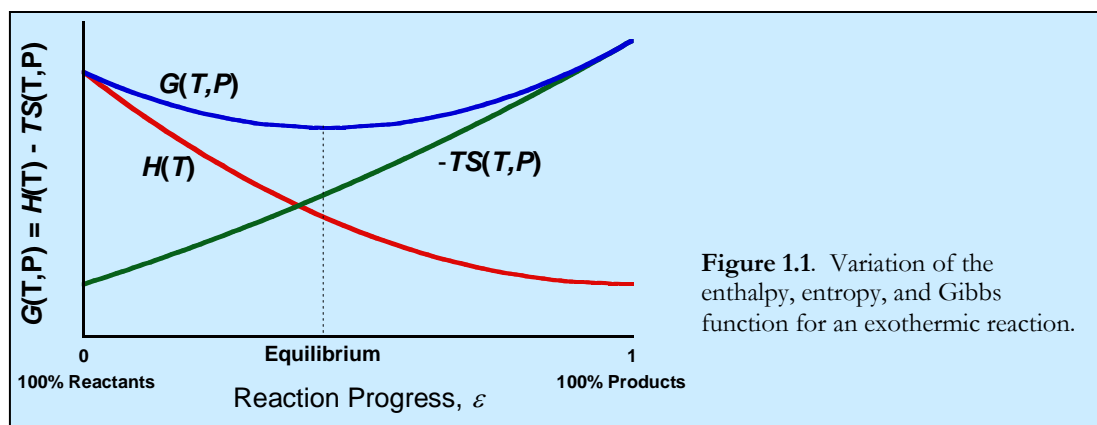


produces the largest heat but with a smaller entropy change, whereas reaction (1.27) produces less heat but with a larger change of entropy upon reaction:



We learned from the second law of thermodynamics that without heat release or absorption, a spontaneous process will proceed in the direction to increase entropy. Therefore a compromise between enthalpy and entropy releases must be made.

This compromise is responsible for chemical equilibrium. It may be quantified by the Gibbs function or Gibbs free energy,



$$G \equiv H - TS , \quad (1.28a)$$

$$g \equiv h - Ts , \quad (1.28b)$$

$$\bar{g} \equiv \bar{h} - T\bar{s} , \quad (1.28c)$$

Figure 1.1 shows a possible scenario for variation of the enthalpy, entropy times temperature, Gibbs function for an exothermic reaction as it progresses to completion at a given T and P . We define here a reaction progress variable ε , such that $\varepsilon = 0$ for pure reactants and $\varepsilon = 1$ for pure products. If the reaction is exothermic, the total enthalpy of the reacting gases (reactants and products) decreases as ε increases. Here the spontaneous release of chemical energy is driving the reaction towards completion.

If the reaction is accompanied by a decrease in the entropy (e.g., $\text{H}_2 + 1/2\text{O}_2 \rightarrow \text{H}_2\text{O}$), the $-TS(T,P)$ function would monotonically increase as reaction progresses. This entropy reduction gives resistance towards the completion of reaction. Overall the Gibbs function must decrease initially, but because of the rise of the $-TS$ term, it eventually will have to go up as ε increases. In other words, the Gibbs function must reach a minimum at some point. The definition of chemical equilibrium is therefore

$$\frac{dG(T,P)}{d\varepsilon} = 0 , \quad (1.29a)$$

or simply

$$dG(T,P) = 0 . \quad (1.29b)$$

Again, the above equilibrium criterion represents a compromise of H and $-ST$, since both of them prefer to minimize themselves. Therefore, the driving force of chemical reaction lies in the minimization of the Gibbs function.

Now let us consider an arbitrary reaction given by Eq. (1.26). The Gibbs function of the reacting gas may be written as

$$G(T,P) = \sum_{\text{react.}} n_i \bar{g}_i(T,P) + \sum_{\text{prod.}} n_{i'} \bar{g}_{i'}(T,P) , \quad (1.30)$$

where n_i is the molar number of the i^{th} species. Putting Eq. (1.30) into (1.29a), we obtain, for constant T and P ,

$$\frac{dG(T,P)}{d\varepsilon} = \sum_{\text{react.}} \bar{g}_i(T,P) \frac{dn_i}{d\varepsilon} + \sum_{\text{prod.}} \bar{g}_{i'}(T,P) \frac{dn_{i'}}{d\varepsilon} = 0 , \quad (1.31)$$

Conservation of mass requires that

$$-\frac{1}{\nu_1} \frac{dn_1}{d\varepsilon} = -\frac{1}{\nu_2} \frac{dn_2}{d\varepsilon} \dots = -\frac{1}{\nu_n} \frac{dn_N}{d\varepsilon} = \frac{1}{\nu_{1'}} \frac{dn_{1'}}{d\varepsilon} = \frac{1}{\nu_{2'}} \frac{dn_{2'}}{d\varepsilon} = \frac{1}{\nu_{n'}} \frac{dn_{N'}}{d\varepsilon} = \gamma(\varepsilon), \quad (1.32)$$

where N and N' are the total numbers of reactants and products, respectively, and $\gamma(\varepsilon)$ is a function that depends only on ε . Combining equations (1.31) and (1.32), we obtain

$$\gamma(\varepsilon) \left[-\sum_{\text{react.}} \nu_i \bar{g}_i(T, P) + \sum_{\text{prod.}} \nu_{i'} \bar{g}_{i'}(T, P) \right] = 0. \quad (1.33)$$

Since $\gamma(\varepsilon) \neq 0$, we see that equilibrium state is given by

$$-\sum_{\text{react.}} \nu_i \bar{g}_i(T, P) + \sum_{\text{prod.}} \nu_{i'} \bar{g}_{i'}(T, P) = 0. \quad (1.34)$$

The function \bar{g}_i is the Gibbs function of species i , which may be expressed by

$$\bar{g}_i(T, P) = \bar{h}_f^\circ(T) - T\bar{s}_i(T) = \bar{h}_f^\circ(T) - T \left[\bar{s}_i^\circ(T) - R_u \ln \left(\frac{P}{P^\circ} \right) \right]. \quad (1.35)$$

We now define a standard Gibbs function $\bar{g}^\circ(T, P^\circ = 1 \text{ atm})$ as

$$\bar{g}^\circ(T) = \bar{h}_f^\circ(T) - T\bar{s}_i^\circ(T), \quad (1.36)$$

and re-write Eq. (1.35) as

$$\bar{g}_i(T, P) = \bar{g}^\circ(T) + R_u T \ln \left(\frac{P}{P^\circ} \right). \quad (1.37)$$

Putting Eq. (1.37) into (1.34) and rearranging, we have

$$\sum_{\text{prod.}} \nu_{i'} \bar{g}_{i'}^\circ(T) - \sum_{\text{react.}} \nu_i \bar{g}_i^\circ(T) = -R_u T \left[\sum_{\text{prod.}} \nu_{i'} \ln \left(\frac{P_{i'}}{P^\circ} \right) - \sum_{\text{react.}} \nu_i \ln \left(\frac{P_i}{P^\circ} \right) \right], \quad (1.38)$$

where P_i is the partial pressure of species i , and of course, $P^\circ = 1 \text{ atm}$. The left-hand side of the above equation may be defined as the standard Gibbs function change of reaction,

$$\Delta G_r^\circ(T) \equiv \sum_{\text{prod.}} \nu_{i'} \bar{g}_{i'}^\circ(T) - \sum_{\text{react.}} \nu_i \bar{g}_i^\circ(T) \quad (1.39)$$

The right-hand side of Eq. (1.38) may be re-arranged to yield

$$\Delta G_r^\circ(T) = -R_u T \ln \left(\frac{\prod_{\text{prod.}} P_{i'}^{\nu_{i'}}}{\prod_{\text{react.}} P_i^{\nu_i}} \right). \quad (1.40)$$

or

$$K_p(T) \equiv \frac{\prod_{\text{prod.}} P_{i'}^{\nu_{i'}}}{\prod_{\text{react.}} P_i^{\nu_i}} = \exp \left[-\frac{\Delta G_r^\circ(T)}{R_u T} \right]. \quad (1.41)$$

where $K_p(T)$ is the *equilibrium constant* of the reaction. Note that by neglecting P° in Eqs. (1.40) and (1.41), we have forced P_i to take the unit of atm.

The equilibrium constant may also be defined by the concentrations of the reactants and products,

$$K_c(T) \equiv \frac{\prod_{\text{prod.}} c_{i'}^{\nu_{i'}}}{\prod_{\text{react.}} c_i^{\nu_i}} = \frac{\prod_{\text{prod.}} P_{i'}^{\nu_{i'}}}{\prod_{\text{react.}} P_i^{\nu_i}} (R_u T)^{-\Delta \nu} = K_p(T) (R_u T)^{-\Delta \nu}, \quad (1.42)$$

where

$$\Delta \nu = \sum_{\text{prod.}} \nu_{i'} - \sum_{\text{react.}} \nu_i.$$

There are several important facts about the equilibrium constant.

(a) While K_p is defined as the pressure ratio of the products and reactants (Eq. 1.41), this equilibrium constant is a function of temperature only.

(b) Consider the reaction



The equilibrium constant for the forward direction of the reaction is

$$K_{p,f}(T) = \frac{P_{\text{H}_2} P_{\text{O}_2}^{1/2}}{P_{\text{H}_2\text{O}}}.$$

We may also write the reaction in the back direction,



and its equilibrium constant

$$K_{p,b}(T) = \frac{P_{\text{H}_2\text{O}}}{P_{\text{H}_2} P_{\text{O}_2}^{1/2}} .$$

Obviously,

$$K_{p,f}(T) = \frac{1}{K_{p,b}(T)} .$$

(c) Reaction (43f) may be written alternatively as



with its equilibrium constant

$$K'_{p,f}(T) = \frac{P_{\text{H}_2}^2 P_{\text{O}_2}}{P_{\text{H}_2\text{O}}^2} .$$

Comparing the equilibrium constants for the two forward reactions, we see that

$$K'_{p,f}(T) = [K_{p,f}(T)]^2 .$$

(d) Consider the following two reactions



(where the \bullet denotes that the species is a *free radical*). We have

$$K_{p,44f}(T) = \frac{P_{\text{H}\bullet}^2}{P_{\text{H}_2}} \quad \text{and} \quad K_{p,45f}(T) = \frac{P_{\text{H}\bullet} P_{\text{OH}\bullet}}{P_{\text{H}_2\text{O}}} .$$

A linear combination of reactions (43f-45f) yield



A little algebra tells us that

$$K_{p,46f}(T) = \frac{K_{p,45f}(T)}{\sqrt{K_{p,44f}(T)}} .$$

- (e) While K_p is not a function of pressure, K_c generally is dependent on pressure so long as $\Delta \nu \neq 0$. On the other hand, if $\Delta \nu = 0$, $K_c(T) = K_p(T)$.
- (f) The equilibrium constant of a given reaction may be determined if the enthalpy of formation and the entropy of reactants and products are known through Eqs. (1.36), (1.39) and (1.41).
- (g) The definition of K_p tells us that the reaction would be more complete if K_p is larger. A larger K_p may be accomplished with a larger, negative $\Delta G_r^\circ(T)$. Combining Eqs. (1.36) and (39), we see that

$$\begin{aligned}\Delta G_r^\circ(T) &\equiv \left[\sum_{\text{prod.}} \nu_i \bar{b}_{f,i}^\circ(T) - \sum_{\text{react.}} \nu_i \bar{b}_{f,i}^\circ(T) \right] - T \left[\sum_{\text{prod.}} \nu_i \bar{s}_i^\circ(T) - \sum_{\text{react.}} \nu_i \bar{s}_i^\circ(T) \right], \\ &= \Delta H_r^\circ(T) - T \Delta S_r^\circ(T)\end{aligned}\quad (1.47)$$

where $\Delta S_r^\circ(T)$ is termed as the entropy of reaction. Therefore a large, negative $\Delta H_r^\circ(T)$ (reaction being highly exothermic) favors a large K_p , whereas a large, positive $\Delta S_r^\circ(T)$ (reaction creating a large amount of entropy) also favors a large K_p or promotes the completion of the reaction.

1.6 Adiabatic Flame Temperature

With the concepts of chemical equilibrium understood, we may now try to calculate the equilibrium composition of a combustion reaction. In doing so, we wish to define the adiabatic flame temperature. Consider an adiabatic combustion process whereby the reactants enter into a combustor at temperature T_0 , and products exit the combustor at the adiabatic flame temperature T_{ad} . Since the process is adiabatic ($Q = 0$), we have

$$H_{\text{prod.}}(T_{ad}) - H_{\text{react.}}(T_0) = 0. \quad (1.48)$$

We now expand Eq. (1.48) using the total enthalpy equation for each species (Eq. 1.25b),

$$\begin{aligned}\sum_{\text{prod.}} \nu_i \bar{b}_{T_{ad},i} - \sum_{\text{react.}} \nu_i \bar{b}_{T_0,i} &= \left[\sum_{\text{prod.}} \nu_i \bar{b}_{f,298,i}^\circ - \sum_{\text{react.}} \nu_i \bar{b}_{f,298,i}^\circ \right] + \sum_{\text{prod.}} \nu_i [\bar{b}(T_{ad}) - \bar{b}(298)]_i \\ &\quad - \sum_{\text{react.}} \nu_i [\bar{b}(T_0) - \bar{b}(298)]_i = 0\end{aligned}\quad (1.49)$$

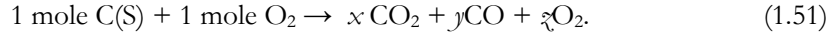
Obviously the first term on the right-hand side of Eq. (1.49) is the standard enthalpy of reaction $\Delta H_{r,298}^\circ$. The second term determines the sensible heat needed to heat the products from 298 K to the adiabatic flame temperature T_{ad} . To simplify our analysis, we shall assume that the reactants enter into the reactor at $T_0 = 298$ K so the third term becomes 0. Rearranging Eq. (1.49), we see that

$$-\Delta H_{r,298}^{\circ} = \sum_{\text{prod.}} \nu_i' [\bar{h}(T_{ad}) - \bar{h}(298)]_i. \quad (1.50)$$

In other words, the adiabatic flame temperature is obtained when all the heat released from a combustion reaction is used to raise the product temperature from 298 to T_{ad} .

The existence of chemical equilibrium makes the calculation of this adiabatic flame temperature a bit more involved. Specifically, while the values of ν_i are always well defined, ν_i' is not since it is dependent on the equilibrium composition of the products.

Consider the combustion of 1 mole of carbon (graphite) in 1 mole of oxygen at a pressure of 1 atm.



The reactant temperature is 298 K. The principle of chemical equilibrium states that the products cannot be entirely CO₂. Rather, a small amount of CO (y moles) must be produced along with z moles of O₂ unused. These products are in equilibrium at the adiabatic flame temperature among themselves through



with its equilibrium constant given by

$$K_p(T_{ad}) = \frac{P_{\text{CO}} P_{\text{O}_2}^{1/2}}{P_{\text{CO}_2}} = \frac{y z^{1/2}}{x} P^{1/2} = \exp(-\Delta G_r^0 / R_u T_{ad}). \quad (1.53)$$

(We need to recognize that the products of a combustion process cannot be in equilibrium with the reactants of the process. Rather it is the products that are in equilibrium among themselves.)

Since there are four unknowns in Eq. (1.53) (i.e., x , y , z and T_{ad}), we need to provide three more equations to solve this problem. Two of these equations come from mass conservation:

$$\text{Carbon: } x + y = 1 \text{ mol}, \quad (1.54)$$

$$\text{Oxygen: } 2x + y + 2z = 2 \text{ mol}. \quad (1.55)$$

The last equation is given by Eq. (1.50), which may be expanded to give

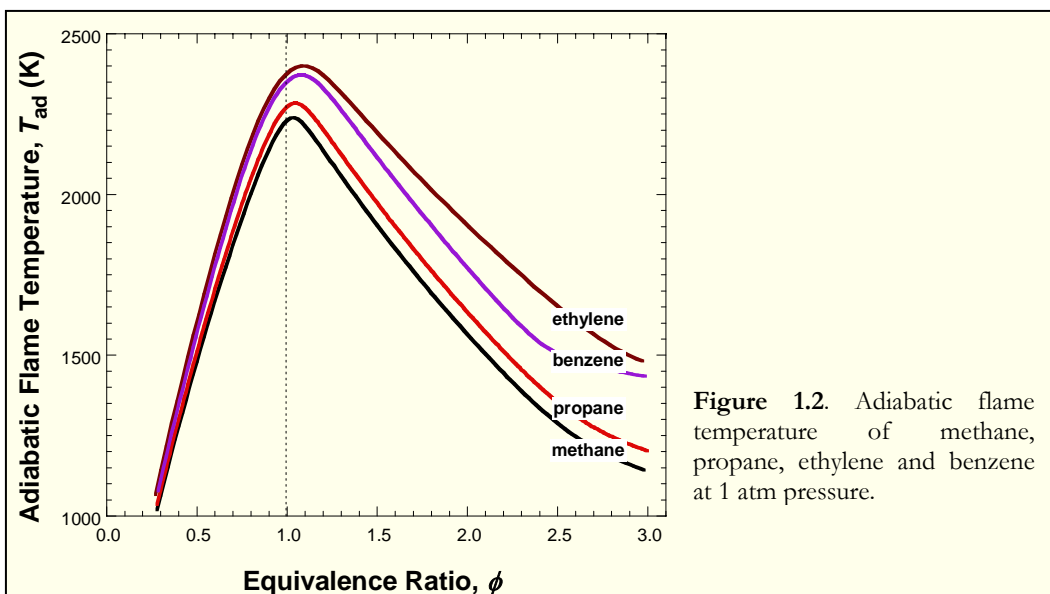
$$-[x \bar{h}_{f,298}^{\circ}(\text{CO}_2) + y \bar{h}_{f,298}^{\circ}(\text{CO})] = x [\bar{h}(T_{ad}) - \bar{h}(298)]_{\text{CO}_2} + y [\bar{h}(T_{ad}) - \bar{h}(298)]_{\text{CO}} + z [\bar{h}(T_{ad}) - \bar{h}(298)]_{\text{O}_2}. \quad (1.56)$$

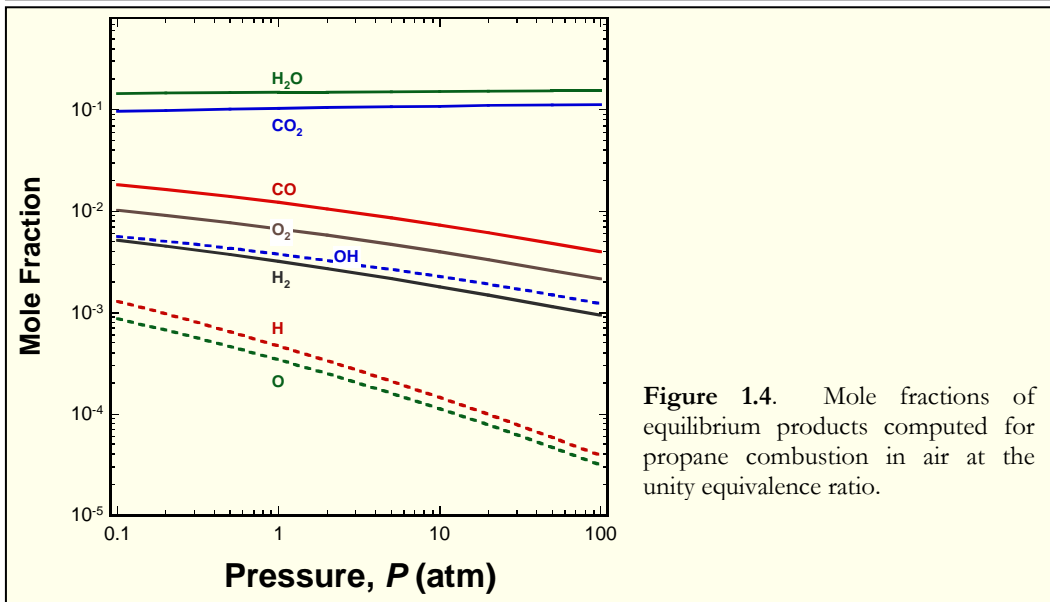
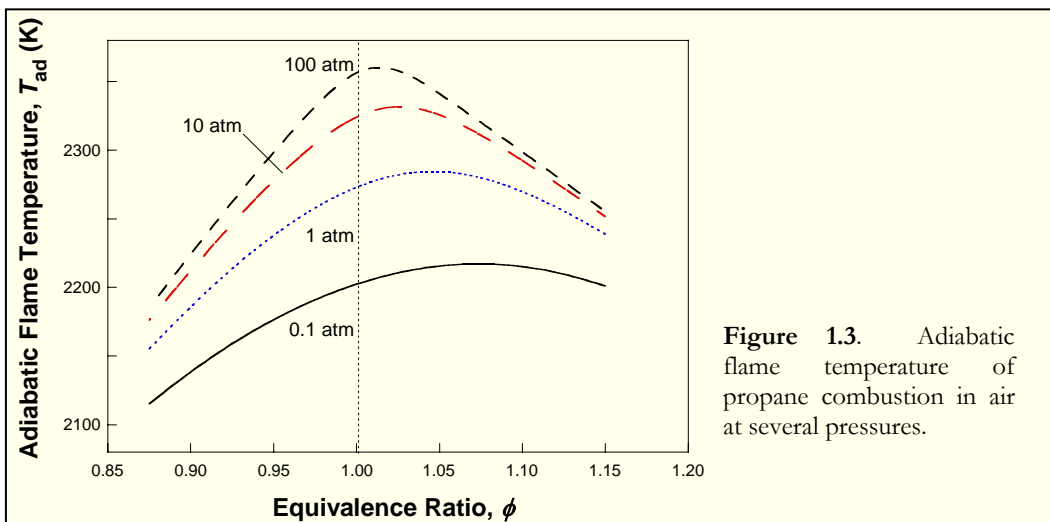
Clearly the coupled Eqs (1.53-1.56) cannot be solved analytically. We shall defer to section 1.8 and use Excel to solve the equation. Any more realistic combustion equilibrium

problems will have to be solved numerically by a computer—a topic we will discuss also in section 1.8.

Figure 1.2 shows the variation of the adiabatic flame temperature as a function of equivalence ratio for the combustion of methane, propane, ethylene and benzene in air at 1 atm pressure. As expected, the flame temperature peaks at an equivalence ratio around unity, slightly on the fuel rich side. The decrease of T_{ad} towards smaller ϕ is caused by dilution of unused oxygen as well as the greater amount of nitrogen brought into the combustor with oxygen. The decrease of the flame temperature towards larger ϕ is because of oxygen deficiency, which does not allow the fuel to be fully oxidized.

Figure 1.3 shows the effect of pressure on the adiabatic flame temperature. It is seen that as pressure increases, (a) the adiabatic flame temperature becomes higher and (b) the peak shifts towards $\phi = 1$. Here it may be noted that the pressure serves to reduce the extent of dissociation of CO_2 and H_2O , and in doing so, force the reaction towards better completion. To explain the variation of T_{ad} as a function of pressure, we plot in Figure 1.4 the equilibrium composition at $\phi = 1$. It is seen that as pressure decreases, the extent of CO_2 and H_2O dissociation into H_2 , O_2 , CO , and even highly unstable free radical species, including $\text{H}\bullet$, $\text{O}\bullet$, and $\text{OH}\bullet$ becomes more and more significant.





1.7 Tabulation and Mathematical Parameterization of Thermochemical Properties

Key thermodynamic or thermochemical properties discussed so far include the constant-pressure specific heat, sensible enthalpy, enthalpy of formation, and entropy under the standard condition. It is important to recognize that under the ideal gas condition, \bar{c}_p is not a function of pressure, but it is a function of temperature.

A common method is to tabulate, among others, $\bar{c}_p(T)$, $\bar{s}^\circ(T)$, $h(T) - h(298)$ and $\bar{h}_f^\circ(T)$ as a function of temperature. Such table is known as the JANAF table.⁸ Appendix 1.A gives a truncated version of these tables for species listed in Table 1.2. In research publications, these tables are usually condensed to something that looks like Table 1.3.

⁸ Chase, M. W., Jr., *J. Phys. Chem. Ref. Data*, 4th Edition, **Mono. 9**, Suppl. 1 (1998a).

Table 1.3. Thermochemical properties of selected species in the vapor state.

Species	$\bar{h}_f^\circ (298\text{K})$	$\bar{s}^\circ (298\text{K})$	$\bar{c}_p (T) \text{ (J/mol-K)}$					
	(kJ/mol)	(J/mol-K)	298	500	1000	1500	2000	2500
C(S)	0	5.730	8.523	14.596	21.624	23.857	25.167	25.976
H ₂	0	130.663	28.834	29.297	30.163	32.358	34.194	35.737
O ₂	0	205.127	29.377	31.082	34.881	36.505	37.855	38.999
H ₂ O	-241.8	188.810	33.587	35.214	41.294	47.333	51.678	54.731
CO	-110.5	197.640	29.140	29.811	33.163	35.132	36.288	36.917
CO ₂	-393.5	213.766	37.128	44.628	54.322	58.222	60.462	61.640
CH ₄	-74.6	186.351	35.685	46.494	73.616	90.413	100.435	106.864
C ₂ H ₆	-83.9	229.051	52.376	77.837	122.540	144.761	158.280	165.774
C ₃ H ₈	-103.8	270.141	73.530	112.409	174.614	204.334	222.359	232.305
C ₄ H ₁₀	-125.8	309.686	98.571	148.552	227.379	264.424	286.823	299.106
C ₈ H ₁₈	-208.7	466.772	187.486	286.282	431.399	494.910	534.404	557.447
C ₂ H ₄	52.3	219.156	42.783	62.321	93.860	109.190	118.563	123.799
C ₂ H ₂	227.4	200.892	43.989	54.715	67.908	75.906	81.045	84.262
CH ₃ OH	-200.9	239.785	44.030	59.526	89.656	105.425	113.891	118.560
C ₆ H ₆	82.8	269.020	82.077	138.240	210.948	240.242	257.667	267.023
H•	218.0	114.706	20.786	20.786	20.786	20.786	20.786	20.786
O•	249.2	161.047	21.912	21.247	20.924	20.846	20.826	20.853
OH•	39.3	183.722	29.887	29.483	30.694	32.948	34.755	36.077

The thermochemical data of a large number of species has been compiled by the National Institute of Standards and Technology. These data may be found at <http://webbook.nist.gov/chemistry/>. Another web-based source of data is the Active Tables (ATcT): https://cmcs.ca.sandia.gov/cmcs/portal/user/anon/js_pane.

For combustion calculations, a very good source of thermochemical data is: Alexander Burcat and Branko Ruscic “Third Millennium Thermodynamic Database for Combustion and Air-Pollution Use,” 2005 (<http://www.technion.ac.il/~aer0201/> or <http://garfield.chem.elte.hu/Burcat/burcat.html>).

The database is the result of extensive work by Professor Alexander Burcat of Technion University, Israel over the last 20 years. In this database, the thermochemical data are expressed in the form of polynomial function and are thus more compact than the JANAF table. A typical record of thermochemical data may look like the following:

Species name	Reference source	Composition	Phase	$T_{\text{Low}}, T_{\text{high}}, T_{\text{mid}}$	
CO2	L 7/88C	10 2 0	0G	200.000 6000.000 1000.	1
				0.46365111E+01 0.27414569E-02-0.99589759E-06 0.16038666E-09-0.91619857E-14	2
				-0.49024904E+05-0.19348955E+01 0.23568130E+01 0.89841299E-02-0.71220632E-05	3
				0.24573008E-08-0.14288548E-12-0.48371971E+05 0.99009035E+01-0.47328105E+05	4
$a_i (i = 1,7) \text{ for } T_{\text{mid}} < T < T_{\text{high}}$					
$a_i (i = 1,7) \text{ for } T_{\text{low}} < T < T_{\text{mid}}$					

The polynomial fits are made for two separate temperature ranges ($T_{\text{low}} \leq T \leq T_{\text{mid}}$ and $T_{\text{mid}} \leq T \leq T_{\text{high}}$). There are 7 polynomial coefficients, a_i ($i=1,..7$), for each temperature range. The thermochemical data are calculated from these fits as

$$\bar{c}_p/R_u = a_1 + a_2 T + a_3 T^2 + a_4 T^3 + a_5 T^4, \quad (1.57)$$

$$\bar{s}^\circ/R_u = a_1 \ln T + a_2 T + a_3 T^2/2 + a_4 T^3/3 + a_5 T^4/4 + a_7. \quad (1.58)$$

$$\bar{h}_T/R_u = a_1 T + a_2 T^2/2 + a_3 T^3/3 + a_4 T^4/4 + a_5 T^5/5 + a_6 \quad (1.59)$$

where \bar{h}_T is the total enthalpy (Eq. 1.25b), \bar{s}° is the standard entropy (1 atm). Note that these equations are in strict agreement with known relationships among the thermochemical properties, i.e.,

$$\bar{h}_T(T) = \int_{298.15}^T \bar{c}_p dT + \bar{h}_{f,298.15}^\circ, \quad (1.60)$$

$$\bar{s}^\circ(T) = \int_{298.15}^T \bar{c}_p d \ln T + \bar{s}^\circ(298.15). \quad (1.61)$$

To calculate and tabulate the thermochemical data properties in the JANAF type form, \bar{c}_p and \bar{s}° are directly calculated with Eqs. (1.57) and (1.58). The sensible enthalpy is determined as

$$\bar{h}(T) - \bar{h}(298.15) = \bar{h}_T(T) - \bar{h}_T(298.15), \quad (1.62)$$

where \bar{h}_T is calculated using Eq. (1.59). For enthalpy of formation, we use

$$\bar{h}_f^\circ(T) = \bar{h}_T(T) - \sum_{\text{elements}} \nu_i \bar{h}_{T,i}(T) \quad (1.63)$$

where ν_i represents the molecular composition of the substance. For example, a $C_xH_yO_z$ species has $\nu_C = x$, $\nu_{H_2} = y/2$ and $\nu_{O_2} = z/2$.

An EXCEL spreadsheet has been prepared for the JANAF like tabulation. The file may be downloaded from the course web site

http://ame-www.usc.edu/crs/Fall06/599/Week_2/NASA_poly%20to%20JANAF.xls.

Burcat's database may also be downloaded in text form

http://ame-www.usc.edu/crs/Fall06/599/Week_2/Burcat%20Thermo.txt,

and in Excel form

http://ame-www.usc.edu/crs/Fall06/599/Week_2/Burcat%20Thermo.xls.

1.8 Solution of an Equilibrium and Adiabatic Flame Temperature Problem

We shall now return to the problem of carbon (graphite) oxidation in section 1.6. We wish to calculate the adiabatic flame temperature for combustion of 1 mole of carbon (graphite)

in 1 mole of oxygen at a pressure of 1 atm. The initial temperature is 298 K. The four equations are

$$\begin{cases} x + y = 1 \\ 2x + y + 2z = 2 \\ \frac{y z^{1/2}}{x} \left(\frac{P}{x + y + z} \right)^{1/2} = \exp(-\Delta G_r^0 / R_u T_d) \\ -[x \bar{h}_{f,298}^\circ(\text{CO}_2) + y \bar{h}_{f,298}^\circ(\text{CO})] = x [\bar{h}(T_{ad}) - \bar{h}(298)]_{\text{CO}_2} \\ + y [\bar{h}(T_{ad}) - \bar{h}(298)]_{\text{CO}} + z [\bar{h}(T_{ad}) - \bar{h}(298)]_{\text{O}_2} \end{cases}.$$

Solution of the above problem is provided in an Excel sheet downloadable from http://ame-www.usc.edu/crs/Fall05/599/week_2/carbon_oxidation.xls. Note that to run the Excel solver requires the user to download the thermochemical property tables from http://ame-www.usc.edu/crs/Fall05/599/week_2/NASA_poly_to_JANAF.xls. This file should be placed in the same directory as the carbon_oxidation.xls file.

The solution of this set of nonlinear algebraic equations gives

$$\begin{cases} x = 0.233 \text{ mol} \\ y = 0.767 \text{ mol} \\ z = 0.384 \text{ mol} \\ T_{ad} = 3537 \text{ K} \end{cases}$$

Now suppose that the carbon is burned in air, instead of pure oxygen, the set of nonlinear algebraic equations may be revised by including the molar number of N₂ (=1 mole O₂×79/21) and the sensible enthalpy required to heat up the nitrogen,

$$\begin{cases} x + y = 1 \\ 2x + y + 2z = 2 \\ \frac{y z^{1/2}}{x} \left(\frac{P}{x + y + z + 79/21} \right)^{1/2} = \exp(-\Delta G_r^0 / R_u T_d) \\ -[x \bar{h}_{f,298}^\circ(\text{CO}_2) + y \bar{h}_{f,298}^\circ(\text{CO})] = x [\bar{h}(T_{ad}) - \bar{h}(298)]_{\text{CO}_2} \\ + y [\bar{h}(T_{ad}) - \bar{h}(298)]_{\text{CO}} + z [\bar{h}(T_{ad}) - \bar{h}(298)]_{\text{O}_2} + 79/21 [\bar{h}(T_{ad}) - \bar{h}(298)]_{\text{N}_2} \end{cases}.$$

The solution is

$$\begin{cases} x = 0.893 \text{ mol} \\ y = 0.107 \text{ mol} \\ z = 0.053 \text{ mol} \\ T_{ad} = 2312 \text{ K} \end{cases}$$

Comparing the two sets of solution, we find that (a) the adiabatic flame temperature is notably lower when air is used, and (b) the reaction is less complete when pure oxygen is used because the higher adiabatic flame temperature forces a greater extent of CO_2 dissociation into CO and O_2 .

Two commonly used equilibrium solvers are Stanjan (or the equilibrium solver – EQUIL - of the ChemKin suite of package) and the NASA Equilibrium code (cec86). We will use the equilibrium solver of the ChemKin suite of package for the current class. Instructions about the computer code can be found on p. 30.

Homework Problems # 1

- (1) Determine the enthalpy of formation of CO at 298 K, if the enthalpy of formation for CO₂ is known (Table 1.2), and the enthalpy of the following reaction



is measured to be -283 kJ per mol of CO₂ produced.

- (2) Tabulate the enthalpies of combustion of methane (CH₄) and octane (C₈H₁₈) in the units of kJ/mol and kJ/kg.
- (3) Solve (by hand or using EXCEL) the equilibrium composition and the adiabatic flame temperature for H₂ oxidation in air at a pressure of 1 atm, equivalence ratio ϕ equal to 1.5. The reactants enter the combustor at the room temperature (298.15 K). The equilibrium mixture is composed of H₂, O₂, and H₂O(v).
- (4) Using the EQUIL code, calculate the adiabatic flame temperature for H₂ and methane (CH₄) oxidation in air and plot the adiabatic flame temperature over an equivalence ratio range of $0.5 < \phi < 2$. Other conditions are identical to those of problem (3). Compare the results for H₂ from your hand or EXCEL calculation (problem 3) with those of EQUIL.
- (5) **Optional:** Can you explain why the adiabatic flame temperature peaks on the fuel-rich side and why the peak shifts further to the fuel-rich side as the pressure is decreased.

Procedure for downloading, compiling and running the EQUIL code on almaak:

- (a) Download all files to your almaak account from
<http://www-rcf.usc.edu/~haiw/cec86/>
- (b) To compile the code, execute the compeq script, i.e., at the UNIX prompt, type compeq and return. This will generate two executables: ckintp.exe and equil.exe. ckintp.exe is a ChemKin preprocessor and you need to run it only once to generate a binary cklink file from input files, including fort.15 (a list of chemical species considered in the calculation) and thermdat (the thermochemical database).
- (c) Run the ChemKin interpreter to pre-process the thermochemical data. At the UNIX prompt, type
 >ckintp.exe
This should generate a binary file named cklink for subsequent EQUIL calculation.
- (d) Edit the eqinp file to define the reaction conditions. This file contains the condition of the reactants and the reactor. An example file is seen below:

```
/This is an adiabatic problem where the enthalpy is a constant (H2 - H1 = 0)
CONH
/This is an isobaric problem
CONP
/The temperature of the reactants
TEMP 298.15
/The reactant composition (moles or mole fraction)
REAC C-GR 1.0
REAC O2 1.0
/The pressure
PRES 1.0
END
```

- (e) Run the EQUIL code by issue the command “equil.exe” at the UNIX prompt. The output file (eqout) is quite self-explanatory.

Appendix A1. Truncated JANAF tables

Graphite (C(S))					
T (K)	$\bar{c}_p(T)$ (J/mol-K)	$\bar{s}^\circ(T)$ (J/mol-K)	$h(T)-h(298)$ (kJ/mol)	$\bar{h}_f^\circ(T)$ (kJ/mol)	$\bar{g}_f^\circ(T)$ (kJ/mol)
298	8.523	5.730	0.000	0.000	0.000
300	8.592	5.787	0.017	0.000	0.000
400	11.832	8.713	1.042	0.000	0.000
500	14.596	11.659	2.368	0.000	0.000
600	16.836	14.526	3.944	0.000	0.000
700	18.559	17.257	5.717	0.000	0.000
800	19.835	19.823	7.640	0.000	0.000
900	20.794	22.217	9.674	0.000	0.000
1000	21.624	24.451	11.795	0.000	0.000
1100	22.169	26.538	13.985	0.000	0.000
1200	22.660	28.489	16.227	0.000	0.000
1300	23.102	30.320	18.515	0.000	0.000
1400	23.499	32.047	20.846	0.000	0.000
1500	23.857	33.681	23.214	0.000	0.000
1600	24.177	35.231	25.616	0.000	0.000
1700	24.465	36.705	28.048	0.000	0.000
1800	24.724	38.111	30.508	0.000	0.000
1900	24.957	39.454	32.992	0.000	0.000
2000	25.167	40.740	35.498	0.000	0.000
2100	25.358	41.972	38.025	0.000	0.000
2200	25.531	43.156	40.569	0.000	0.000
2300	25.691	44.295	43.131	0.000	0.000
2400	25.838	45.391	45.707	0.000	0.000
2500	25.976	46.449	48.298	0.000	0.000

Hydrogen (H ₂)					
T (K)	$\bar{c}_p(T)$ (J/mol-K)	$\bar{s}^\circ(T)$ (J/mol-K)	$h(T)-h(298)$ (kJ/mol)	$\bar{h}_f^\circ(T)$ (kJ/mol)	$\bar{g}_f^\circ(T)$ (kJ/mol)
298	28.834	130.663	0.000	0.000	0.000
300	28.850	130.856	0.058	0.000	0.000
400	29.277	139.229	2.969	0.000	0.000
500	29.297	145.768	5.900	0.000	0.000
600	29.254	151.105	8.827	0.000	0.000
700	29.344	155.619	11.755	0.000	0.000
800	29.615	159.553	14.702	0.000	0.000
900	29.970	163.062	17.681	0.000	0.000
1000	30.163	166.232	20.690	0.000	0.000
1100	30.634	169.130	23.730	0.000	0.000
1200	31.089	171.815	26.817	0.000	0.000
1300	31.527	174.320	29.948	0.000	0.000
1400	31.950	176.672	33.122	0.000	0.000
1500	32.358	178.891	36.337	0.000	0.000
1600	32.752	180.992	39.593	0.000	0.000
1700	33.132	182.989	42.887	0.000	0.000
1800	33.499	184.893	46.219	0.000	0.000
1900	33.853	186.714	49.586	0.000	0.000
2000	34.194	188.459	52.989	0.000	0.000
2100	34.525	190.135	56.425	0.000	0.000
2200	34.843	191.749	59.893	0.000	0.000
2300	35.151	193.305	63.393	0.000	0.000
2400	35.449	194.807	66.923	0.000	0.000
2500	35.737	196.260	70.483	0.000	0.000

Oxygen (O ₂)					
T (K)	$\bar{c}_p(T)$ (J/mol-K)	$\bar{s}^\circ(T)$ (J/mol-K)	$h(T)-h(298)$ (kJ/mol)	$\bar{h}_f^\circ(T)$ (kJ/mol)	$\bar{g}_f^\circ(T)$ (kJ/mol)
298	29.377	205.127	0.000	0.000	0.000
300	29.387	205.323	0.059	0.000	0.000
400	30.120	213.870	3.031	0.000	0.000
500	31.082	220.692	6.090	0.000	0.000
600	32.080	226.448	9.249	0.000	0.000
700	32.990	231.463	12.503	0.000	0.000
800	33.747	235.919	15.842	0.000	0.000
900	34.355	239.930	19.248	0.000	0.000
1000	34.881	243.578	22.710	0.000	0.000
1100	35.232	246.919	26.216	0.000	0.000
1200	35.569	249.999	29.756	0.000	0.000
1300	35.893	252.859	33.329	0.000	0.000
1400	36.205	255.530	36.934	0.000	0.000
1500	36.505	258.038	40.569	0.000	0.000
1600	36.795	260.404	44.234	0.000	0.000
1700	37.074	262.643	47.928	0.000	0.000
1800	37.343	264.769	51.649	0.000	0.000
1900	37.604	266.795	55.396	0.000	0.000
2000	37.855	268.731	59.169	0.000	0.000
2100	38.098	270.584	62.967	0.000	0.000
2200	38.334	272.361	66.789	0.000	0.000
2300	38.562	274.070	70.634	0.000	0.000
2400	38.784	275.716	74.501	0.000	0.000
2500	38.999	277.304	78.390	0.000	0.000

Water vapor (H ₂ O(v))					
T (K)	$\bar{c}_p(T)$ (J/mol-K)	$\bar{s}^\circ(T)$ (J/mol-K)	$h(T)-h(298)$ (kJ/mol)	$\bar{h}_f^\circ(T)$ (kJ/mol)	$\bar{g}_f(T)$ (kJ/mol)
298	33.587	188.810	0.000	-241.821	-228.585
300	33.596	189.034	0.067	-241.841	-228.496
400	34.268	198.783	3.458	-242.849	-223.896
500	35.214	206.527	6.930	-243.836	-219.043
600	36.320	213.044	10.506	-244.767	-213.996
700	37.508	218.731	14.197	-245.632	-208.798
800	38.733	223.819	18.008	-246.435	-203.481
900	39.986	228.453	21.944	-247.182	-198.066
1000	41.294	232.733	26.007	-247.859	-192.571
1100	42.659	236.734	30.206	-248.454	-187.013
1200	43.941	240.501	34.536	-248.979	-181.404
1300	45.145	244.066	38.991	-249.442	-175.753
1400	46.275	247.454	43.563	-249.847	-170.070
1500	47.333	250.683	48.244	-250.199	-164.359
1600	48.324	253.770	53.027	-250.504	-158.626
1700	49.251	256.727	57.907	-250.766	-152.875
1800	50.117	259.567	62.876	-250.989	-147.110
1900	50.925	262.299	67.928	-251.178	-141.334
2000	51.678	264.930	73.059	-251.336	-135.548
2100	52.380	267.469	78.262	-251.468	-129.756
2200	53.034	269.921	83.533	-251.576	-123.957
2300	53.641	272.292	88.867	-251.664	-118.154
2400	54.206	274.587	94.260	-251.735	-112.348
2500	54.731	276.811	99.707	-251.792	-106.539

Carbon monoxide (CO)					
T (K)	$\bar{c}_p(T)$ (J/mol-K)	$\bar{s}^\circ(T)$ (J/mol-K)	$h(T)-h(298)$ (kJ/mol)	$\bar{h}_f^\circ(T)$ (kJ/mol)	$\bar{g}_f^\circ(T)$ (kJ/mol)
298	29.140	197.640	0.000	-110.529	-137.155
300	29.143	197.835	0.058	-110.518	-137.334
400	29.375	206.246	2.982	-110.105	-146.344
500	29.811	212.844	5.940	-110.002	-155.421
600	30.415	218.330	8.950	-110.147	-164.495
700	31.133	223.071	12.027	-110.472	-173.529
800	31.894	227.278	15.178	-110.912	-182.509
900	32.606	231.077	18.404	-111.423	-191.428
1000	33.163	234.543	21.694	-111.985	-200.288
1100	33.637	237.726	25.035	-112.588	-209.089
1200	34.069	240.672	28.420	-113.214	-217.835
1300	34.460	243.414	31.847	-113.862	-226.527
1400	34.813	245.981	35.311	-114.531	-235.168
1500	35.132	248.394	38.808	-115.220	-243.761
1600	35.418	250.671	42.336	-115.926	-252.308
1700	35.674	252.826	45.891	-116.651	-260.810
1800	35.903	254.872	49.470	-117.392	-269.268
1900	36.107	256.818	53.071	-118.149	-277.685
2000	36.288	258.675	56.691	-118.922	-286.062
2100	36.447	260.449	60.327	-119.710	-294.400
2200	36.589	262.148	63.979	-120.514	-302.699
2300	36.713	263.778	67.645	-121.332	-310.962
2400	36.822	265.342	71.321	-122.166	-319.189
2500	36.917	266.848	75.009	-123.014	-327.381

Carbon dioxide (CO ₂)					
T (K)	$\bar{c}_p(T)$ (J/mol-K)	$\bar{s}^\circ(T)$ (J/mol-K)	$h(T)-h(298)$ (kJ/mol)	$\bar{h}_f^\circ(T)$ (kJ/mol)	$\bar{g}_f^\circ(T)$ (kJ/mol)
298	37.128	213.766	0.000	-393.505	-394.372
300	37.218	214.015	0.074	-393.506	-394.377
400	41.286	225.297	4.006	-393.572	-394.658
500	44.628	234.881	8.307	-393.655	-394.920
600	47.359	243.268	12.911	-393.786	-395.162
700	49.589	250.741	17.762	-393.963	-395.378
800	51.425	257.487	22.816	-394.171	-395.566
900	52.970	263.635	28.038	-394.389	-395.727
1000	54.322	269.288	33.404	-394.606	-395.865
1100	55.268	274.510	38.884	-394.821	-395.980
1200	56.124	279.356	44.454	-395.033	-396.076
1300	56.899	283.880	50.106	-395.243	-396.154
1400	57.596	288.122	55.831	-395.453	-396.217
1500	58.222	292.118	61.623	-395.665	-396.264
1600	58.782	295.894	67.473	-395.882	-396.297
1700	59.281	299.473	73.377	-396.104	-396.316
1800	59.724	302.874	79.328	-396.334	-396.322
1900	60.116	306.114	85.320	-396.573	-396.314
2000	60.462	309.206	91.349	-396.823	-396.294
2100	60.765	312.164	97.411	-397.086	-396.262
2200	61.031	314.997	103.501	-397.362	-396.216
2300	61.263	317.715	109.616	-397.653	-396.157
2400	61.464	320.326	115.753	-397.960	-396.086
2500	61.640	322.839	121.908	-398.285	-396.001

Methane (CH ₄)					
T (K)	$\bar{c}_p(T)$ (J/mol-K)	$\bar{s}^\circ(T)$ (J/mol-K)	$h(T)-h(298)$ (kJ/mol)	$\bar{h}_f^\circ(T)$ (kJ/mol)	$\bar{g}_f^\circ(T)$ (kJ/mol)
298	35.685	186.351	0.000	-74.594	-50.544
300	35.760	186.590	0.071	-74.655	-50.383
400	40.530	197.488	3.871	-77.704	-41.830
500	46.494	207.161	8.217	-80.544	-32.527
600	52.730	216.190	13.179	-83.013	-22.685
700	58.650	224.769	18.752	-85.070	-12.462
800	63.998	232.957	24.889	-86.749	-1.970
900	68.850	240.778	31.535	-88.096	8.711
1000	73.616	248.277	38.656	-89.114	19.525
1100	77.713	255.489	46.226	-89.814	30.425
1200	81.404	262.412	54.185	-90.269	41.378
1300	84.728	269.061	62.495	-90.510	52.360
1400	87.720	275.452	71.120	-90.564	63.353
1500	90.413	281.597	80.029	-90.454	74.344
1600	92.839	287.511	89.194	-90.202	85.323
1700	95.028	293.206	98.589	-89.828	96.282
1800	97.007	298.695	108.192	-89.348	107.217
1900	98.802	303.989	117.984	-88.775	118.122
2000	100.435	309.099	127.947	-88.124	128.994
2100	101.929	314.036	138.066	-87.403	139.833
2200	103.302	318.809	148.329	-86.622	150.635
2300	104.573	323.430	158.724	-85.788	161.401
2400	105.756	327.906	169.241	-84.908	172.130
2500	106.864	332.246	179.872	-83.986	182.821

Ethane (C ₂ H ₆)					
T (K)	$\bar{c}_p(T)$ (J/mol-K)	$\bar{s}^\circ(T)$ (J/mol-K)	$h(T)-h(298)$ (kJ/mol)	$\bar{h}_f^\circ(T)$ (kJ/mol)	$\bar{g}_f(T)$ (kJ/mol)
298	52.376	229.051	0.000	-83.854	-31.884
300	52.642	229.402	0.105	-83.956	-31.534
400	65.627	246.340	6.024	-88.822	-13.313
500	77.837	262.313	13.205	-93.084	6.072
600	89.040	277.511	21.558	-96.664	26.250
700	99.101	292.007	30.974	-99.580	46.975
800	107.983	305.833	41.338	-101.902	68.077
900	115.743	319.010	52.533	-103.711	89.438
1000	122.540	331.564	64.455	-105.061	110.975
1100	127.823	343.495	76.977	-106.039	132.629
1200	132.662	354.827	90.005	-106.753	154.359
1300	137.081	365.623	103.495	-107.232	176.139
1400	141.106	375.932	117.408	-107.503	197.949
1500	144.761	385.794	131.704	-107.589	219.771
1600	148.069	395.244	146.348	-107.516	241.593
1700	151.053	404.311	161.307	-107.305	263.407
1800	153.735	413.023	176.549	-106.978	285.204
1900	156.138	421.400	192.045	-106.553	306.981
2000	158.280	429.465	207.768	-106.050	328.733
2100	160.183	437.234	223.693	-105.486	350.459
2200	161.866	444.725	239.797	-104.877	372.156
2300	163.347	451.954	256.059	-104.236	393.825
2400	164.644	458.934	272.460	-103.579	415.466
2500	165.774	465.679	288.982	-102.916	437.079

Propane (C3H8)					
T (K)	$\bar{c}_p(T)$ (J/mol-K)	$\bar{s}^\circ(T)$ (J/mol-K)	$h(T)-h(298)$ (kJ/mol)	$\bar{h}_f^\circ(T)$ (kJ/mol)	$\bar{g}_f(T)$ (kJ/mol)
298	73.530	270.141	0.000	-103.842	-23.472
300	73.949	270.634	0.147	-103.977	-22.932
400	94.097	294.707	8.564	-110.281	5.058
500	112.409	317.709	18.906	-115.638	34.533
600	128.644	339.671	30.976	-120.004	64.993
700	142.749	360.587	44.563	-123.452	96.111
800	154.863	380.460	59.459	-126.111	127.667
900	165.312	399.318	75.480	-128.108	159.515
1000	174.614	417.224	92.483	-129.506	191.554
1100	181.688	434.203	110.303	-130.416	223.707
1200	188.162	450.294	128.801	-130.989	255.927
1300	194.072	465.592	147.917	-131.262	288.184
1400	199.452	480.174	167.598	-131.268	320.450
1500	204.334	494.104	187.791	-131.042	352.709
1600	208.751	507.435	208.449	-130.612	384.947
1700	212.732	520.212	229.527	-130.009	417.151
1800	216.308	532.475	250.982	-129.259	449.316
1900	219.508	544.257	272.776	-128.389	481.436
2000	222.359	555.590	294.872	-127.422	513.507
2100	224.889	566.502	317.237	-126.380	545.529
2200	227.124	577.016	339.840	-125.285	577.499
2300	229.090	587.157	362.653	-124.155	609.418
2400	230.809	596.944	385.649	-123.008	641.288
2500	232.305	606.397	408.807	-121.861	673.110

Normal butane (C4H10)					
T (K)	$\bar{c}_p(T)$ (J/mol-K)	$\bar{s}^\circ(T)$ (J/mol-K)	$h(T)-h(298)$ (kJ/mol)	$\bar{h}_f^\circ(T)$ (kJ/mol)	$\bar{g}_f(T)$ (kJ/mol)
298	98.571	309.686	0.000	-125.767	-16.535
300	99.112	310.347	0.198	-125.926	-15.802
400	125.064	342.467	11.425	-133.355	22.056
500	148.552	372.947	25.128	-139.607	61.658
600	169.281	401.906	41.043	-144.631	102.403
700	187.205	429.383	58.890	-148.521	143.898
800	202.523	455.407	78.397	-151.440	185.882
900	215.684	480.039	99.323	-153.544	228.181
1000	227.379	503.378	121.485	-154.914	270.675
1100	236.202	525.470	144.670	-155.689	313.275
1200	244.275	546.373	168.700	-156.057	355.927
1300	251.642	566.221	193.502	-156.064	398.595
1400	258.344	585.119	219.006	-155.751	441.252
1500	264.424	603.154	245.150	-155.158	483.876
1600	269.920	620.398	271.872	-154.322	526.452
1700	274.871	636.913	299.116	-153.280	568.969
1800	279.314	652.752	326.829	-152.063	611.420
1900	283.287	667.962	354.963	-150.705	653.800
2000	286.823	682.585	383.472	-149.234	696.104
2100	289.958	696.656	412.314	-147.677	738.333
2200	292.722	710.210	441.451	-146.061	780.486
2300	295.148	723.277	470.847	-144.409	822.565
2400	297.267	735.884	500.470	-142.742	864.572
2500	299.106	748.058	530.291	-141.081	906.509

Normal octane (C8H18)					
T (K)	$\bar{c}_p(T)$ (J/mol-K)	$\bar{s}^\circ(T)$ (J/mol-K)	$h(T)-h(298)$ (kJ/mol)	$\bar{h}_f^\circ(T)$ (kJ/mol)	$\bar{g}_f(T)$ (kJ/mol)
298	187.486	466.772	0.000	-208.731	16.269
300	188.566	468.029	0.376	-209.011	17.780
400	240.137	529.457	21.852	-221.937	95.386
500	286.282	588.108	48.222	-232.547	175.994
600	326.349	643.939	78.905	-240.815	258.516
700	360.219	696.868	113.285	-246.981	342.252
800	388.302	746.862	150.756	-251.414	426.749
900	411.539	793.980	190.783	-254.468	511.715
1000	431.399	838.389	232.950	-256.354	596.959
1100	446.430	880.221	276.852	-257.332	682.343
1200	460.225	919.665	322.195	-257.701	767.789
1300	472.856	957.009	368.858	-257.523	853.243
1400	484.394	992.480	416.730	-256.861	938.664
1500	494.910	1026.265	465.703	-255.773	1024.023
1600	504.469	1058.515	515.680	-254.313	1109.297
1700	513.136	1089.363	566.567	-252.534	1194.470
1800	520.974	1118.919	618.279	-250.484	1279.530
1900	528.044	1147.279	670.736	-248.210	1364.470
2000	534.404	1174.529	723.865	-245.755	1449.285
2100	540.110	1200.743	777.596	-243.159	1533.973
2200	545.217	1225.989	831.867	-240.461	1618.536
2300	549.775	1250.328	886.621	-237.695	1702.974
2400	553.836	1273.813	941.805	-234.894	1787.291
2500	557.447	1296.497	997.373	-232.087	1871.491

Ethylene (C ₂ H ₄)					
T (K)	$\bar{c}_p(T)$ (J/mol-K)	$\bar{s}^\circ(T)$ (J/mol-K)	$h(T)-h(298)$ (kJ/mol)	$\bar{h}_f^\circ(T)$ (kJ/mol)	$\bar{g}_f(T)$ (kJ/mol)
298	42.783	219.156	0.000	52.298	68.280
300	42.992	219.443	0.086	52.234	68.387
400	53.098	233.213	4.897	49.173	74.241
500	62.321	246.070	10.676	46.440	80.832
600	70.529	258.174	17.327	44.085	87.938
700	77.685	269.597	24.746	42.100	95.408
800	83.843	280.383	32.831	40.445	103.141
900	89.153	290.572	41.487	39.075	111.063
1000	93.860	300.213	50.641	37.968	119.123
1100	97.500	309.332	60.212	37.079	127.283
1200	100.836	317.961	70.131	36.342	135.517
1300	103.885	326.154	80.369	35.742	143.807
1400	106.664	333.956	90.899	35.262	152.138
1500	109.190	341.403	101.694	34.890	160.500
1600	111.479	348.524	112.729	34.610	168.884
1700	113.546	355.346	123.982	34.410	177.282
1800	115.406	361.889	135.431	34.276	185.691
1900	117.074	368.174	147.057	34.198	194.105
2000	118.563	374.218	158.840	34.164	202.522
2100	119.889	380.036	170.764	34.163	210.940
2200	121.062	385.640	182.813	34.185	219.358
2300	122.097	391.045	194.972	34.222	227.774
2400	123.005	396.261	207.228	34.265	236.188
2500	123.799	401.299	219.569	34.306	244.601

Acetylene (C2H2)					
T (K)	$\bar{c}_p(T)$ (J/mol-K)	$\bar{s}^\circ(T)$ (J/mol-K)	$h(T)-h(298)$ (kJ/mol)	$\bar{h}_f^\circ(T)$ (kJ/mol)	$\bar{g}_f(T)$ (kJ/mol)
298	43.989	200.892	0.000	227.397	209.884
300	44.134	201.187	0.088	227.393	209.766
400	50.268	214.772	4.825	227.170	203.922
500	54.715	226.492	10.086	226.848	198.146
600	58.110	236.780	15.734	226.417	192.444
700	60.916	245.954	21.688	225.896	186.822
800	63.429	254.254	27.907	225.322	181.279
900	65.775	261.862	34.369	224.737	175.808
1000	67.908	268.905	41.055	224.172	170.402
1100	69.787	275.467	47.941	223.638	165.051
1200	71.517	281.614	55.008	223.135	159.748
1300	73.108	287.402	62.240	222.659	154.485
1400	74.568	292.874	69.625	222.209	149.258
1500	75.906	298.065	77.150	221.782	144.062
1600	77.130	303.004	84.802	221.375	138.894
1700	78.248	307.714	92.572	220.986	133.751
1800	79.269	312.216	100.449	220.612	128.631
1900	80.199	316.527	108.423	220.249	123.530
2000	81.045	320.662	116.486	219.897	118.449
2100	81.816	324.636	124.629	219.552	113.385
2200	82.516	328.458	132.847	219.211	108.338
2300	83.153	332.140	141.131	218.873	103.306
2400	83.733	335.692	149.475	218.535	98.288
2500	84.262	339.121	157.875	218.194	93.285

Methanol vapor (CH ₃ OH(v))					
T (K)	$\bar{c}_p(T)$ (J/mol-K)	$\bar{s}^\circ(T)$ (J/mol-K)	$h(T)-h(298)$ (kJ/mol)	$\bar{h}_f^\circ(T)$ (kJ/mol)	$\bar{g}_f^\circ(T)$ (kJ/mol)
298	44.030	239.785	0.000	-200.932	-162.241
300	44.155	240.080	0.088	-201.005	-161.981
400	51.400	253.735	4.852	-204.576	-148.427
500	59.526	266.074	10.397	-207.747	-134.013
600	67.334	277.628	16.746	-210.407	-119.008
700	74.146	288.534	23.830	-212.581	-103.597
800	79.807	298.817	31.536	-214.360	-87.902
900	84.681	308.502	39.764	-215.827	-72.003
1000	89.656	317.675	48.475	-216.987	-55.958
1100	93.611	326.410	57.642	-217.843	-39.811
1200	97.125	334.709	67.183	-218.487	-23.597
1300	100.239	342.608	77.054	-218.953	-7.336
1400	102.994	350.140	87.219	-219.269	8.955
1500	105.425	357.330	97.642	-219.463	25.264
1600	107.570	364.204	108.294	-219.556	41.583
1700	109.459	370.783	119.148	-219.571	57.905
1800	111.124	377.088	130.178	-219.523	74.226
1900	112.593	383.136	141.366	-219.429	90.543
2000	113.891	388.945	152.691	-219.301	106.854
2100	115.042	394.530	164.139	-219.151	123.158
2200	116.067	399.906	175.696	-218.987	139.455
2300	116.984	405.086	187.349	-218.817	155.744
2400	117.810	410.083	199.089	-218.647	172.025
2500	118.560	414.908	210.908	-218.482	188.300

Benzene (C6H6)					
T (K)	$\bar{c}_p(T)$ (J/mol-K)	$\bar{s}^\circ(T)$ (J/mol-K)	$h(T)-h(298)$ (kJ/mol)	$\bar{h}_f^\circ(T)$ (kJ/mol)	$\bar{g}_f(T)$ (kJ/mol)
298	82.077	269.020	0.000	82.818	129.707
300	82.718	269.572	0.165	82.707	130.023
400	112.650	297.567	9.968	77.627	146.585
500	138.240	325.536	22.550	73.463	164.325
600	159.404	352.677	37.468	70.145	182.823
700	176.423	378.577	54.292	67.540	201.817
800	189.948	403.052	72.636	65.507	221.144
900	200.995	426.081	92.198	63.930	240.698
1000	210.948	447.775	112.798	62.775	260.405
1100	217.961	468.215	134.249	61.966	280.209
1200	224.361	487.458	156.370	61.377	300.077
1300	230.183	505.651	179.101	60.985	319.986
1400	235.466	522.905	202.388	60.767	339.918
1500	240.242	539.317	226.178	60.701	359.860
1600	244.545	554.961	250.421	60.766	379.803
1700	248.408	569.905	275.072	60.940	399.738
1800	251.863	584.203	300.089	61.203	419.660
1900	254.939	597.905	325.432	61.538	439.566
2000	257.667	611.052	351.065	61.925	459.452
2100	260.074	623.683	376.955	62.349	479.318
2200	262.187	635.832	403.070	62.791	499.163
2300	264.033	647.528	429.383	63.237	518.988
2400	265.637	658.800	455.869	63.673	538.794
2500	267.023	669.673	482.503	64.085	558.582

Hydrogen Atom (H•)					
T (K)	$\bar{c}_p(T)$ (J/mol-K)	$\bar{s}^\circ(T)$ (J/mol-K)	$h(T)-h(298)$ (kJ/mol)	$\bar{h}_f^\circ(T)$ (kJ/mol)	$\bar{g}_f^\circ(T)$ (kJ/mol)
298	20.786	114.706	0.000	217.995	203.281
300	20.786	114.845	0.042	218.007	203.183
400	20.786	120.825	2.120	218.630	198.146
500	20.786	125.463	4.199	219.243	192.955
600	20.786	129.253	6.277	219.859	187.639
700	20.786	132.457	8.356	220.473	182.220
800	20.786	135.232	10.435	221.078	176.714
900	20.786	137.681	12.513	221.667	171.133
1000	20.786	139.871	14.592	222.241	165.488
1100	20.786	141.852	16.670	222.801	159.785
1200	20.786	143.660	18.749	223.340	154.032
1300	20.786	145.324	20.828	223.858	148.235
1400	20.786	146.865	22.906	224.355	142.399
1500	20.786	148.299	24.985	224.830	136.529
1600	20.786	149.640	27.063	225.284	130.627
1700	20.786	150.900	29.142	225.718	124.698
1800	20.786	152.088	31.221	226.131	118.743
1900	20.786	153.212	33.299	226.525	112.766
2000	20.786	154.278	35.378	226.900	106.769
2100	20.786	155.293	37.456	227.257	100.754
2200	20.786	156.260	39.535	227.596	94.722
2300	20.786	157.184	41.614	227.920	88.675
2400	20.786	158.068	43.692	228.227	82.614
2500	20.786	158.917	45.771	228.520	76.541

Oxygen atom (O•)					
T (K)	$\bar{c}_p(T)$ (J/mol-K)	$\bar{s}^\circ(T)$ (J/mol-K)	$h(T)-h(298)$ (kJ/mol)	$\bar{h}_f^\circ(T)$ (kJ/mol)	$\bar{g}_f^\circ(T)$ (kJ/mol)
298	21.912	161.047	0.000	249.171	231.743
300	21.900	161.194	0.044	249.185	231.626
400	21.462	167.427	2.209	249.864	225.669
500	21.247	172.190	4.344	250.469	219.548
600	21.138	176.053	6.462	251.008	213.312
700	21.062	179.306	8.572	251.491	206.991
800	20.987	182.113	10.675	251.924	200.604
900	20.923	184.581	12.770	252.316	194.165
1000	20.924	186.785	14.861	252.677	187.684
1100	20.903	188.778	16.953	253.014	181.168
1200	20.885	190.596	19.042	253.329	174.623
1300	20.870	192.267	21.130	253.626	168.052
1400	20.857	193.813	23.216	253.905	161.458
1500	20.846	195.252	25.301	254.169	154.846
1600	20.838	196.597	27.385	254.418	148.216
1700	20.832	197.860	29.469	254.653	141.571
1800	20.828	199.051	31.552	254.875	134.913
1900	20.826	200.177	33.635	255.085	128.242
2000	20.826	201.245	35.717	255.283	121.561
2100	20.827	202.261	37.800	255.471	114.871
2200	20.831	203.230	39.883	255.647	108.171
2300	20.837	204.156	41.966	255.813	101.464
2400	20.844	205.043	44.050	255.968	94.750
2500	20.853	205.894	46.135	256.113	88.029

Hydroxyl radical (OH•)					
T (K)	$\bar{c}_p(T)$ (J/mol-K)	$\bar{s}^\circ(T)$ (J/mol-K)	$h(T)-h(298)$ (kJ/mol)	$\bar{h}_f^\circ(T)$ (kJ/mol)	$\bar{g}_f^\circ(T)$ (kJ/mol)
298	29.887	183.722	0.000	39.346	34.631
300	29.878	183.922	0.060	39.348	34.599
400	29.573	192.469	3.030	39.376	33.010
500	29.483	199.056	5.982	39.333	31.422
600	29.534	204.434	8.931	39.240	29.848
700	29.684	208.997	11.892	39.108	28.292
800	29.916	212.975	14.871	38.945	26.758
900	30.240	216.516	17.878	38.759	25.246
1000	30.694	219.724	20.923	38.569	23.754
1100	31.174	222.672	24.017	38.389	22.282
1200	31.641	225.405	27.157	38.217	20.825
1300	32.093	227.955	30.344	38.052	19.382
1400	32.529	230.350	33.575	37.895	17.952
1500	32.948	232.608	36.850	37.744	16.533
1600	33.349	234.748	40.165	37.599	15.124
1700	33.730	236.781	43.519	37.459	13.723
1800	34.091	238.719	46.910	37.324	12.331
1900	34.433	240.572	50.336	37.193	10.946
2000	34.755	242.346	53.796	37.065	9.568
2100	35.056	244.049	57.287	36.939	8.196
2200	35.339	245.686	60.806	36.813	6.830
2300	35.602	247.263	64.354	36.687	5.470
2400	35.848	248.784	67.926	36.560	4.116
2500	36.077	250.252	71.523	36.432	2.767