

**COMBUSTION-GENERATED
AIR POLLUTION**

COMBUSTION-GENERATED AIR POLLUTION

*A Short Course on Combustion-Generated Air Pollution
held at the University of California, Berkeley
September 22-26, 1969*

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INTRODUCTION

This collection of notes was assembled as a supplement and guide to a five-day short course presented at the University of California at Berkeley, September 22-26, 1969. The scope of subject matter, while limited to combustion as a source of air pollution, at the same time is intended to give the broadest possible exposure within that area. The spectrum is deliberately wide, ranging from fundamentals of combustion and combustion reactions through performance of combustion systems and to legal and administrative control.

Contributors to this compendium and lecturers in the subject were solicited from academic and public organizations. Most of the authors are from the statewide University of California and the California Department of Public Health. Notable individuals with particular expertise, from other institutions, were also invited to contribute. The choice of instructor in each case was based upon a desire to collect a cross-section of outstanding individuals, each highly qualified technically in his field. These notes reflect the freedom which each author was encouraged to follow in providing supplementary material for his lecture.

The staff of Continuing Education in Engineering, Professor Thomas Hazlett and Daphne Stern, deserve commendation for their effective and successful handling of the innumerable details which were encountered. Professors Robert Sawyer and Laurence Caretto are herewith gratefully acknowledged for their support in the seemingly uncountable tasks necessary to assemble the entity which is represented.

The material here outlined is intended to be only a beginning. It is the desire to expose each individual to the fundamentals and practicalities of combustion-generated air pollution as it is understood today. The objective is to provide to each thereby a better array of equipment to be used in understanding and attacking the problems of air pollution.

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COMBUSTION THERMODYNAMICS

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INTRODUCTION

The majority of man's energy long has become available through combustion processes. In the United States over 95% of the energy consumed involves the combustion of fossil fuels (1). On a world-wide basis, more than 99% of the energy consumed is released through combustion processes (2). While increased development of nuclear power will occur during the remainder of this century, fossil fuels are predicted to provide more than 75% of the energy requirements of the United States in the year 2000. In 35 years the consumption of fossil fuels will be 2 to 3 times the current rate (1).

In a general sense, combustion is taken to include all fast exothermic reactions. "Fast" implies that the time scale is of the order of seconds, or less. More often, "fast" means milliseconds or less. "Exothermic," in this same vague sense, implies that the energy involved is sufficient to be of interest.

Recent intensification of the study of combustion has been associated with advent and development of aerospace propulsion, primarily rocketry. While the problems of space and atmosphere propulsion will continue to place new demands upon the field of combustion, the primary requirement for improved understanding of combustion is likely to result from air pollution problems.

Many of the problems of understanding and describing the nature of combustion remain unsolved. This lack of progress results from the intrinsic complexity of combustion phenomena rather than from a lack of interest or effort. These complexities are traceable directly to the result of the simultaneous interaction in the com-

bustion process of (1) chemical reaction, (2) fluid flow, (3) heat transfer, and (4) mass transfer.

It is natural that the work in combustion has been carried on by a group in which chemists, thermodynamicists, and aerodynamicists are represented. The resulting mix of metric and English dimension persists in the combustion literature. No attempt is made here to promote the consistent use of a particular system.

LAWS OF THERMODYNAMICS

Pertinent laws of thermodynamics and basic thermodynamic definitions and concepts are presented in their simplest forms. The material is recorded in the form of a review. If a more detailed or rigorous presentation is sought, a number of suitable references exist, for example (3) or (4).

Equation of state: Combustion products generally are high temperature gases and as such may be treated adequately as perfect gases, i.e. fluids obeying the law, $PV = nRT$. A corollary relation for a perfect gas is that its internal energy be a function of temperature alone, $U = U(T)$ alone. The term "calorically perfect gas" is reserved for a gas with a constant specific heat, $C_v = \text{constant}$.

Work: Work in a combustion system is limited to mechanical work of the form, $\delta W = P dV$. The amount of work produced by a system depends upon the path taken, in terms of, say, the thermodynamic coordinates P and V . Work, therefore, is not a function of the thermodynamic coordinates of the initial and final states of the system alone. The differential quantity of work is an inexact differential and represented by the notation, δW , rather than dW which is reserved for an exact differential.

Heat: The term heat refers to energy in transit because of a temperature difference. Since heat cannot be expressed as a function of the thermodynamic coordinates, the infinitesimal quantity of heat is an inexact differential and therefore represented as δQ .

First law of thermodynamics: An expression of conservation of energy, the first law of thermodynamics merely states that the difference between the heat added to a system and the work produced by the system is the change in the associated internal energy function, U .

$$\delta Q = dU + \delta W \quad (1)$$

The sign convention adopted is that heat transferred to the system and work done by the system are positive. In a combustion system, work is limited to PdV work so that the first law of thermodynamics takes the form $\delta Q = dU + PdV$. The equivalence

between mechanical energy and thermal energy is expressed as 4.1858 joules/cal or 778 ft-lb/Btu.

Heat capacity: The heat capacity of a system is defined by the ratio of heat transfer to resultant temperature change, $C = dQ/dT$. The heat capacity takes on unique values for processes occurring at constant pressure and at constant volume. The heat capacity at constant pressure, $C_P = (dQ/dT)_P$, and the heat capacity at constant volume, $C_V = (dQ/dT)_V$. For a perfect gas the difference between these specific heats is a constant, $C_P - C_V = R$. Note, however, that only for calorically perfect gases are the specific heats themselves constant. High temperature gases characteristic of combustion products have specific heats which depend strongly upon temperature and therefore do not qualify as calorically perfect gases. Heat capacities may be measured experimentally at moderate temperatures and calculated with good accuracy at high temperatures from the spectroscopic characteristics of the gas. An extensive tabulation of heat capacities as a function of temperature is available in the JANAF^F Thermochemical Tables (5).

Second law of thermodynamics: The second law of thermodynamics places limitation upon the amount of work derivable in a thermodynamic process. More important among the consequences of the second law is the relation of heat transfer to the thermodynamic coordinates of the system. For a reversible process,

$$\frac{dQ_{rev}}{T} = dS \quad (2)$$

The differential change in the entropy, dS , is exact. Equation (2) is a definition for the thermodynamic property, the entropy. For an ideal gas, the entropy change is related in a simple fashion to the other thermodynamic coordinates.

$$dS = C_P \frac{dT}{T} + nR \frac{dP}{P} \quad (3)$$

$$dS = C_V \frac{dT}{T} + nR \frac{dV}{V} \quad (4)$$

Reversible processes are those for which the entropy of the system and its surroundings remain unchanged. Reversible adiabatic processes are necessarily isentropic. Chemical reaction and therefore combustion processes are irreversible and accompanied by an entropy increase. In a microscopic consideration of thermodynamics, the entropy is given an additional significance -- entropy is a measure of the disorder of the system.

The most important idea of the second law is that the entropy of an isolated system is a maximum at equilibrium. This principle

allows the prediction of the final equilibrium state that will obtain in a system. If the entropy maximum principle is applied to a simple system with two parts one finds the expected result that

$$T(2) = T(1)$$

for equilibrium when energy transfer is allowed and

$$P(2) = P(1)$$

for equilibrium when the two subsystems can exchange volume. The entropy maximum principle can be reformulated in terms of other thermodynamic functions but the second law always gives an extremum principle which can be used to find a final equilibrium state.

It is necessary to use such a principle to determine the equilibrium composition of a reactive mixture.

Enthalpy: The enthalpy of a system is defined by $H = U + PV$. The enthalpy is a particularly useful quantity in the description of constant pressure processes. The differential of enthalpy is exact. The enthalpy, therefore, may be evaluated as the integral of an analytic function. In particular, for an ideal gas,

$$dH = C_P dT \quad (5)$$

which may be integrated to give

$$H_T = H_0 + \int_{T_0}^T C_P dT \quad (6)$$

As was mentioned previously, the specific heat for high temperature gases is a function of the temperature. The integral, therefore, may be evaluated only if the dependence of the specific heat upon temperature, $C_P = C_P(T)$, is known. Only for the special case of the calorically perfect gas is $H_T - H_0 = C_P(T - T_0)$.

In chemically reactive systems, the enthalpy arising from temperature change, the "sensible enthalpy" or $\int C_P dT$, is not sufficient to describe completely the enthalpy of the system. To account for the capacity of the system to undergo chemical reactions one must identify the constant of integration in equation (6) as the enthalpy of formation of the specie. In standard notation, then,

$$H_0 = \Delta H_{fT_0}^0 \quad (7)$$

The enthalpy of formation, $\Delta H_{f,T_0}^{\circ}$, is the enthalpy required to form the specie from the standard state elements at a pressure of one atmosphere and at a temperature, T_0 . By convention, the standard state elements are taken to be the elements in their natural forms. For example, standard state elements are: gaseous molecular nitrogen, $N_2(g)$; gaseous molecular hydrogen, $H_2(g)$; graphitic carbon, $C(gr)$; etc. The reference temperature, T_0 is taken to be 298.15°K (25°C. or 77°F.). The superscript (\circ) denotes the standard state condition of 1 ATM. The enthalpies of formation for ideal gases are independent of pressure, i.e., functions of temperature alone. Some enthalpies of formation of species of interest to combustion processes are recorded in Table 1.

Enthalpies of formation are measured experimentally by calorimetric means, deduced from measured enthalpies of formation of related species, or estimated from bond energies. The enthalpy of formation is an index of the potential of the specie to undergo an exothermic reaction. The larger the enthalpy of formation, the more likely is the specie to enter into an exothermic reaction. Nearly non-reactive species, such as water or carbon dioxide, have negative enthalpies of formation. Once again, the JANAF Thermochemical Tables (5) provide an excellent source for enthalpies of formation.

Internal energy: The internal energy, U , was first mentioned in connection with the statement of the first law of thermodynamics. For combustion studies, it is generally necessary only to include sensible and chemical energies in the accounting of internal energies. The differential of internal energy is exact. For an ideal gas,

$$dU = C_V dT \quad (8)$$

and may be integrated to give,

$$U_T = U_0 + \int_{T_0}^T C_V dT \quad (9)$$

As for the enthalpy, the constant of integration is related to a capacity to undergo an exothermic reaction.

$$U_0 = \Delta U_{f,T_0}^{\circ} \quad (10)$$

other forms of internal energy, e.g., gravitational potential energy and kinetic energy, may be neglected in most combustion

Table 1. Enthalpies of formation of species of interest as combustion reactants or products. Formation from assigned reference elements, 298.15°K, in kcal/mole. Gas phase unless otherwise noted.

C	171.3	C ₆ H ₆ (l)	19.8
C(gr)	0	n-C ₆ H ₁₄	-40.0
CH	142.4	n-C ₇ H ₁₆	-44.9
CHO	-3.2	n-C ₈ H ₁₈	-49.8
CH ₂	69.0	H	52.1
CH ₃	33.4	HN	78.9
CH ₃ OH	-48.1	HNO	23.8
CH ₃ NO ₂ (l)	-26.7	HNO ₃ (l)	-41.4
CH ₄	-17.9	HO	9.3
CH ₄ (l)	-20.3	HO ₂	5.0
CN	96.4	H ₂	0
CO	-26.4	H ₂ O	-57.8
CO ₂	-94.1	H ₃ N	-11.0
C ₂	200.0	H ₄ N ₂ (l)	12.05
C ₂ H ₂	54.9	N	113.0
C ₂ H ₄	12.5	NO	21.6
C ₂ H ₆	-20.2	NO ₂	8.0
C ₂ H ₅ OH	-50.2	N ₂	0
C ₂ N ₂	73.8	N ₂ O	19.5
C ₃	189.7	N ₂ O ₄	2.3
C ₃ H ₈	-24.8	O	59.6
C ₃ H ₇ OH(l)	-71.9	O ₂	0
n-C ₅ H ₁₂	-35.0		

problems. Should the need arise, then any other form of internal energy could be included in the "energy accounting system" described above.

Helmholtz and Gibbs functions: These two functions, often called the Helmholtz free energy and the Gibbs free energy, are used to determine equilibrium conditions for systems under specified constraints. The Helmholtz function, A , is defined as

$$A = U - TS \quad (11)$$

and obeys the following extremum principle: the Helmholtz function is a minimum for the final equilibrium state of a system at constant volume and constant temperature.

The Gibbs function, G , is defined as

$$G = H - TS \quad (12)$$

the Gibbs function is a minimum for the final equilibrium state of a system at constant temperature and pressure.

The symbol F is commonly used for the Helmholtz function by physicists and for the Gibbs function by chemists. (The JANAF tables use F for the Gibbs function).

The (exact) differentials of the various thermodynamic properties are given by the following relations:

$$dU = TdS - PdV \quad (13)$$

$$dH = TdS + VdP \quad (14)$$

$$dA = -PdV - SdT \quad (15)$$

$$dG = VdP - SdT \quad (16)$$

Mixtures: It is convenient to relate the thermodynamic properties of a mixture to the thermodynamic properties of its components. To do this in the general case requires the use of so-called partial

molar quantities (4). Fortunately most combustion problems involve high temperature gases which are adequately described by ideal gas laws. For ideal gases the mixture property is simply the weighed sum of the component properties at the same temperature and partial pressure of the component in the mixture. The partial pressure, p_i , is defined as

$$p_i = x_i P = (n_i/n)P \quad (17)$$

where x_i is the mole fraction of species i , n_i is the number of moles of species i , and n is the total number of moles; obviously,

$$\sum_{i=1}^m n_i = n \quad (18)$$

$$\sum_{i=1}^m x_i = 1 \quad (19)$$

$$\sum_{i=1}^m p_i = P \quad (20)$$

where m is the number of species in the mixture.

The internal energy of the ideal gas mixture is given by

$$U(T,x) = \sum_{i=1}^m n_i u_i(T) \quad (21)$$

and the mixture entropy is given by

$$S(T,P,x) = \sum_{i=1}^m n_i x_i(T,p_i) \quad (22)$$

The lower case symbol denotes the quantity per mole. Note that the entropy of a species must be evaluated at the partial pressure of that species. The temperature and total pressure are uniform throughout an equilibrium thermodynamic system.

Composition change. For open systems and systems where the composition changes due to chemical reactions equations 13-16 must be augmented to account for the effects of composition change on the thermodynamic properties. This is done by introducing the chemical potential defined as

$$\mu_i = \left(\frac{\partial U}{\partial n_i} \right)_{S, V, n_{j \neq i}} = \left(\frac{\partial H}{\partial n_i} \right)_{S, P, n_{j \neq i}} = \left(\frac{\partial A}{\partial n_i} \right)_{T, V, n_{j \neq 1}} = \left(\frac{\partial G}{\partial n_i} \right)_{T, P, n_{j \neq 1}}$$

The notation $n_{j \neq i}$ implies that the differentiation with respect to n_i is taken holding all the other moles numbers n_j ($j \neq i$) constant. With this definition the differentials of the thermodynamic properties become

$$dU = TdS - PdV + \sum_{i=1}^m \mu_i dn_i \quad (23)$$

$$dH = TdS + VdP + \sum_{i=1}^m \mu_i dn_i \quad (24)$$

$$dA = PdV - SdT + \sum_{i=1}^m \mu_i dn_i \quad (25)$$

$$dG = VdP - SdT + \sum_{i=1}^m \mu_i dn_i \quad (26)$$

Note that these equations are completely general and reduce to equations 13-17 for constant composition (all $dn_i = 0$).

The chemical potential is a somewhat abstract quantity which is best understood as the mass transfer analog of the temperature. We consider heat to flow from higher to lower temperatures and thermal equilibrium to be reached when temperatures are equal. Similarly, if it is possible for matter of species i to be transferred between two systems, the matter will flow from the system with the higher value of chemical potential, μ_i , to that with the lower value of μ_i , and equilibrium with respect to mass transfer of species i occurs when the value of μ_i is the same for both systems.

STOICHIOMETRY

When chemical reactions take place all the mole number changes are no longer independent. The conservation of chemical elements places restrictions on the allowed variations of the dn_i . Analysis of the composition change in a chemical reactions comes under the name of "stoichiometry." It is important to distinguish between the actual composition change in a reactive process and the use of balanced chemical reactions which are a tool used in solving problems.

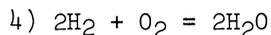
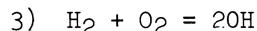
As an example consider the reaction of hydrogen and oxygen. The possible species include H_2 , O_2 , H_2O , OH , H , and O . (It is

also possible to consider peroxy species HO_2 and H_2O_2 , but these will be neglected in this example.) We have 6 species to consider in this case, but not all are independent since we must have conservation of H atoms and O atoms, i.e.

$$n_{\text{H}} + 2n_{\text{H}_2} + 2n_{\text{H}_2\text{O}} + n_{\text{OH}} = \text{constant}$$

$$n_{\text{H}_2\text{O}} + n_{\text{OH}} + n_{\text{O}} + 2n_{\text{O}_2} = \text{constant}$$

The two equations of constraint reduce the number of independent composition variables from six to four. We could differentiate the two equations immediately above and obtain a relation between the dn_i which would allow us to eliminate two of them. The general procedure, which is completely equivalent, is to consider balanced chemical equations. One then defines a reaction progress variable for each equation. In this case we need four independent variables so we would require four reactions, e.g.



The composition changes are then related to the degrees of advancement, ξ , of the chemical reactions as follows

$$dn_{\text{H}} = 2d\xi_1$$

$$dn_{\text{O}} = 2d\xi_2$$

$$dn_{\text{OH}} = 2d\xi_3$$

$$dn_{\text{H}_2\text{O}} = 2d\xi_4$$

$$dn_{\text{H}_2} = -d\xi_1 - d\xi_3 - 2d\xi_4$$

$$dn_{\text{O}_2} = -d\xi_2 - d\xi_3 - d\xi_4$$

The above equations indicate that we are effectively regarding dn_{H} , dn_{O} , dn_{OH} , and $dn_{\text{H}_2\text{O}}$ as the independent variables in this system. The use of balanced chemical reactions provides a straightforward, general scheme for taking atom conservation into account. (This is to be expected as atom conservation forms the basis for balanced chemical reactions.)

In the general case we can write our reactions as

$$\sum_{i=1}^m \nu'_{ij} R_i = \sum_{i=1}^m \nu''_{ij} P_i \quad j=1 \dots r \quad (27)$$

where R_i denotes a reactant species, P_i denotes a product species and the quantities ν'_{ij} and ν''_{ij} are called the stoichiometric coefficients for reaction j . The number of reactions, r , which must be considered is simply equal to the number of chemical species less the number of different atoms present in the system. Any choice of linearly independent chemical reactions will suffice for a thermodynamic analysis. It is usually easiest to choose the set of chemical reactions where species are formed from their naturally occurring chemical elements. This provides a consistent scheme which is readily adapted to machine computation.

In terms of the reaction progress variables for our general scheme the changes in mole number are given by

$$dn_i = \sum_{j=1}^r (\nu''_{ij} - \nu'_{ij}) d\xi_j \quad (28)$$

Note that we formally consider each species to be written on both sides of every chemical equation. This is done to provide easy extension to a computer solution. Of course, most of the stoichiometric coefficients will be zero.

In the example of hydrogen-oxygen reaction we have the following tables:

		ν'_{ij}			
		1	2	3	4
species i	reaction j				
	H	0	0	0	0
	O	0	0	0	0
	OH	0	0	0	0
	H ₂ O	0	0	0	0
	H ₂	1	0	1	2
	O ₂	0	1	1	1

		ν''_{ij}			
		1	2	3	4
species i	reaction j				
	H	2	0	0	0
	O	0	2	0	0
	OH	0	0	2	0
	H ₂ O	0	0	0	2
	H ₂	0	0	0	0
	O ₂	0	0	0	0

From equation 28 we can write

$$\sum_{i=1}^m \mu_i dn_i = \sum_{i=1}^m \mu_i \sum_{j=1}^r (\nu_{ij}'' - \nu_{ij}') d\xi_j = \sum_{j=1}^r \left(\sum_{i=1}^m (\nu_{ij}'' - \nu_{ij}') \mu_i \right) d\xi_j \quad (29)$$

This can be substituted into equations 23-26. In particular we can write dG as

$$dG = SdT + VdP + \sum_{j=1}^r \left(\sum_{i=1}^m (\nu_{ij}'' - \nu_{ij}') \mu_i \right) d\xi_j \quad (30)$$

The fundamental difference between the mole numbers, n_i , which represent the actual composition in a given problem, and the stoichiometric coefficients, ν_{ij}' and ν_{ij}'' , which represent the mathematical coefficients in a balanced chemical equation should be clearly recognized. The stoichiometric coefficients are simply numerical tools which allow us to calculate the composition.

Specification of the initial reactant composition usually is made in terms of mixture ratio. A quantity such as the fuel-oxidizer mass ratio may be used. The equivalence ratio is a particularly useful quantity to specify the reactant composition. Defined as

$$\phi = \frac{\frac{\text{fuel}}{\text{oxidizer}}}{\left(\frac{\text{fuel}}{\text{oxidizer}} \right)_{\text{stoichiometric}}} \quad (31)$$

the equivalence ratio is a normalized, non-dimensional quantity and may therefore be formed from the mass, mole, or volume ratios of the fuel and oxidizer. The stoichiometric mixture ratio corresponds to complete reaction, that is, to the reactant quantities which would allow reaction to normal oxidation state products. (For systems with C, H, O, and N atoms only the stoichiometric reactant composition is the one which could produce only CO_2 , H_2O , and N_2 on the basis of atom conservation.) An equivalence ratio of less than one is fuel lean; greater than one, fuel rich; and equal to one, stoichiometric. For the hydrogen/oxygen reaction

$$\phi = (n_{\text{O}_2} / n_{\text{H}_2}) / (1/2) = (m_{\text{O}_2} / m_{\text{H}_2}) / (4/32)$$

(m = mass; subscript (o) denotes initial composition).

THERMOCHEMISTRY

In calculations of changes of the thermodynamic properties in reacting systems one can simply write

$$Y_2 - Y_1 = \sum_{i=1}^m n_{i2} y_i(T_2, P_2, n_2) - \sum_{i=1}^m n_{i1} y_i(T_1, P_1, n_1) \quad (32)$$

where Y denotes any extensive thermodynamic property. In particular the enthalpy change for a process is given by

$$H_2 - H_1 = \sum_{i=1}^m n_{i2} h_i(T_2) - \sum_{i=1}^m n_{i1} h_i(T_1) \quad (33)$$

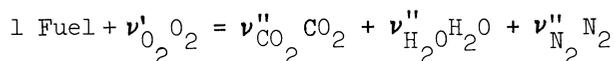
where the enthalpy is given by equations 6 and 7.

One also speaks of the standard enthalpy of reaction which is defined for a balanced chemical reaction, at a given temperature; this is defined as

$$\Delta H_{Rj}^{\circ}(T) = \sum_{i=1}^m (\nu''_{ij} - \nu'_{ij}) h_i^{\circ}(T) \quad (34)$$

again the enthalpies are given by equations 6 and 7. Note the difference between the two definitions of an enthalpy change; one involves the actual change in mole numbers and two thermodynamic states; the other involves the stoichiometric coefficients and has both reactants and products at the same temperature and standard state pressure.

The values of ΔH_R for balanced stoichiometric combustion reactions are usually given for the reaction of 1 mole of fuel (i.e. $\nu'_{\text{fuel}} = 1$). The general stoichiometric reaction for a fuel with some combination of C, H, O, or N, atoms is



for which (subscript F denotes fuel)

$$\begin{aligned} \Delta H_{R}^{\circ}(T_0) = & \nu_{CO_2}'' h_{CO_2}^{\circ}(T_0) + \nu_{H_2O}'' h_{H_2O}^{\circ}(T_0) + \nu_{N_2}'' h_{N_2}^{\circ}(T_0) \\ & - \nu_{O_2}' h_{O_2}^{\circ}(T_0) - h_F(T_0) \end{aligned} \quad (35)$$

Combustion reactions are by definition always exothermic. The enthalpy of formation of the reactants must therefore exceed the enthalpy of formation of the products. From equation (35), en-