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Fundamentals of Combustion for Environmental Applications - Part 1 of 2

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Fundamentals of Combustion for Environmental Applications - Part 1 of 2

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COURSE CONTENT

Purification by fire is an ancient concept, its applications noted in the earliest chapters of recorded history. Modern application of high temperature processes to achieve this end [1] reflect the increasing awareness by modern health and environmental professionals of the importance of effective biological sterilization of bacteria, viruses, prions and other pathological infectious agents; of the achievement of high levels of destruction of toxic, carcinogenic, teratogenic, and mutagenic organic matter that adversely impacts on the quality and duration of human and other animal and plant life; and of the substantial neutralization of the flame and explosion hazards associated with highly volatile combustible materials.

This course assumes a basic understanding of chemistry and mathematics. It presumes basic engineering analysis perspectives but, through text and examples guides the student an understanding of the processes and interactions of burning systems. The course includes:

- The basics of units and fundamental relationships for mass and energy;
- The special issues in waste characterization for combustion applications;
- Mass and energy balances; and
- The basics of equilibrium and chemical kinetics.

Part 2 of the course carries the student further into furnace behavior, fluid mechanics, refractory and other more applied issues in combustor design and operation.

Many texts on combustion fall back on the “3-T’s” . . . a simplistic rule stating that all you need for good combustion is Time, Temperature and Turbulence. WOW! If that were all there is to it, the course would be over, you would collect your PDH’s (and I my course fee) and we would retire to the bar to celebrate. But high temperature processes are too complex and the consequences of partial success too profound to allow one to depend on such imprecise (but not wrong) design principles:

- The ever-changing chemical and physical characteristics of wastes (“fuels” is a more productive way to think of them) makes for an uncertain statement of the combustion scenario;
- The materials handling of irregular and inconsistent materials with aggressive and problematic properties creates a major challenge in formulating a reliable equipment strategy that achieves the uniform feed rates needed to achieve good performance by high temperature, combusting systems with heat recovery;
- The vigorous attack of materials of construction, exacerbated by elevated temperatures and a destructive mix of erosive and corrosive mechanisms risks the on-line availability of combustion systems and escalates maintenance expense;
- The complexity of combustion chemistry and reaction rates (kinetics) for mixtures of compounds often containing halogens, sulfur, metals, double and triple bonds, polynuclear aromatic structures etc. makes assured achievement of “four, or six, 9’s” (99.99% or 99.9999% destruction removal efficiency) uncertain.

- Complexity arising from fluid mechanical considerations (laminar and turbulent regions involving both eddy and diffusional transport mechanisms; buoyancy effects; jet flow dynamics; plug, recirculating and swirling flow, etc.) considering that combustion's chemical reactions require the collision of molecules of fuel and oxidant at an atomic scale and not coarse mixing as "jelly-rolls" of air and fuel, broadly drawn, encourages conservative designs.

- Complex physical processes, including evaporation, sublimation, and all three forms of heat transfer mechanisms (radiant, convective and conductive) that, again, fosters conservatism in design and in the formulation of operational strategy.

- All of the above physical and chemical processes and events take place in enclosures with significant gradients in temperature (with its profound effect on reaction rate, gas density, vapor pressure of evaporating fuels etc.), in oxygen concentration and in residence time. As important, all of these and most other process parameters are usually time-variant.

With this grim view of the complexity of the process, one is tempted to retreat to the 3 T's and go forth. Yet application of basic chemical and physical laws, use of the resources of the technical literature and a significant body of correlations and data on both the chemistry and mixing processes in combustors are available that give those designing, troubleshooting, or regulating combustion systems the tools to analyze, size and select equipment and anticipate and/or solve operational problems. This course is intended to provide you with these basic engineering analysis tools. It is well to remember that pencils and paper are ever so much cheaper than concrete and steel.

A. Units

The U.S. engineering literature is still ambivalent in its use of English or metric units. While chemical engineers use mols (the mass of a compound divided by its molecular weight), mechanical engineers often favor weight units. Reporting temperature in Fahrenheit or Centigrade (Celsius) units varies and, depending on the processes being analyzed, 460 is added for Rankin or 273.15 for Kelvin, respectively, to yield the "absolute temperature" if a reference of absolute zero is appropriate. Energy is reported in Btu or kilocalorie (or joule) units. Pressure is reported in pounds per square inch (psi) as "gauge" (i.e. the pressure above normal atmospheric pressure) or "absolute" (referenced to zero pressure), in atmospheres or Pascals. Table 1 has several important conversion factors.

Table 1 Conversion Factors

Temperature	**Length**	**Area**	**Volume**
°C =5/9(°F -32)	1 m =3.281 ft	1 m^2 = 10.76 ft^2	1m^3 = 35.31 ft^3
°F =9/5 °C +32	1ft = 30.48cm	1 ft^2 = 909 cm^2	1 gal = 3.785 liters

Pressure (absolute)	**Mass**	**Energy**
1 atm. = 14.7 psi = 1.0133 bar	1 kg = 2.2046 lb	1 Btu = 0.252 kcal
1 atm. = 760 mm Hg	1 lb = 454 grams	1 kcal = 4.184 kilojoules
1 atm. = 101.33 kilopascals	1 metric ton = 2205 lb	1 kcal/kg = 1.8 Btu/lb

B. Fundamental Relationships

1. The Perfect Gas Law

The behavior of "ideal gases" is described by Equation 1 -The "Perfect Gas Law"

$$PV = n\mathcal{R}T \qquad (1)$$

Where P is the absolute pressure of the gas, V is its volume, n is the number of mols and T is the absolute temperature (R or K degrees). $\mathcal{R}$ is the Universal Gas Constant. For high temperature combustion systems and, indeed, even for most room temperature situations, the statistical thermodynamic assumptions implicit in the Perfect Gas Law are quite satisfactory. The Universal Gas Constant is the same for all gases. Note, however, that in some of the mechanical engineering literature the gas constant used equals the universal constant $\mathcal{R}$ divided by the molecular weight of the compound of interest and, instead of using the number of mols (n), one uses the mass of the compound. Table 2 includes values of the Universal Gas Constant for different energy, pressure, volume, mols and temperatures.

Table 2 Values of the Universal Gas Constant ($\mathcal{R}$)

Energy	Pressure	Volume	Mols	Temp.	Constant	Units
----	atm	m^3	kg mol	K	0.08205	m^3 atm/kg mol K
----	atm	liters	g mol	K	0.08205	l^3 atm/gram mol K
----	kPa	m^3	kg mol	K	8.3137	m^3 kPa/kg mol K
kcal	----	----	kg mol	K	1.9872	kcal/kg mol K
joules	----	----	g mol	K	8.3144	joules/g mol K
ft-lb	psia	ft^3	lb mol	R	1545.0	ft lb/lb mol R
Btu	----	----	lb mol	R	1.9872	Btu/lb mol R
---	atm	ft^3	lb mol	R	0.7302	ft^3 atm/lb mol R

In combustion calculations, one commonly knows the number of mols and the temperature and need to calculate the volume. For these calculations, it is convenient to obtain the answer by adjusting a unit volume at specified standard conditions to the conditions of interest. For such calculations, one can use the gas laws expressed in terms of the volume of one kg mol (or one lb mol) of an ideal gas at the standard temperature (T_o) of 0 °C (32 °F) and standard pressure of 1 atm (P_o). The molecular volume V_o is 22.4 m^3 (359.3 ft^3) per kg (lb) mol. The volume V at an arbitrary temperature T and pressure P is given by Equation 2:

$$V = n \; x \; V_o \; x \; \frac{P_o}{P} \; x \; \frac{T}{T_o} \qquad (2)$$

where pressure and temperature are expressed in any consistent absolute units.

2. Standard Conditions

In the literature, in regulations, in industrial data sheets, etc. one frequently finds references to the term "Standard Conditions." This nomenclature implies standardization but one should be cautioned that the meaning is not at all consistent. U.S. fan manufacturers and the U.S. natural gas industry refer to 60 °F and 14.7 psi (absolute). The manufactured gas industry uses 60 °F but adds that the gas is saturated with water vapor at 30 inches of mercury (absolute) for marketing but dry at 1 atm for combustion calculations. Other important appearances of the term "standard conditions" are found in the calculations and reports associated with permits for atmospheric discharges (air permits). In that case, for the USEPA and in most states, the reference is dry at 20 °C (68 °F) and 1 atm (dscm).

The reference states used to specify and report pollutant concentrations in regulations and permits often generate another set of "standard conditions." In the U.S., this often involves calculation of volume in standard cubic feet (scf) at a reference temperature of 32 °F and 1 atm. Europeans use the metric equivalent (0°C and 1 atm and report in "normal cubic meters" or Nm^3). Most regulations also correct the gas volume to a specified oxygen concentration (to prevent the use of "dilution as the solution to pollution" approach to meeting concentration-based emission limits). This reference concentration is usually 7% O_2 in the U.S. but is often 11% O_2 in Europe and Asia. In some cases, correction to a reference CO_2 concentration (often 12%) is required. Correction of a measured volume to these reference concentrations can be readily effected using the following correction factors (C_{O_2} and C_{CO_2} respectively) applied to the base gas volume:

$$C_{O_2} = {[21.0 - measured \; \%O_2]}\Big/{[21.0 - reference \; \%O_2]} \qquad (3)$$

$$C_{CO_2} = {[measured \; \%CO_2]}\Big/{[reference \; \%CO_2]} \qquad (4)$$

C. Energy

Clearly, the availability and release of chemical energy in fuels and wastes is a core matter in combustion analysis and system behavior. We need to know how much energy is available from a given material and, when released, what the impact is: the ultimate gas temperature and the heat available to heat materials or generate steam. In this discussion, the basic unit of heat energy will be the kcal: the amount of heat necessary to heat one kilogram of water 1 °C. The English unit equivalent (the British thermal unit or Btu) relates to heating one pound of water 1 °F.

Analysis of the processes and consequences of releasing of heat energy through combustion involves several technical matters:

- Assessing the Heat of Combustion ΔH_c (the energy released in oxidation).
- Assessing the Sensible Heat of Gases (most of the released energy ends up as an elevated temperature of the flue gases generated in combustion: a mixture of N_2 and excess O_2, and the products of combustion . . . usually a mix of CO_2, H_2O, SO_2, and HCl and lesser amounts of CO and nitrogen oxides).
- Assessing secondary energy sinks such as (1) latent heat (the energy, for example, to vaporize any liquid water); (2) the sensible heat in "ash" residues; and (3) heat losses by conduction through the walls of the combustor's enclosure, ducts, etc.

1. Heat of Combustion

The ΔH_c is defined as the net enthalpy change resulting from the complete oxidation of a material starting at a reference temperature of 20 °C. Such an oxidation process can, in most cases, be expected to result in the oxidation of carbon in the material to carbon dioxide (CO_2), of hydrogen to water (H_2O), of sulfur to sulfur dioxide (SO_2), and of chlorine to hydrochloric acid (HCl). One must be a bit careful in making this assumption since, some of the carbon may be present in the feed material not as, for example, in hydrocarbons but as inorganic carbonates (such as in calcium carbonate). Some of the hydrogen may already be fully oxidized (such as the bound water in crystals of copper sulfate hexahydrate ($CuSO_4 \cdot 6\ H_2O$). Some of the sulfur may be present not in pyritic (sulfide) form or in proteins or other organic compounds but as inorganic sulfur in compounds such as in the gypsum in sheetrock ($CaSO_4$) which is already oxidized. Also, some of the chlorine may not be as organic chlorine (such as in the plastic PVC) that reacts with available hydrogen to form HCl but as inorganic chloride salts such as deicing calcium chloride ($CaCl_2$) or table salt (NaCl) which stays in the ash. Also, some of the oxygen for combustion may be already present in the waste itself (e.g. the oxygen in the sugar sucrose: $C_{12}H_{22}O_{11}$).

The fuel heat content of a given material is released in the oxidation process. In most cases, the majority of the heat of combustion finds itself elevating the temperature of the products of combustion but a portion is devoted to vaporizing any water brought in with the fuel or formed in the combustion of hydrogen in the fuel chemistry. The heat of combustion can, therefore, be expressed either with the water condensed where it is known as the *Higher Heating Value* (HHV) or with the water as vapor (the *Lower Heating Value* (LHV). The HHV is the common way to report ΔH_c data in the U.S. and British literature. Clearly, however, in a real furnace, the sensible heat content of the flue gases is lower than would be suggested by the HHV by an amount of energy equivalent to the latent heat of vaporization of the water (10,507 kcal/kg mol at 25 °C). For methane, the primary constituent of natural gas, this corresponds to 21,014 kcal per kg mol of methane: about 10% of the HHV or 212,950 kcal/kg mol. The LHV is the energy release value commonly reported in the literature of continental Europe and the Far East.
For a fuel with a dry basis hydrogen content of % H_2 (expressed as a percent), the HHV and LHV (dry basis) are related by:

$$LHV = HHV - 94.315\ [\%\ H_2] \quad \text{for LHV and HHV in Btu/lb and} \qquad (5a)$$
$$LHV = HHV - 52.397\ [\%\ H_2] \quad \text{for LHV, HHV in kcal/kg} \qquad (5b)$$

The three heating value estimation relationships that follow were developed to estimate the higher heat of combustion (ΔH_c) of the combustible fraction of industrial and municipal wastes (kcal/kg) on a moisture and ash-free or "MAF" basis. *One must use the weight percent of hydrogen (*H*), oxygen (*O*), organic and pyritic sulfur (*S*) etc. on a dry, ash-free basis and substitute the percent (*not *the decimal percent) value in the equations.*

Chang Equation

$$\Delta H_c = 8561.11 + 179.72\ H - 63.89\ S - 111.17\ O - 90.00\ Cl - 66.94\ N \qquad (6)$$

Modified Dulong Equation

$$\Delta H_c = 78.31\ C + 359.32\ (H - O/8) + 22.12\ S + 11.87\ O + 5.78\ N \qquad (7)$$

Boie Equation

$$\Delta H_c = 83.22\ C + 276.48\ H - 25.8\ O + 25.0\ S + 15.0\ N + 9.4\ Cl + 18.5\ F + 65.0\ P + 12.2\ Fe \qquad (8)$$

The Chang Equation [2], the Modified Dulong Equation and the Boie Equation [3] were tested [1] against one another for the prediction of the HHV of 150 pure organic compounds where laboratory data were available to test the accuracy of prediction. In this comparison, the average error relative to the laboratory value was: for Chang 1.48%; for Dulong 5.54%; and for Boie, 11.38%.

Chang's Equation was clearly superior for this task. However, the Boie Equation was originally developed and is well regarded for estimation of the HHV of mixed wastes (esp. high cellulosic material) such as refuse or wood. The Modified Dulong Equation is generally best for fuel-like, high carbon and hydrogen-containing materials such as coal, peat or lignite but less accurate for refuse predictions.

2. Sensible Heat of Gases

In analyzing temperature scenarios in combustion systems it is often necessary to calculate the sensible heat (enthalpy) associated with the combustion gases or preheated air at elevated temperatures or to calculate the change in enthalpy (Δh) between, say, temperatures T_1 and T_2. These calculations can be based on the approximation that the heat content per mol of each gas (kcal/kg mol) which incidentally is numerically identical to the heat capacity in Btu/lb mol °F is given by:

$$\Delta h = \int_{T_1}^{T_2} Mc_p^o\, dT \ \frac{kcal}{kg\ mol} \qquad (9)$$

This integration can be carried out using an analytical expression for the heat capacity (Mc_p^o kcal/kg mol °C) as a function of temperature. Values of a quadratic (3-constant) form of the heat capacity are given in Table 3 for several common gases. Using this heat capacity function, the heat content (Δh) of a mixture of i gases (containing n_i mols of each gas) in a gas mixture is calculated from:

$$\Delta h = \sum_{1}^{i} n_i \left[a_i(T_2 - T_1) + \frac{b_i(T_2^2 - T_1^2)}{2} + \frac{c_i(T_2^3 - T_1^3)}{3} \right] \frac{kcal}{kg\ mol} \qquad (10a)$$

One can easily carry out such computations using a spreadsheet program such as Excel. The heat content can be calculated at each of a series of temperatures and a graph constructed of the flue gas heat content vs. temperature. Reductions must be made in the total heat content column for (1) the latent heat of any water formed in the combustion, (2) by the heat content of any solid residues (including heats of fusion if the melting points are exceeded) and (3) the system heat losses (see below for estimation methods for the latter two quantities). An example of such a calculation and its utility is shown in the material and energy balance below.

3. Average Heat Capacity

If the enthalpy change in Equation 10a is calculated between a reference temperature such as 15.56 °C (or 60 °F) and some higher temperature (T) and the resulting enthalpy is divided by the arithmetic temperature difference (T – 15.56), the average molal heat capacity ($Mc_{p,ave}^o$) results. Then,

$$\Delta h = n\, Mc_{p,ave}^o\ (\mathrm{T} - 15.56)\ \mathrm{kcal} \qquad (10b)$$

The average molal heat capacity can be plotted vs. temperature as a handy resource in rough energy calculations [1]

4. Sensible Heat of Solids

Kopp's Rule (Equation 11) can be used to estimate the heat content per mol of solid compounds (Mc_p) containing n atoms.

$$Mc_p = 6\mathrm{n\ kcal/kg\ mol\ °C} \qquad (11)$$

For many inorganic compounds (e.g. "ash"), a mean heat capacity of 0.2 to 0.3 kcal/kg °C is a reasonable assumption.

Table 3 Constants in Molal Heat Capacity (Mc_p^o) Relationship with Temperature ($Mc_p^o = a + bT + cT^2$ where T is in °C)

Compound	A	b	c
H_2	6.92	0.153E-3	+0.279E-6
O_2	6.95	2.326E-3	-0.770E-6
N_2	6.77	1.631E-3	-0.345E-6
Air	6.81	1.777E-3	-0.434E-6
CO	6.79	1.840E-3	-0.459E-6
CO_2	9.00	7.183E-3	-2.475E-6
H_2O	7.76	3.096E-3	-0.343E-6
SO_2	9.29	9.334E-3	-6.380E-6
HCl	6.45	1.975E-3	-0.547E-6
CH_4	8.00	15.695E-3	-4.300E-6

5. Latent Heat

The change in state of elements and compounds, for example, from solid (s) to liquid (l), or from liquid (l) to gas (g) is accompanied by a heat effect: the latent heat of fusion, sublimation, or vaporization for the state changes (s) → (l), (s) → (g), and (l) → (g), respectively. Latent heat effects in many industrial processes are negligible. For example, the heat of vaporization of fuel oil is usually neglected in combustion calculations. Particularly for incinerator design calculations involving wastes or fuels with a high hydrogen content and/or high moisture content, latent heat effects are very significant. For reference, several latent heat values are given in Table 4.

Table 4 Latent Heat Effects for Changes in State of Common Materials

			Latent heat of indicated state change		
Material	State Change	Temp. (°C)	kcal/kg	kcal/kg mol	Btu/lb
Water	Fusion	0	80	1,435	144
Water	Vaporization	100	540	9,712	971
Acetone	Vaporization	56	125	7,221	224
Benzene	Vaporization	107	94	7,355	170
Methanol	Vaporization	65	60	12,614	473
Zinc	Fusion	419	28	1,839	51

6. Heat Losses

Real combustors are not perfectly insulated and some heat (called the "radiation loss") is lost to the surroundings by a combination of conduction through the containing ductwork and chamber walls followed by natural or forced convection and radiation from the outer surfaces. The American Boiler Manufacturer's Association developed a dimensional algorithm (Equation 12) with which to estimate heat losses from boilers and similar combustors. The estimate is generally conservative (high) for large furnaces.

$$Radiation\ loss = \left(\frac{3.6737}{C}\right)\left(\frac{HR \cdot C}{F_{OP}}\right)^{0.6303} e^{kW_{type}} \qquad (12)$$

Where for the radiation loss calculated in kcal/hr (or Btu/hr):

C = Constant: 1.0 for kcal/hr (0.252 for Btu/hr)

HR = Design Total Energy Input (fuel + waste heat of combustion+ air preheat) in kcal/hr (or Btu/hr)

F_{OP} = Operating Factor (actual HR as decimal percent of design HR)

k = Constant dependent on the method of wall cooling and equal to:

Wall Cooling Method	k
Not cooled	+ 0.0
Air cooled	- 0.0013926
Water cooled	- 0.0028768

W_{type} = Decimal fraction of furnace or boiler wall that is air- or water-cooled

D. Systems Analysis

1. General Approach

● Basic Data
The basic information used in the analysis of combustion systems can include tabulated thermochemical data, the results of several varieties of laboratory and field analyses (concerning fuel, waste, residue, gases in the system) and basic rate data (usually, the flow rates of feed, flue gases etc.). Guiding the use of these data are fundamental relationships that prescribe the combining proportions in molecules (e.g., two atoms of oxygen with one of carbon in one molecule of carbon dioxide), and those that indicate the course and heat effect of chemical reactions.

● Basis of Computation
To be clear and accurate in combustor analysis it is important to specifically identify the system being analyzed. This should be the first step in setting down the detailed statement of the problem. In this course, the term ***basis*** will be used. In the course of prolonged analyses, it may appear useful to shift bases. Often, however, the advantages are offset by the lack of a consistent, one-to-one relationship between intermediate and final results, side calculations etc.

As the first step, therefore, the analyst should choose and *write down* the reference basis: a given weight of the feed material (e.g., 100 kg of waste) or an element, or a unit time of operation. The latter is usually equivalent to a weight, however, and in general, the weight basis is preferred. Note that this need not equal to actual throughput rate (kg/hr) but may be selected, for example, for the computational simplicity of a "round" rate basis.

● Approach to Computation
Although the skilled analyst may elect to skip one or more steps because of limited data or lack of utility, the following sequence of steps is strongly recommended:

- Sketch a flow sheet. Indicate all flows of heat and material, including recirculation streams. Document all basic data on the sketch including special features of analytical data and heat effects.
- Select a basis and annotate the sketch to show all known flows of heat or material relative to that basis.
- Apply material, elemental, and component balances. Recognize that the use of average values for quantities and characteristics is necessary but that variations from the average are most likely the norm rather than the exception. Explore alternative assumptions.
- Use energy balances. Here too, explore alternative assumptions.
- Apply known equilibrium and other thermodynamically useful relationships.
- Apply known reaction rate relationships.
- Review the previous steps incorporating the refinements from subsequent stages into the simpler, earlier work.

2. Analyses

Combustion systems for wastes (incinerators), unlike more convention combustors, are often charged with materials where the composition varies widely over time and that are highly complex mixtures of waste streams, off-specification products, plant trash, and so forth. The analysis of these wastes must often be a compromise.

In residential waste incineration, for example, what is a shoe? Is it (1) a shoe (i.e. a waste category easily identified by untrained field personnel in a waste sorting program)? (2) 0.5 kg in the "leather and rubber" category (i.e., a group characterization)? (3) 0.2 kg leather, 0.18 kg rubber, 0.02 kg iron nails, etc. (i.e. a detailed, component-by-component characterization that, often, can be tied to data on heating value and combustion chemistry)? (4) 8% moisture, 71% combustible, 21% residue, heating value of 3,800 kcal/kg? (5) The composition as given by ultimate analysis (see below)? (6) Properties as given by a proximate analysis (see below)? or (7) A non-hazardous waste constituent? These are the questions the waste engineer must ponder as they impinge upon the adequateness of his design in all sectors (heat release capacity, air pollution needs, materials of construction, energy recovery potential, etc), the need for rigorous detail (in consideration of feed variability), permitting issues, and, importantly, the sampling and analysis budget allocation.

The final decision should be based on the impact of errors on:

- *Regulatory and Permit definitions*: hazardous or non-hazardous designations
- *Materials handling*: bulk density, storability, explosion and fire hazard etc.

- *Fan requirements*: combustion air and draft fans
- *Heat release rate*: per square meter, per cubic meter of the combustor
- *Materials problems*: refractory or fireside boiler tube attack, corrosion in tanks, pipes, or storage bins, etc.
- *Secondary environmental problems*: air, water, and residue-related pollution
- *Process economics*: heat recovery rate, labor requirements, utility usage, etc.

There are no simple rules in this matter. Judgments are necessary on a case-by-case basis. The techniques described below, however, give the analyst tools to explore many of these effects on paper. The cost is much lower than detailed field testing and laboratory analysis and far less than is incurred after an incineration furnace has been installed and fails to operate satisfactorily.

The data generated for the evaluation of waste streams present problems to the analyst. The problem begins with the largely uncontrollable characteristics of the waste generators, the unusual nature of the waste itself and imperfections in the field sampling and waste analysis processes. These difficulties make it problematical to secure proper samples, to adequately preserve and reduce the gross samples from the field to the relatively small quantities submitted to the laboratory and to conduct the physical or chemical analyses themselves.

One of the first problems of concern is the need for a representative sample. Domestic waste composition has been shown to vary between urban and rural areas; between different economic and cultural groups; from month to month through the year; in different geographic, political and climatological areas. There is a profound variation in the quantities and characteristics of wastes generated by different industries and even between different process alternatives for manufacture of the same product.

This inherent variability in the basic waste composition is only the starting point in illustrating the difficulty in securing a sample (ultimately in the 1 to 50 gram size) that properly reflects the chemistry, heating value and other significant characteristics of "average" waste. Often, waste streams include constituents that are relatively massive and hard to subdivide (e.g., tree stumps or automobile engine blocks). Other constituents may be volatile or may biodegrade on standing. If trace elements or compounds are important, a single waste item (e.g., a single auto battery affecting the lead content of the waste) may be the repository of almost all of the material of interest in many tons of waste. If the item is included, the waste is "typical"; if not, the analysis is faulty.

Concern should also be given to the reported moisture level to assure that it typifies the material "as-fired." Often, wastes are supplied to the laboratory after air drying. This is either because the sampling team decided (without consultation) that such a step would be "good" or because insufficient attention was given to moisture loss during and after the waste was sampled. Not uncommonly, a waste sample may not be representative because the sampling team wanted to give you the "best they could find" or because they did not wish to handle some undesirable (e.g., decaying garbage) or awkward (e.g., a large pallet) waste components.

Let us leave this topic with an injunction to the engineer:

> *Know the details of the sampling methodology, the sample conditioning protocols, and the laboratory analysis and reporting methods before trusting the data.*

A second and as important consideration in the development and use of waste data relates to the definition of “average” as applied to waste parameters:

> *“Average” is the quality of a measurement that while often reported and relied upon as “the design basis,” as the assumed characteristics of the feed etc. is never observed in nature.*

Several types of waste analysis are available in support of combustion system analysis. The different analytical protocols characterize the waste materials from different perspectives to meet different appraisal objectives.

- Waste Component Analysis

For many waste streams, an acceptable and useful analysis is obtained by weighing the waste after separation into visually definable components. For municipal solid waste, the component categories often include: newsprint, corrugated cardboard, "other paper," food waste, yard waste, aluminum, metal (excluding aluminum and mostly ferrous metal), glass, leather, rubber, textiles, plastics, and miscellaneous. The use of these waste categories has obvious advantages in the separation step. Further, the weights in each category are often useful in assessing recycling processes and in monitoring trends in waste sources and composition. References [1] are available to convert composition data in these categories directly into the chemical and energy values needed for more quantitative analysis.

- Proximate Analysis

The balance between moisture, combustible and ash content and the volatilization characteristics of the combustible fraction at high temperatures are important properties affecting combustor design. A simple and relatively low cost laboratory test that reports these properties is called the *proximate analysis* [1]. The formal procedure includes the following steps:

- Heat in a crucible one hour at 104 to 110 °C. Report weight loss as *moisture*.
- Ignite in a covered crucible for seven minutes at 950 °C and report the weight loss (combined water, hydrogen, and the portion of the carbon initially present as or converted to volatile hydrocarbons) as *volatile matter*.
- Ignite in an open crucible at 725 °C to constant weight and report weight loss as *fixed carbon*.
- Report the residual mass as *ash*.

Recognize that the value reported as "moisture" includes not only free water but, inadvertently, any organic compounds (e.g., solvent) with significant vapor pressure at 110 °C. The value for "volatile matter" includes organic compounds driven off or pyrolyzed but may also include water driven off from hydroxides or hydrates. "Fixed carbon" includes the weight of carbon left behind as a char but the value may be reduced by reported weight gain for the crucible due to oxidation of metals. In the civil-sanitary engineering literature concerning sewage treatment plant sludge incineration, "volatile matter" data is often treated as though it was equivalent to "combustible matter." For wastewater treatment sludge containing many hydroxides and hydrated organic and inorganic compounds, this is incorrect. It is not surprising, therefore, that one finds a wider than reasonable range in the reported heating value of sludge volatile matter.

The proximate analysis is useful is to understand the patterns of heat release for a grate-type combustor (such as the “mass burn incineration” system). The moisture scales, obviously, the latent heat that must be supplied before the rest of the material can burn since the temperature will be held at or below 100 °C until the liquid water is evaporated. Further, the latent heat of evaporation and the mass of the moisture act to reduce the ultimate flame temperature. The volatile matter scales the fraction of the material that will be rapidly gasified from the feed and that will express a requirement for combustion air supply and mixing energy above the grate surface (overfire air). The fixed carbon scales the fraction of the material that will burn more slowly on the grate and, therefore, may require extended residence time to achieve good burn-out. Ash scales the requirement for materials handling of residue material and for residue disposal.

- Ultimate Analysis

For fuels, the term *ultimate analysis* refers to an analysis routine that reports: moisture (loss in weight, for solid fuels at 105 °C), combined water (equivalent to the oxygen) and the content of several elements. Carbon, available or net hydrogen (hydrogen other than in moisture and combined water), oxygen, total sulfur, nitrogen, and "ash" are always reported. Oxygen is generally determined by difference, and thus both the value for "percent oxygen" and the "combined water" value may be in error.

One must exercise caution in reviewing ultimate analysis data when significant fractions of the waste are other than C, H, O, N and S. For example, if a waste has 10% chlorine and 5% fluorine, the value reported for “oxygen” may be calculated as:

$$\%\ O_2 = 100 - \%C - \%H - \%N - \%S$$

when it should be calculated as:

$$\%\ O_2 = 100 - \%C - \%H - \%N - \%S - \%Cl - \%F$$

Since the equation used for calculating the percent oxygen is normally not displayed on the analysis sheet, it is important to check with the laboratory to be sure what computational method was used when reviewing ultimate analysis data for wastes with high percentages of halogens, phosphorous and other non-metallic elements.

In calculations relating to waste disposal systems, it may be appropriate to request analyses for chlorine and for environmentally significant elements (such as arsenic, beryllium, cadmium, chromium, nickel and lead), and other waste constituents that could influence the combustion process, affect ash fusion temperature (e.g. phosphorous) or would be important to air pollution permits and control technology selections or to water pollution assessments for scrubber blowdown or residue leachate. In general, several different samples are used to generate the total analysis report. Particularly for waste analysis, therefore, some numerical inconsistencies should not be unexpected and there is merit in considering multiple analyses to develop statistically meaningful averages.

As for the proximate analysis, the testing method can produce uncertain results for several analysis categories. The weight reported as "ash" will be changed by oxidation of metals in the sample, by the release of carbon dioxide from carbonates, by loss of water from hydrates or easily decomposed hydroxides, by oxidation of sulfides and other reactions. Also, volatile organic compounds (e.g., solvent) can be lost in the drying step thus removing a portion of the fuel chemistry from the sample.

- Thermochemical Analysis

The heat of combustion of wastes is, clearly, important information in incineration system analysis. However, one must be cautions in accepting even the mean of a series of laboratory values (noting that a bomb calorimeter uses only about 1 gram of sample) when there are problems in obtaining a representative sample. For both municipal and industrial incineration systems, the analyst must also recognize that within the hardware lifetime waste heat content will almost inevitably change: year-to-year, season-to-season and, even day-to-day. This strongly suggests the importance of evaluating the impact of waste variation on system temperatures, energy recovery etc. Further, such likely variability raises legitimate questions regarding the cost-effectiveness of extensive sampling and analysis programs to develop this type of waste property information.

- Special Analysis

A competent fuels laboratory offers other analysis routines that, for certain types of combustors or process requirements can provide essential information.

The *forms of sulfur* analysis breaks down the total sulfur content of the material into three categories: organic, sulfide (pyritic) and sulfate. The "organic" and "sulfide" sulfur forms will oxidize in an incineration environment thus contributing to the stoichiometric oxygen requirement and will produce SO_2 and, to a lesser extent SO_3 (acid gases) that often have significance in air pollution permits. "Sulfate" sulfur in the waste is already fully oxidized and, barring dissociation at very high temperatures, will not contribute to acid gas emissions or consume alkali in a flue gas scrubbing system.

A test for *forms of chlorine* provides a similar segregation between organically and inorganically bound chlorine in wastes. Chlorine is an important element in waste combustion. Organic chlorine (e.g., in polyvinyl chloride – PVC, saran and other halogenated polymers or pesticides) is almost quantitatively converted by combustion processes to HCl: an acid gas of significance in many state and federal air pollution regulations, an important contributor to corrosion problems in boilers, scrubbers and fans and a consumer of alkali in scrubbers. Inorganic chlorine (e.g., NaCl) is relatively benign but contributes to problems with refractory attack, submicron fume generation etc. Since all but a few inorganic chlorides are water soluble and few organic chloride compounds show any significant solubility, leaching and quantification of the soluble chlorine in the leachate provides a simple and useful differentiation between these two types of chlorine compounds.

An *ash analysis* is another special analysis. The ash analysis reports the content of the mineral residue as the oxides of the principal ash cations. A typical ash analysis is reported as the percent (dry basis) of SiO_2, Al_2O_3, TiO_2, Fe_2O_3, CaO, MgO, P_2O_5, Na_2O, and K_2O. The balance between the acidic and basic oxides in the ash is important in setting ash melting temperatures and in influencing corrosive attack of refractory (fluxing) [1].

A number of other useful *physical properties* may merit determination. These include: ash or material melting point (to assess the potential for wastes to melt at incineration temperatures and run through openings in grates), viscosity (important in atomization of liquid wastes), flash point (important in assessing safety problems and a key parameter in some regulatory definitions of "hazardous" combustible wastes).

Finally, the design of *materials handling* systems can benefit from data such as angle of repose (for bins and belt conveyors), particle size and density (for pneumatic conveyors) and the like (See Chapter 7 in Reference 1).

- Regulatory/Process Definitions

Beyond the materials tests noted above, it may be appropriate to conduct several specialized tests or develop waste characterizations to make specific distinctions that affect the permit requirements of the combustion system or that broadly characterize the waste as a guide in basic combustion process selection.

The permit-generated characterizations are specified in the relevant regulations (e.g., the USEPA hazardous waste regulations). Such characterizations include waste chemistry or industrial process source that might denote the presence of carcinogens or toxic substances, hazardous physical properties (e.g., low flash point or corrosivity), hazardous biological properties (e.g., the presence of pathogenic organisms), or the presence of high or low level radioactive materials.

Process characterizations include designation as "sewage sludge," "office trash," "domestic waste," “medical waste” or "cafeteria waste" which aid in broad incineration concept selection and which may have regulatory significance.

3. Material Balances

A material balance is a quantitative expression of the law of conservation of matter: What goes in comes out (unless it stays behind).

$$\text{Input} = \text{Output} + \text{Accumulation} \qquad (13)$$

This expression is always true for elements flowing through combustion systems (except for minor deviations in the unusual case where radioactive materials are involved). It is often not true for compounds participating in combustion reactions. Because of its fundamental character and intrinsic credibility, the material balance is one of the most useful tools for combustion system analysis.

Balances on elements in the fuel or waste allow one to calculate the amount of air theoretically required to completely oxidize the carbon, net hydrogen, sulfur, etc. This quantity of air (known as the *theoretical or stoichiometric air* requirement) is often insufficient to achieve complete burnout in a practical combustor and *excess air*, defined as a percentage of the stoichiometric air quantity, is usually supplied. For example, an operation at 50% excess air denotes combustion where 1.5 times the stoichiometric air requirement has been supplied.

The percentage excess air can be readily computed from the flue gas analysis for CHO-based fuels/wastes:

$$Percentage\ excess\ air = 100\ x\ \frac{O_2 - 0.5(CO + H_2)}{0.266N_2 - O_2 + 0.5(CO + H_2)} \qquad (14)$$

where O_2, N_2, etc. are the volume percentages of the gases.

Example 1. Calculate the air requirement and products of combustion when burning, at 30% excess air, 75 kg/hr of a waste liquid having an HHV of 9,739 kcal/kg (dry) with the ultimate analysis: 12.2% moisture, 71.0 % carbon, 9.2% hydrogen, 0.3% soluble chlorine, 3.1% sulfur, 2.1% oxygen, 0.6% nitrogen and 1.5% ash. The combustion air is available at 15.56 °C, and 70% relative humidity. We estimate a 2% heat loss factor.

The following should be noted in Table 5 which summarizes the material balance considerations:

Line 1 – Carbon is assumed to burn to CO_2. In reality, some carbon may be found as CO or a range of hydrocarbons but, for most material balance analyses, complete combustion is assumed.

Line 2, 3 – Hydrogen in the waste combustible increases the combustion air requirement but does not appear in the dry basis Orsat (a type of flue gas analysis device) analysis. If the waste contains organic (insoluble) chlorine or fluorine, hydrogen will first react with the halogens to form the corresponding halogen acid (HCl or HF). Beyond this, the hydrogen is assumed to oxidize to H_2O. Soluble chlorine (e.g. the chlorine in NaCl) is included in the ash.

Line 4 – Sulfur present as pyritic or organic sulfur consumes oxygen and forms SO_2. Sulfate sulfur is included in the ash.

Line 5 – Oxygen present in the waste organic matter reduces the required oxygen from combustion air.

Line 12 – Moisture entering with the air is small and often neglected. Psychometric data relating the water content of the air (humidity) may be available, however.

What can we do with the information gathered in the Material Balance? Actually, quite a bit . . . we can:

- Calculate the mols of combustion air we need for basis conditions. It is equal to the sum of the mols of nitrogen in the stoichiometric and excess air times (1/0.79). Multiplying this by 75% (since we are only burning 75 kg/hr and not the 100 kg/hr used as the basis), we get the actual moles of combustion air. From this, using the Perfect Gas Law, we can calculate the volume of combustion air for use in sizing the combustion air fan.

- Calculate the mols of flue gas generated (equal to 75% of 54.671mols) with which we can calculate the requirements of the fan used to handle the flue gas and develop sizing on any air pollution control devices . . . once we know the temperature (see the Energy Balance below). We can also use this information to conduct dispersion analysis to evaluate stack gas dispersion and ground level air quality impacts.

- Calculate the concentration of SO_2 and HCl in the flue gases for comparison with air pollution regulations to see of control is needed. If so, we can calculate the quantity of these acid gases that are generated (equal to 75% of 0.097 and 0.008 mols, respectively) from which we can calculate the amount of lime or other alkali needed to capture it in our air pollution control system.

- Calculate the amount of ash we generate to size the ash handling and ash storage facilities and the quantities needing landfill or other disposal means.

Pretty impressive, is it not? And, since these calculations are based on the "Law of the Conservation of Mass," we can be pretty sure they are quite accurate and believable.

4. Energy Balances

An energy balance is a quantitative expression of the law of conservation of energy. In waste incineration system analysis, five energy quantities are of prime interest:

- Chemical Energy: the heat of chemical reactions (importantly, oxidation reactions) that include combustion and dissociation. This quantity must be corrected for any "unreleased" fuel value in the residue or off-gases;

- Latent Heat: the heat to change the state of materials, which includes sublimation, fusion, and vaporization;

- Sensible Heat: the heat content related to the temperature of materials;

- Heat Losses: to the walls of combustion systems; and

- Useful Heat: delivered to boiler tubes or to materials being heated by the combustion process.

The only truly basic energy reference condition for energy calculations is for the case where the materials are at absolute zero (- 273.15°C, - 460°F). For convenience, however, a condition of 1 atmosphere and 15.56°C (60 °F) is often used as the reference for sensible heat content. Most laboratory data on chemical reaction and latent energy are reported at reference temperatures of 15 to 25 °C. In the latter case, although theory would dictate that correction to a consistent temperature base is always appropriate, the errors incurred are generally minor. Thus, tabulated values of heat of combustion and latent heat are ordinarily used without correction.

Continuing with the Example 1 analysis, we can construct a table of the heat content of the flue gas constituents (kcal/100 kg waste burned) using the numbers of mols from Table 5 and, via a spreadsheet, integrating the heat capacity functions to yield the heat content from a reference of 15.56 °C to a series of temperatures. To that we add the fixed latent heat of the water vapor (10,595 kcal/mol for 5.889 mols) and the sensible heat of the 1.5 kg of ash (@ 0.2 kcal/kg/°C). Such a table is shown as Table 6.

We deduct 2% for heat loss and plot the total gas enthalpy vs. temperature in Fig. 1. The total HHV heat input for 100 kg of waste is 855,084 kcal. Without consideration of heat losses, the gas sensible heat content is 799,598 kcal (855,084 less 55,487 latent heat) and the *adiabatic flame temperature* is 1713 °C. With 2% heat loss (17,102 kcal) , the heat content is 782,496 and the actual peak temperature is 1680 °C.

Let us look at two other ways we could use this technique to evaluate system options. First, let us consider installation of a boiler in the system to generate saturated steam at 40.83 atmospheres (600 psig). With feedwater at 130°C, steam tables [1] show the enthalpy gain from feedwater to steam is 538 kcal/kg. If we draw the flue gas temperature down to 180 °C, the table (or the figure) shows that the flue gas enthalpy drops to 121,452 kg/100 kg of waste burned so the heat transferred to the feedwater is 661,104 kcal/100 kg waste. This corresponds to 1,229 kg of steam. Therefore, for the actual burn rate of 75 kg/hr, the steaming rate will be 920 kg/hr.

A second alternative to investigate would involve preheat of the combustion air to, say, 200°C using a portion of the steam. By using the same calculation method for the nitrogen, oxygen and moisture in the combustion air, this air preheat would add 66,646 to the input heat balance and 91 lb/hr to the steaming rate (don't forget to take the 2% heat loss).

What can we do with the information gathered in the Energy Balance? Again, quite a bit . . . we can:

- Estimate the peak temperatures achieved in the flame to assess the potential for slagging (melting) of the ash or ash particles elutriated into the flue gas flow which could foul the boiler tubes or accumulate on any cooler refractory surfaces. These temperatures, coupled with ash properties and gas composition assists in refractory selection and in making judgments regarding boiler corrosion potential.
- Estimate the potential for energy recovery and the effects on both flame temperature and energy recovery of air preheat. The energy used for air preheat ("lost steam") can also be estimated.
- Estimate the needed combustion chamber volume which is often related [1] to the heat release rate (so many m^3 per million kcal/hr heat release).
- With the gas temperatures in hand, we can now calculate the volumetric flow rate of the flue gases as input to duct and fan sizing, air pollution control system selection and sizing and dispersion modeling.

5. Equilibrium

It is a recognized property of chemical reactions that no reactions go "to completion." Often the concentrations of the products are so much greater than those of the reactants that, from a practical viewpoint, the reaction is complete. Yet, in fact, as reactants combine to form products, the products themselves begin to react in accord with the law of mass action to reform the original reactants. At the *equilibrium condition*, the concentrations of reactants and products are constant as the rates of the forward and backward reactions become equal.

Thermodynamic analysis shows that the extent of the reaction of ideal gases is described by an equilibrium constant K_p that is a function only of temperature. The equilibrium constant for the reaction:

$$aA + bB \leftrightarrow cC + dD \qquad (15)$$

expressed in terms of the partial pressures of reactants A and B and the products C and D is given in Equation 16. By convention, the partial pressure terms for the reaction products are always placed in the numerator of the expression.

$$K_p = \frac{p_C^c p_D^d}{p_A^a p_B^b} \qquad (16)$$

The dimensions of K_p depend on the algebraic sum of the exponents given by the sum of the stoichiometric coefficients: [c + d - a - b]. If the total is zero, Kp is dimensionless. If the total is non-zero, Kp will have the units of pressure (atmospheres) raised to the appropriate integer or fractional power.

Table 5 Calculations for Example 1[a]

Line	Component	kg	Atoms or mols	Product	Mols O_2	Mols formed in stoichiometric combustion						
						CO_2	H_2O	SO_2	HCl	N_2	O_2	Total
1	Carbon (C)	71.0	5.912	CO2	5.912	5.912						5.912
2	Hydrogen (H)[b]	9.2	4.559	H_2O	2.280		4.559					4.559
3	Chlorine (Cl)	0.3	0.004	HCl	0.0				0.008			0.008
4	Sulfur	3.1	0.097	SO_2	0.097			0.097				0.097
5	Oxygen	2.1	0.066	---	(0.066)							0.0
6	Nitrogen	0.6	0.021	N_2	0.0					0.021		0.021
7	Moisture	12.2	0.678	H_2O	0.0		0.678					0.678
8	Ash	1.5	N/A	---	0.0							0.0
9	Total	100.0	11.387		8.222[c]	5.912	5.237	0.097	0.008	0.021	0.0	11.275
10	Mols N_2 in stoichiometric air 8.234 (79/21) [d]									30.932		30.932
11	Mols N_2 in excess air 0.3(8.234) (79/21)									9.280		9.280
12	Mols O_2 in excess air 0.3(8.234)										2.467	2.467
13	Mols moisture in combustion air [e]						0.652					0.652
14	Total mols in wet flue gas					5.912	5.889	0.097	0.008	40.233	2.467	54.606
15	Volume (mol) percent in wet flue gas					10.83	10.78	0.18	0.02	73.68	4.52	100.00
16	Flue gas analysis (vol %) on a dry basis (Orsat analysis)					12.15	0.0	0.20	0.02	82.59	5.06	100.00

NOTES:

a Basis: 100 kg waste

b The mols of hydrogen (used to calculate oxygen requirement) are reduced by the mols of insoluble chlorine (which reacts with hydrogen to form HCl)

c 8.222 mols O_2 corresponds to the stoichiometric oxygen

d Throughout this course, atmospheric air is assumed to contain 21.0% oxygen and 79.0% nitrogen by volume

e Calculated as follows (0.008/18.016)[(mols N_2 in air)(28.016) + (1 + % excess air)(stoichiometric mols O_2)(32.00)] based on the assumption of 0.008 kg water vapor per kg bone-dry air; found from standard psychometric charts.

Table 6 Enthalpy Calculations for Flue Gases

Line	Assumed Temperature (°C)	**180**	**500**	**1000**	**1500**	**2000**	**2500**
A	A – 15.5	164.5	484.5	984.5	1484.5	1984.5	2484.5
B	$Mc^{o}_{p,ave}$ for N_2 at A°C using Equation 10b	6.93	7.16	7.48	7.74	7.95	8.10
C	$Mc^{o}_{p,ave}$ for O_2 at A °C	7.17	7.48	7.87	8.13	8.26	8.26
D	$Mc^{o}_{p,ave}$ for H_2O at A °C	8.06	8.53	9.22	9.85	10.42	10.93
E	$Mc^{o}_{p,ave}$ for CO_2 at A °C	9.67	10.64	11.81	12.57	12.91	12.85
F	$Mc^{o}_{p,ave}$ for HCl at A °C	6.64	6.91	7.27	7.53	7.71	7.79
G	$Mc^{o}_{p,ave}$ for ash at A °C	0.20	0.20	0.20	0.20	0.20	0.20
H	Heat content of N_2 (mols x M_{cp} x ΔT)	45,834	139,583	296,330	462,543	634,750	809,481
I	Heat content of O_2 (mols x M_{cp} x ΔT)	2909	8,944	19,113	29,767	40,431	50,630
J	Heat content of H_2O (mols x M_{cp} x ΔT)	7807	24,335	53,433	86,079	121,769	159,997
K	Heat content of CO_2 (mols x M_{cp} x ΔT)	9,407	30,471	68,731	110,290	151,492	188,678
L	Heat content of HCl (mols x M_{cp} x ΔT)	9	28	60	94	129	163
M	Heat content of ash (kg x M_{cp} x ΔT)	49	145	295	445	723	873
N	Latent Heat of Water (mols x 10,595)	55,487	55,487	55,487	55,487	55,487	55,487
O	Total heat content of gas (H+I+J+K+L+N)	121,452	258,847	493,154	744,260	1,004,057	1,264,437

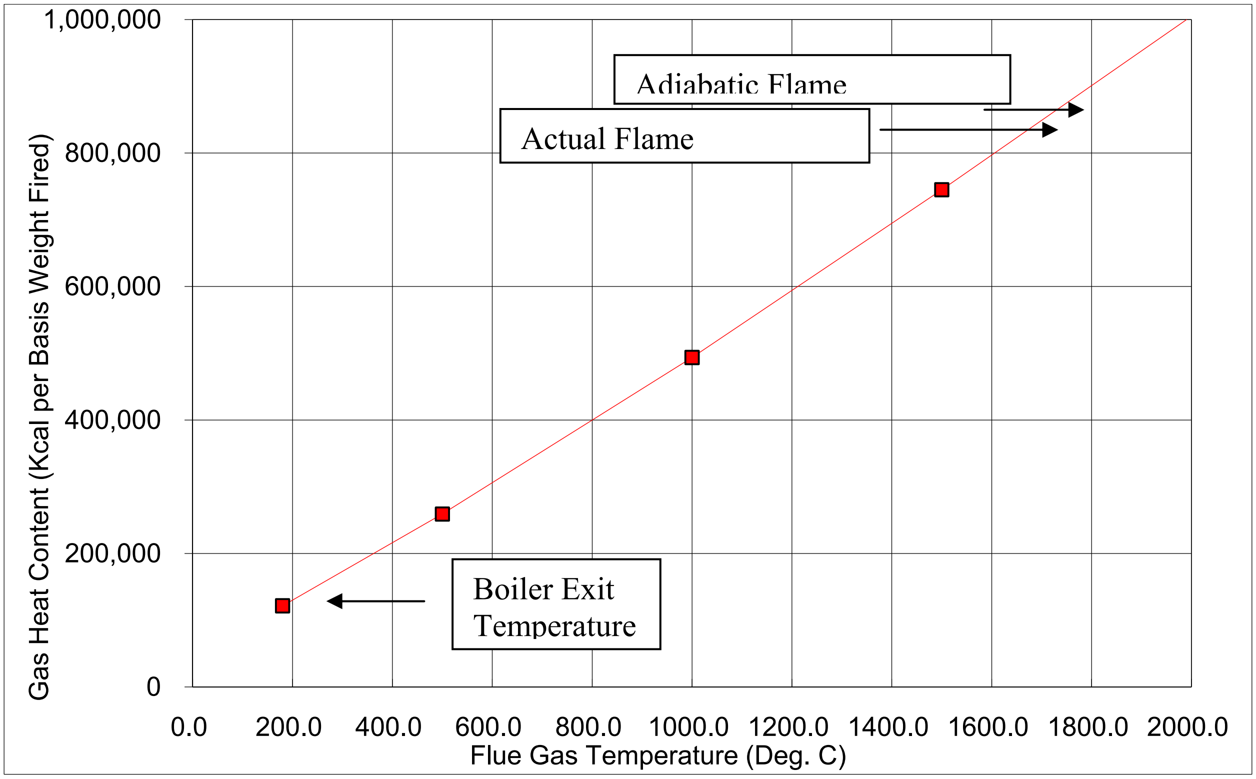


Figure 1 Example 1 Flue gas Enthalpy-Temperature Graph

The reader is directed to other texts [1] for a more detailed development of the thermodynamic basis and relationships concerning equilibrium. In combustion system analysis relating to environmental problems, however, it is sometimes useful to understand the temperature dependence of the equilibrium constant and to know how to estimate K_p for an arbitrary reaction of interest at any given temperature.

It can be shown that K_p is related to the free energy change ΔF^o when all of the reactants and products are in their standard states by:

$$-\Delta F^o = RT \ln K_p \qquad (17)$$

Further, the variation in free energy with temperature at constant pressure is given by:

$$\left[\frac{\partial}{\partial T}\left(\frac{\Delta F^o}{T}\right)\right]_p = = \frac{-\Delta H^o}{RT^2} \qquad (18)$$

Equations 17 and 18 can be combined to form an expression for the variation of K_p with temperature (T) and the enthalpy change of the reaction ΔH^o:

$$\left[\frac{\partial \ln K_p}{\partial T}\right]_p = \frac{d(\ln K_p)}{dT} = \frac{\Delta H^o}{RT^2} \qquad (19)$$

Clearly, if the reaction is exothermic (ΔH_o is positive), K_p increases with temperature. If the reaction is endothermic, (ΔH_o is negative) and the reverse is true.
Rearranging Equation 19 gives:

$$\frac{d(\ln K_p)}{d(\frac{1}{T})} = \frac{-\Delta H^o}{R} \qquad (20)$$

Equation 20 shows that if the logarithm of K_p is plotted against the reciprocal of absolute temperature, the slope is equal to - $\Delta H_o/R$. The K_p - T relationships shown in Fig. 2 show almost straight lines for most reactions. This suggests that ΔH_o is often approximately constant over relatively long temperature ranges.

So where do equilibrium calculations fit into the analysis of combustion situations? The equations shown in Table 7 (those graphed in Figure 2) show a number of situations where equilibria impact on gas compositions or result in pollutant formation. K_p is based on partial pressures in atmospheres. Water is as the vapor. Carbon (solid) is beta-graphite. For combustion calculations, several reactions merit consideration in evaluating heat and material flows, especially the gas phase reactions of H_2, H_2O, CO, CO_2, O_2 . Note that for reactions involving solids, the activity of the solid compounds is assumed to be unity. Thus the "concentration" or "partial pressure" of carbon or other solids do not enter into the mathematical formulation.

The partial pressure of the gases in a mixture at atmospheric pressure can be conveniently equated with the mol fraction (mols of the component divided by the total number of mols in the mixture). This equivalence (Dalton's Law) and its use in the equilibrium constant formulation is strictly true only for ideal gases. Fortunately, at the temperatures and pressures typical of most combustion calculations, this is a valid assumption. Let us look at an important example:

Example 2. For the combustion chamber conditions of Example 1, what is the emission rate of thermal NO due to the reaction ½ N_2 + ½ O_2 = NO?

The thermal NO emission rates for a real combustor will fall somewhere between the equilibrium value calculated at combustion chamber effluent temperatures and that for stack temperatures. NO is not formed in the high temperature zones quite to the theoretical equilibrium level due to local temperature or concentration variations and to reaction rate limitations. The NO concentration also does not follow the theoretical equilibrium curve as the gas temperature falls (in traversing the boiler) due to reaction rate limitations. The calculations below, therefore, illustrate the "worst case" scenario: equilibrium NO formation at peak furnace temperature and "frozen equilibrium" through the boiler.

From Example 1, the concentrations of N_2, O_2, and NO are:

Component	Mols	Mol Percent (Partial Pressure)
NO	x	x /54.606
N_2	40.233 - 0.5x	(40.233 - 0.5x)/54.606
O_2	2.467 - 0.5x	(2.467 - 0.5x)/54.606
Total (CO_2, H_2O, O_2, N_2)$_{(a)}$	54.606	

(a) Note that for this reaction, the total number of mols of gas does not change.

From Fig. 2, (Reaction Number 16) at 1680°C (1953 K), $\log_{10}(Kp) = -1.85$ and $Kp = 0.0141$ where:

$$K_p = \frac{p_{NO}}{p_{O_2}^{1/2} p_{N_2}^{1/2}} \qquad (21)$$

and p_{O2} , p_{N2} and p_{NO} are the partial pressures of O_2, N_2 and NO, respectively, each expressed in atmospheres. At equilibrium, then,

$$(2.467 - 0.5\text{x})^{1/2}(40.233 - 0.5\text{x})^{1/2} = \frac{\text{x}}{(0.0141)(54.606)}$$

Solving this equation gives x = 4.0705 mol of NO at equilibrium. This is equivalent to 7.45 mol percent or 74,500 parts per million (ppm) NO by volume. The heat of formation of NO is -21,600 kcal/mol of NO formed. Thus, this reaction will absorb 87,922 kcal or 10.28% of the heat of combustion calculated per basis weight in Example 2. Clearly, an set of iterative recalculations of flame temperature, the NO formation and the heat absorption in NO formation is merited. In any event, it is also clear that a significant NO/NO_x generation potential may exist under this combustion scenario and appropriate consideration as to NO_x control technology is appropriate.

Figure 2 Equilibrium Constants of Importance in Combustion Reactions

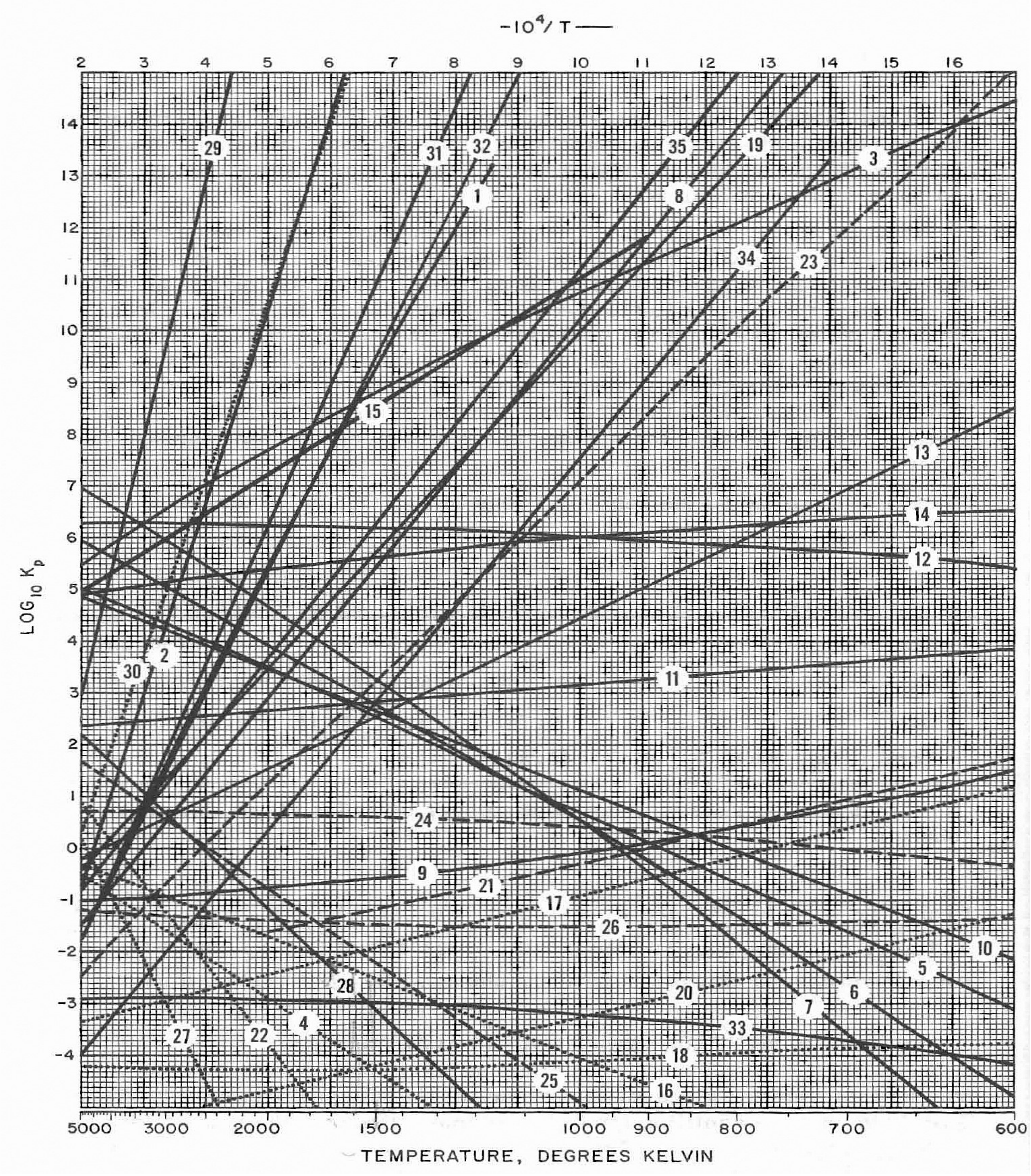
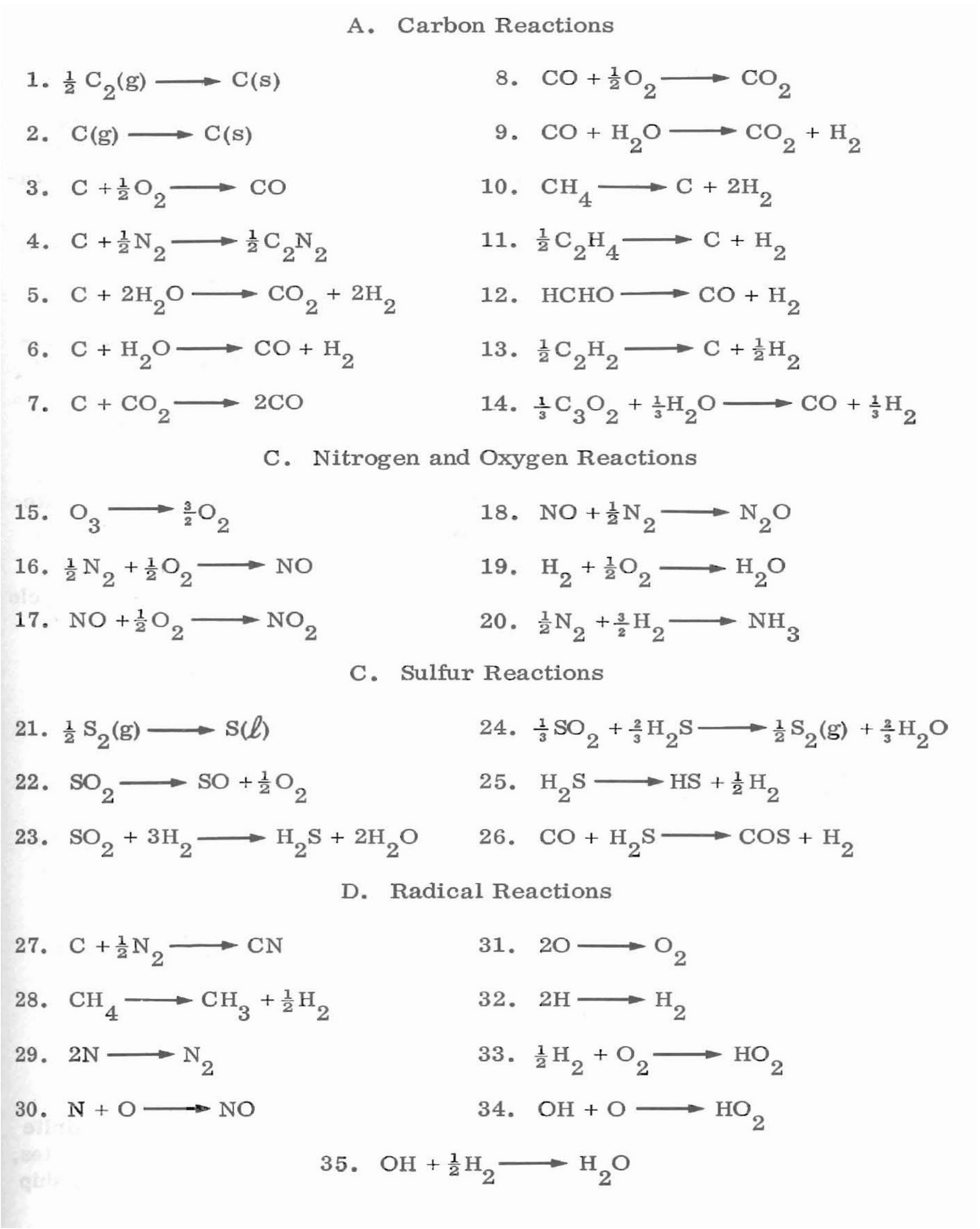


Table 7 Reaction Equilibria described in Figure 2



A. Carbon Reactions

1. $\frac{1}{2} C_2(g) \longrightarrow C(s)$
2. $C(g) \longrightarrow C(s)$
3. $C + \frac{1}{2} O_2 \longrightarrow CO$
4. $C + \frac{1}{2} N_2 \longrightarrow \frac{1}{2} C_2N_2$
5. $C + 2H_2O \longrightarrow CO_2 + 2H_2$
6. $C + H_2O \longrightarrow CO + H_2$
7. $C + CO_2 \longrightarrow 2CO$
8. $CO + \frac{1}{2} O_2 \longrightarrow CO_2$
9. $CO + H_2O \longrightarrow CO_2 + H_2$
10. $CH_4 \longrightarrow C + 2H_2$
11. $\frac{1}{2} C_2H_4 \longrightarrow C + H_2$
12. $HCHO \longrightarrow CO + H_2$
13. $\frac{1}{2} C_2H_2 \longrightarrow C + \frac{1}{2} H_2$
14. $\frac{1}{3} C_3O_2 + \frac{1}{3} H_2O \longrightarrow CO + \frac{1}{3} H_2$

C. Nitrogen and Oxygen Reactions

15. $O_3 \longrightarrow \frac{3}{2} O_2$
16. $\frac{1}{2} N_2 + \frac{1}{2} O_2 \longrightarrow NO$
17. $NO + \frac{1}{2} O_2 \longrightarrow NO_2$
18. $NO + \frac{1}{2} N_2 \longrightarrow N_2O$
19. $H_2 + \frac{1}{2} O_2 \longrightarrow H_2O$
20. $\frac{1}{2} N_2 + \frac{3}{2} H_2 \longrightarrow NH_3$

C. Sulfur Reactions

21. $\frac{1}{2} S_2(g) \longrightarrow S(\ell)$
22. $SO_2 \longrightarrow SO + \frac{1}{2} O_2$
23. $SO_2 + 3H_2 \longrightarrow H_2S + 2H_2O$
24. $\frac{1}{3} SO_2 + \frac{2}{3} H_2S \longrightarrow \frac{1}{2} S_2(g) + \frac{2}{3} H_2O$
25. $H_2S \longrightarrow HS + \frac{1}{2} H_2$
26. $CO + H_2S \longrightarrow COS + H_2$

D. Radical Reactions

27. $C + \frac{1}{2} N_2 \longrightarrow CN$
28. $CH_4 \longrightarrow CH_3 + \frac{1}{2} H_2$
29. $2N \longrightarrow N_2$
30. $N + O \longrightarrow NO$
31. $2O \longrightarrow O_2$
32. $2H \longrightarrow H_2$
33. $\frac{1}{2} H_2 + O_2 \longrightarrow HO_2$
34. $OH + O \longrightarrow HO_2$
35. $OH + \frac{1}{2} H_2 \longrightarrow H_2O$

6. Kinetics

Combustion involves chemical reactions. Indeed, key steps in the combustion process proceed at finite rates that are dependent upon local temperature, the concentrations of the reacting species, and in some cases, the static pressure. Combustion kinetics describe the relationships between the combustion reaction rate and basic system and environmental parameters.

Incineration applications of the combustion process pursue the ideal of 100% reaction completeness: total destruction of the feed material. An argument could be made that this goal is the same for all combustion-based processes (What utility boiler engineer wants unburned combustible in the off-gas or ash?). For incineration applications, however, the primary purpose of the system is destruction of the feed, not the release of energy as a means to other ends (such as the generation of electricity). For hazardous waste incineration systems, the focus on completeness of destruction is intense. This difference in the "rules" leads to a distinctive set of design objectives and evaluation tools when compared to those appropriate for non-incineration applications.

It is useful for the incinerator designer to have a basic understanding of the principles involved in combustion reaction kinetics. At a minimum, one should understand the concepts of an ignition temperature; the situations that lead to "quenching" of combustion reactions; and the significance of oxygen depletion on burnout.

a. Basic Kinetic Theory and Mathematical Formulations

For the generalized, gas phase chemical reaction

$$bB + cC \leftrightarrow dD + eE$$

The rate of decline in the concentration of reactant “B” or “C” (r) of the forward reaction (to the right) can often be described by equations of the form:

$$r = \frac{dc_B}{dt} = k[B]^b[C]^c \qquad (22)$$

where the value in the brackets (for ideal gases) is the concentration (gm mol/liter) of the components. Thermodynamic reasoning by Van’t Hoff [1] led to the formulation of the Arrhenius equation:

$$k = A\,exp(-\Delta E/RT) \qquad (23)$$

The quantity ΔE (kcal/kg mol) was interpreted by Arrhenius as an excess over the average energy that the reactants must possess in a molecule-to-molecule collision to allow the reaction to occur. He termed this the *activation energy* (actually an enthalpy) and related its significance to the critical energy required to form an activated complex or transition state between reactants and products. The exponential term is usually interpreted as the fraction of collisions that manage to obtain the necessary energy. One might picture such an intermediate as the stressed, energy-rich assembly of two colliding molecules just before the bonding electrons had shifted to form the product. The only constraint on the enthalpy change of the forward reaction (E) and of the backward reaction (E’) (where ΔE = E – E’) is that their difference should be equal to the net heat of reaction. Their individual magnitudes depend on the particular structures of the molecules involved.

The term "A" (the "pre-exponential factor") should be interpreted as a combination of molecular collision frequency parameters, steric factors (reflecting the orientation of the reacting molecules at the instant of collision) and other influences on reaction rate. Thus, although "A" appears in Eqn. (23) as a constant, the value of “A” includes the mass and effective cross-sectional area of the specific molecules involved and, from collision theory, has a dependency on the square-root of absolute temperature. The temperature sensitivity of the exponential term, however, is so powerful that “A” is usually treated as a constant.

The significant trends which one can draw from an examination of the Arrhenius expression are:

- Rate always increases as temperature increases.

- For large ΔE (more typical of exothermic combustion reactions), the increase in rate can be very dramatic over a relatively narrow temperature range. This gives rise to the useful concept of an "ignition temperature."

The Arrhenius concept, developed in 1889 [10], has been used successfully to correlate a wide variety of kinetic data (i.e., by plotting ln(k) vs. 1/T to give a straight line with a slope of -ΔE/R). Indeed, most failures to follow such a form have been successfully traced to previously unknown side reactions or catalytic effects.

Since the activation energy ΔE is associated with the energy required to form an activated intermediate, it is not unexpected that the value of ΔE changes if means are provided to change the amount of energy required. Specifically, the function of a catalyst is to reduce the activation energy for a given reaction. This facilitates and increases the rate of the reaction at lower temperatures.

Since reaction rate is proportional to the concentrations of the reacting substances, it is reasonable to divide the study of kinetics into classes determined either by molecularity (the number of atoms or molecules taking part in each act leading to chemical reaction) or the order of the reaction (the number of atoms or molecules whose concentrations determine the rate of the process). In a *first order reaction*, the rate is directly proportional to the concentration of the reacting substance or:

$$-\frac{dc}{dt} = kc \qquad (24)$$

where *c* is the concentration of the reacting substance. For a system with an initial concentration c_o and a concentration at time t of c_t , one has:

$$c_t = c_o e^{-kt} \qquad (25)$$

Many reactions of importance in combustion studies follow the first order mathematics of Equation 25. This includes many pyrolysis-type decomposition reactions. An important consequence of first order reactions is that the time taken to complete a definite fraction of the reaction is independent of the starting concentration. For example, the time required to achieve 50% destruction (the "half-life") t_{50} or the time to achieve 99% destruction (t_{99}) are:

$$t_{50} = \frac{\ln 2}{k} \qquad (26)$$

$$t_{99} = \frac{\ln 100}{k} \qquad (27)$$

If the rate of reaction depends on two concentrations, the process is said to be of the *second order*. For the generalized reaction:

$$A + B \rightarrow \text{products}$$

and for the reaction at some time when the concentrations of A and B are c_A and c_B the rate is given by:

$$-\frac{dc_A}{dt} = k \bullet C_A^a C_B^b \qquad (28)$$

where the exponents "a" and "b" show the *degree* of the reaction. This mathematical formulation is often useful to describe combustion processes where "A" is, say, the fuel or feed and "B" is oxygen. In many cases, the process runs very fuel lean such that the oxygen concentration is almost unchanged across the flame front. For simplicity, one can describe such a case as pseudo-first order and lump the numerical value of the oxygen concentration into the "k" term.

Example 3. Calculate the percent reduction after 1.5 seconds in the concentration of DDT being burned in a thermal oxidizer as a dilute (oxygen concentration does not change significantly) fume at 750 K. The DDT starts at a concentration of 100 ppm (parts per million, by volume) and the oxygen is at 8% (by volume, wet basis) in the combustion gases of the oxidizer. The kinetic parameters are: A = 9.319E7 liter/gram mol-sec and the ΔE is16,659 kcal/gram mol.

The combustion process is described by:

$$-\frac{dc_{DDT}}{dt} = k(c_{DDT})(c_{O_2}) \text{ , where}$$

$$k = A\left(exp\,\frac{-\Delta E}{RT}\right) = 9.319E7\left(\exp\frac{-16{,}659}{(1.986)(750)}\right) = 1{,}294.5 \text{ liter/gram mol} - \text{sec}$$

The oxygen concentration (c_{O_2}) which is assumed to be constant and the initial DDT concentration (c_{DDT_o}) are given by:

$$c_{O_2} = \frac{p_{O2}}{RT} = \frac{0.08}{(0.08206)(750)} = 0.0013\ gram\,\frac{mol}{liter}\ \ and$$

$$c_{DDT_o} = \frac{p_{DDT_o}}{RT} = \frac{10^{-4}}{(0.08206)(750)} = 1.62E - 5\ gram\ mol/liter))$$

Integrating from $c_{DDT} = c_o$ to $c_{DDT} = c$ when time goes from zero to t we have:

$$ln\left[\frac{C_o}{c}\right] = k(c_{O_2})t$$

So the DDT destruction ratio after 1.5 second is 1,294.5 * 0.0015*1.5 = 2.52 or

c_o/c = 12.48, and the DDT has been reduced to 100/12.48 = 8.0 ppm

Note the need for care in the units used for the Gas Constant R and the use of absolute temperature. Clearly, also, the math used for the integration of the rate equation becomes more sophisticated as the equation becomes more complex (as, for example, if the oxygen concentration was also allowed to change as the oxidation proceeded). On the plus side, this simple example shows the power of kinetic analysis for a very real problem where, for example, DDT was driven off contaminated soil and the resulting fume passed to a thermal oxidizer. How hot should it be run? How much residence time do we need? These calculations give answers useful in design or operational troubleshooting. Other kinetic data are found in the literature or references [1].

b. Mechanism

The formulation of reaction rate expressions from the simple stoichiometric relationships drawn from the equation for the reaction may be in error. In such cases, the error may often be eliminated when the full sequence of reactions leading from reactants to products is more fully understood. Exploring the true route of a reaction is the study of *mechanism*. Such studies, particularly in combustion systems, often show the vital role of highly activated species, fragments of molecules, called free radicals. Free radicals, existing individually for only fractions of a second, are nonetheless important intermediates in the initiation and propagation of combustion reactions.

The subject of reaction mechanism is involved and complicated; far beyond the scope or needs of this course. Seldom does the analyst of waste incineration systems have the opportunity or the need to study the kinetic relationships that are operative in their process. However, having a basic understanding of the fundamental processes involved can be useful in interpreting the underlying causes of combustion problems even if the system under study is too complex to allow a priori and quantitative evaluation of reaction rates.

For example, a chlorine atom has a large and diffuse swarm of electrons surrounding the nucleus. This electron "cloud" tends to stabilize free radicals and reduce their reactivity. Thus, we find it more difficult to burn chlorinated compounds than compounds having no halogens. A similar effect is seen for highly branched or aromatic hydrocarbons which stabilize radicals more effectively than their straight chain brothers. As a result, the straight chain compounds burn faster (higher flame speed) than the other type of compounds and, in automobile cylinders, lead to "knock" . . . which is controlled with the slow-burning "Platformate" (a trade name for highly branched gasoline compounds) or aromatic compositions. While we do not necessarily understand or need to understand all of the complexity underlying the basic "fuel + air → products" reaction, it is important to recognize that processes are going on in the background whose characteristics profoundly influence the results we seek: (almost) 100% destruction.

c. Kinetics of Carbon Monoxide Oxidation

Carbon monoxide is an important air pollutant, a poisonous gas in high concentrations, and can be the unwanted repository of considerable combustion energy in inefficient combustors. In many instances where hydrocarbons are burned, the oxidation reactions proceed rapidly to the point where CO is formed and then slow greatly until CO burnout is achieved. Indeed, the kinetics of methane oxidation almost duplicates the CO kinetic expressions.
CO is produced by the incomplete combustion of pyrolysis products of solid or liquid wastes, from the char in a refuse bed, or as an intermediate combustion product. The oxidation kinetics to carbon dioxide have been studied by several investigators and, although there are differences in the rate constant reported, a reasonable estimate can be made of the times required to complete the combustion.

Morgan [4], in studies at MIT developed a useful and conservative overall CO oxidation rate:

$$\frac{-\mathrm{d}f_{CO}}{\mathrm{d}t} = 1.8 \text{ x } 10^{13}\ f_{CO} f_{O_2}^{0.5} f_{H_2O}^{0.5} \left(\frac{P}{R'T}\right)^{2.0} \exp\left(\frac{-25{,}000}{RT}\right) \qquad (29)$$

In equation 29 we calculate the rate of reduction in the mol fraction of CO (f_{CO}) as it relates to the mol fractions of CO, oxygen and water vapor. T is the absolute temperature (K), P is the absolute pressure (atm), t the time in seconds, R is the gas constant (1.986 kcal/kg mol K) and R' is also the gas constant, but in alternate units (82.06 atm cm^3/g mol K). In reviewing the reaction rate expression, it is instructive to note the dependence upon the mol fraction of water vapor. This results from the participation of hydrogen and hydroxyl (OH) free radicals in the reaction.

To the extent that the combustion chamber may be considered as an isothermal reactor, the decline in CO concentration over an interval t (seconds) from an initial mol fraction $f_{CO)\,i}$ to a final mol fraction $f_{CO)\,f}$ is given by:

$$\frac{(f_{CO})_f}{(f_{CO})_i} = \exp(-Kt) \qquad (30a)$$

where

$$K = 1.8 \text{ x } 10^{13} \exp\left(\frac{-25{,}000}{RT}\right) f_{O_2}^{0.5} f_{H_2O}^{0.5} \left(\frac{P}{R'T}\right) \qquad (30b)$$

d. Ignition Temperature

Using a kinetic expression to calculate the destruction rate of a given compound for a series of temperatures, one usually finds that, over a relatively small temperature range, the oxidation rate increases rapidly. The temperature where “breakaway” occurs is denoted the “ignition temperature” which marks the lowest operating temperature where any reasonable degree of material burnout can be expected. Clearly, to allow for quenching effects along cold walls or where tramp air may enter and chill the gas, a margin of conservatism in setting the working temperature is appropriate. For CO, data suggest an ignition temperature of about 600°C. Data for other compounds are available from the literature [1]. Note that the ignition temperature depends to a degree (pardon the pun) on the oxygen concentration.

e. Destruction and Removal Efficiency

Changes in the specific hazardous materials feed to an incineration system place an important question before the operator: Will the burnout be better, the same or worse if the waste changes from feed "A" where testing has shown acceptable burnout under their normal operating conditions (defined, say, by the temperature, oxygen concentration and feed rate) to a new feed "B"? This is not a rhetorical question in view of the legal and moral liability for exposed, downwind individuals. Also, there is the requirement to meet the terms of operating permits under legislation that can impose severe fines and/or perhaps invoke criminal penalties if there are excessive emissions of hazardous substances.
This practical need to be able to determine the "relative incinerability" of chemical compounds has led to considerable laboratory and field investigation of the efficiency and rate of combustion processes. Early investigators

used surrogate parameters such as the heat of combustion or auto ignition temperature to provide a simple, easy-to-use scale. However, data on incinerator performance showed the surrogate parameters to be unreliable. Increasing attention has been given, therefore, to the use of kinetic parameters [1] as an appropriate and direct scale of incinerability.

Incineration systems should not, ideally, be operated such that kinetics limit the degree of burnout achieved. That is, oxygen concentrations and gas temperatures should be high enough that reaction rates are very fast relative to the residence time. This is particularly important for incinerators burning hazardous wastes.

Hazardous waste incinerators are often required by their operating permits to achieve a Destruction and Removal Efficiency (DRE) of "four 9's". This means that the combined effects of the combustion process (destruction) and any settlement in ductwork or the action of air pollution control systems (removal) must assure that the system exhaust stream contains not more than 0.01% of a preselected, environmentally significant organic material in the feed. In the acronym-rich regulatory language of the US Environmental Protection Agency (EPA), the selected material is a Principle Organic Hazardous Constituent or "POHC" and 99.99% of the POHC has been destroyed and/or removed (a DRE of four "9s"). Mathematically, DRE is calculated as follows:

$$DRE = [(W_{in} - W_{out}) / W_{in}] x100 \qquad (31)$$

where: W_{in} = Mass feed rate of the principal organic hazardous constituent (POHC) in the waste stream fed to the incinerator,

W_{out} = Mass emission rate of the POHC in the stack prior to release to the atmosphere.

The inability of a combustion system to attain or exceed the DRE requirement can arise from several "failure modes." These failure modes generally are not visible in the design or operating parameters that characterize the bulk flow. The "mean furnace temperature," the "mean flue gas oxygen concentration" and the "mean residence time" may all be satisfactory. However, some fraction of the system flow does not achieve the critical parameter thresholds that assure burnout. Generally, if only 99% destruction of a feed material is achieved, it is not because 100% of the flow is 99% burned but, more likely, that 99% of the flow is fully burned-out and 1% did not burn at all.

E. Summary

You have started down the path to understanding combustion. There is much more to learn but the tools and insights above give you a strong running start at the evaluation of combustion systems: their fundamental input and output characteristics regarding mass and energy and a peek "under the hood" at the basic processes and controlling thermodynamic principles that make them do what they do. Extended to topics on burners and flame length, fluid mechanics and mixing, refractory, heat recovery, pyrolysis and gasification and other topics in Fundamentals of Combustion -Part 2 will build on these basic principles in their application in incineration furnaces. I hope to see you there.

F. References

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