AN INVESTIGATION OF THE MAXIMUM TEMPERATURES AND PRESSURES ATTAINABLE IN THE COMBUSTION OF GASEOUS AND LIQUID FUELS

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AN INVESTIGATION OF THE MAXIMUM TEMPERATURES AND PRESSURES ATTAINABLE IN THE COMBUSTION OF GASEOUS AND LIQUID FUELS

I. OBJECT AND SCOPE OF THE INVESTIGATION

1. *Statement of the Problem.*—Certain chemical reactions which are associated with high temperatures possess great technical importance. Among these, especially interesting to the engineer, are the combustion reactions such as occur in boiler practice, in the internal combustion engine, in the gas producer, and in the oxy-hydrogen and the oxy-acetylene flame.

Reactions at high temperatures present certain phenomena which have not received the attention they deserve from engineers. The reaction energy, that is, the available work of the reaction, is not generally the exact equivalent of the heat of reaction; however, this is not always recognized. Again, at high temperatures a reaction cannot proceed to completion but must halt when the constituents attain a state of equilibrium. The maximum temperature that can be attained is thus definitely limited by the law of chemical equilibrium.

A concrete example will serve to illustrate the effect of equilibrium conditions on the temperatures attained. Clerk* has discussed the great discrepancy between the observed and the calculated pressures in the explosion of coal gas with various proportions of air to gas. The figures are as follows:

Ratio of air to gas	14	13	12	11	9	7	6
Observed pressure	40	51.5	60	61	78	87	90
Calculated pressure	89.5	96	103	112	134	168	192

The pressures are in lb. per sq. in. above atmospheric pressure. The calculated pressures are nearly double the observed pressures, and this means that calculated temperatures are likewise nearly double the temperatures actually attained.

The explanation of the large discrepancy lies in the crudeness of the method used in calculating the temperatures. Three assumptions were made, not one of which was justified:

(1) It was assumed that the combustion process was adiabatic; that is, that all the heat of combustion was used in raising the temperature of the products of combustion. The recent experiments of David

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* D. Clerk, "The Gas, Petrol, and Oil Engine," Vol. 1, p. 136.

show that during explosion an appreciable amount of heat is dissipated by conduction and radiation, and is, therefore, not available for raising the temperature of the mixture.

(2) The specific heat of the products mixture was taken as constant. It is now known that the specific heats of all gaseous constituents increase with the temperature. The effect of such variation in the specific heat is a considerable reduction in the calculated temperature.

(3) Complete combustion at the end of the explosion period was assumed. This assumption is also untenable. According to the law of chemical equilibrium the mixture at the point of maximum pressure must contain a considerable amount of uncombined carbon monoxide and a smaller amount of uncombined hydrogen. Consequently, at this point the whole of the heat of combustion has not been developed.

Clerk explained the discrepancy between actual and calculated temperatures as due largely to dissociation of the combustion products.* The following quotation gives a clear statement of the situation:

"It is quite evident, then, that at the highest temperatures produced by combustion, the product cannot exist in a state of complete combination. It will be mixed to a certain extent with the free constituents which cannot combine further until the temperature falls; as the temperature falls, combustion will continue till all the free gases are combined. The subject, from its nature, is a difficult one in experiment, and accordingly different observers do not agree upon temperatures and percentages of dissociation, but all are agreed that dissociation places a rigid barrier in the way of combustion at high temperatures, and prevents the attainment of temperatures, by combustion, which are otherwise quite possible."

At the present time fairly consistent and reliable data on the dissociation of the main products of combustion are available, and apparently there is a possibility of taking account of dissociation phenomena in the calculation of temperatures and pressures. In fact, Tizard and Pye,† using the figures of Nernst on the dissociation of CO_2 and H_2O, have succeeded in calculating the maximum temperatures attained in the combustion of benzene and similar fuels. Though the method was laborious, and a number of approximations were used, the results obtained are surprisingly good.

The equilibrium conditions for a chemical reaction have been determined from the laws of thermodynamics, and for the principal dissociation reactions, as $CO_2 = CO + \tfrac{1}{2}O_2$ and $H_2O = H_2 + \tfrac{1}{2}O_2$,

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* D. Clerk, "The Gas, Petrol, and Oil Engine," Vol. 1, p. 123.

† The Automobile Engineer, I, Feb., 1921, p. 55, II, March, 1921, p. 98, III, April, 1921, p. 134.

these conditions are furnished by equilibrium equations which can be established with a fair degree of accuracy. These equilibrium equations, along with an equation connecting the heat of combustion with various energy changes, furnish a system from which the temperature attained at equilibrium may be calculated in a straightforward manner.

The problem proposed for investigation is, therefore, the following: first, to investigate the conditions of equilibrium and establish the necessary equilibrium equations; and, second, to incorporate these equilibrium equations into a formulation by means of which the maximum temperature resulting from the combustion of a fuel under predetermined conditions may be calculated.

2. *Data Required.*—The constants in the equilibrium equations involve certain thermal data: namely, the heat of combustion and the specific heats of the various constituents. The accuracy of the equilibrium equations depends, therefore, in the first instance, on the accuracy of these thermal data. The available experimental evidence on the specific heats of various constituents has been examined critically, and the discussion is given in Appendix I. In the same way the experimental evidence on heats of combustion is reviewed in Appendix II. One constant in the equilibrium equations is independent of thermal magnitudes, and its determination requires a chemical analysis of a gas mixture in the equilibrium state. In Appendix III, the chemical data for various reactions are assembled, and the unknown constants are determined for such reactions.

3. *Plan and Scope of the Discussion.*—A brief *résumé* of the important laws of gas mixtures is desirable and is given in Chapter II. Then in Chapter III follows the general theory of chemical equilibrium, and the derivation of the equilibrium equations for various reactions. In Chapter IV the energy equation is developed, and the method of solving the system of equations for the maximum temperature is shown. With this section the theoretical discussion is completed. The remaining sections are devoted to comparisons and applications of the theory.

II. The Laws of Gas Mixtures

4. *Universal Gas Constant.*—Calculations relating to gas mixtures are simplified by the introduction of a unit of weight called the *mol.* Let m denote the molecular weight of a gas; then 1 mol $= m$ pounds or m grams, according as the pound or the gram is taken as the unit. Thus, for oxygen, 1 mol $= 32$ lb., for ammonia, 1 mol $= 17$ lb., etc. At a temperature of 32 deg. F. and at normal atmospheric pressure the weight of 1 cubic foot of oxygen is 0.08922 lb.; hence the

volume of 1 mol of oxygen is $32 \div 0.08922 = 358.7$ cu. ft. From the relation between the volumes and molecular weights of gases, it is evident that 358.7 cu. ft. is the volume of 1 mol of *any* gas at 32 deg. F. and atmospheric pressure. If the standard temperature is taken as 62 deg. F. instead of 32 deg. F. the volume of 1 mol is 380.6 cu. ft.

Let both members of the usual gas equation

$$pv = BT$$

be multiplied by the molecular weight m. The resulting equation is

$$p\,mv = mBT$$

Taking now the standard condition, $T = 32 + 459.6 = 491.6$, $p = 2116.3$ lb. per sq. ft. (atmospheric pressure), the product mv is the volume of 1 mol or 358.7 cu. ft.; hence

$$mB = \frac{2116.3 \times 358.7}{491.6} = 1544.$$

Denoting the constant 1544 by R, the equation of a gas is

$$pv = RT \ldots \ldots \ldots \ldots \ldots \ldots \ldots (1)$$

provided v denotes the volume of 1 mol. The constant R is the same for all gases.

In the following sections the thermal unit (B. t. u.) rather than the mechanical unit (ft. lb.) will generally be used. In the preceding equation the product pv is in foot pounds, hence the constant R has the dimension ft. lb. per degree. To change from ft. lb. to B. t. u. we divide by the mechanical equivalent $J = 777.64$. The value of R thus obtained lies between 1.985 and 1.986. The value 1.985 is usually taken.

5.   *Gas Mixtures; Partial Pressures.*—The composition of a gas mixture as determined by chemical analysis is expressed in terms of volumes. That is, the total volume V of the mixture, having a pressure p and temperature T, is divided into partial volumes V_1, V_2, etc., that would be occupied by the individual constituents at the same pressure and temperature. Thus the composition

$$
\begin{aligned}
CO_2 &= 0.30 \\
H_2O &= 0.20 \\
N_2 &= 0.50 \\
\hline
&\ 1.00
\end{aligned}
$$

signifies that if the CO_2 is separated from the mixture its volume will be 30 per cent of the volume of the mixture at the same pressure and temperature.

Another interpretation of a volume composition is useful. Because of the invariable relation between the volume of a gas and its

weight expressed in mols, the numbers in the volume composition are proportional to the number of mols in the several constituents. Thus 1 mol of the mixture just given contains 0.3 mol of CO_2, 0.2 mol of H_2O, and 0.5 mol of N_2.

When the separated constituents having the volumes V_1, V_2, etc., and a common pressure p and temperature T are allowed to mix, the volume V_1 of the first constituent increases to the total volume V of the mixture, and

$$V = V_1 + V_2 + V_3 + \ldots\ldots$$

The pressure of this constituent must change from the original common pressure p to a smaller value p_1, given by the relation

$$pV_1 = p_1V$$

Likewise for the other constituents

$$pV_2 = p_2V$$
$$pV_3 = p_3V$$

A combination of these equations gives the important relation

$$p_1 + p_2 + p_3 + \ldots\ldots = p$$

That is, the pressure of the mixture is the sum of the partial pressures of the constituents (Dalton's law). Also

$$p_1 : p_2 : p_3 \ldots = V_1 : V_2 : V_3 : \ldots\ldots$$

or the partial pressures are proportional to the partial volumes given by the composition. For example, let the pressure of the mixture just quoted be 14.7 lb. per sq. in.; then the partial pressure of the CO_2 constituent is $14.7 \times 0.3 = 4.41$ lb., that of the N_2 constituent $14.7 \times 0.5 = 7.35$ lb.

6. *Specific Heat of Gases.*—In the problems that are attacked in the following sections the mol rather than the pound will be used as the unit; hence the specific heat per mol is required. Let c denote the specific heat referred to the pound, γ the specific heat referred to the mol, and m the molecular weight. Then

$$\gamma = mc \qquad \gamma_p = mc_p \qquad \gamma_v = mc_v$$

The difference $c_p - c_v$ between the specific heats at constant pressure and constant volume is the product AB, where A is the reciprocal of J, the mechanical equivalent of heat; hence taking R in thermal units,

$$\gamma_p - \gamma_v = R = 1.985 \ldots\ldots\ldots\ldots\ldots (2)$$

If for a gas the specific heat at constant pressure is given by an expression such as

$$\gamma_p = a + bT + cT^2,$$

the specific heat at constant volume is given by the expression

$$\gamma_p = a' + bT + cT^2,$$

where

$$a' = a - 1.985.$$

The equations for the specific heats of various gases are examined in Appendix I, and a collection of the equations finally chosen will be found on page 106.

7. *Energy of a Gas Mixture.*—The intrinsic energy of one mol of a single component is given by the expression

$$u = \int \gamma_v dT \dots \dots \dots \dots (3)$$

Thus the energy of one mol of H_2 is

$$u = \int (4.015 + 0.6667 \times 10^{-3} T) \, dT$$
$$= 4.015 T + 0.3333 \times 10^{-3} T^2 + u_0$$

in which u_0 denotes the energy of the gas when $T = 0$.

The energy of a gas mixture is the sum of the energies of the individual constituents. If n_1, n_2, n_3,.... denote the number of mols of the first, second, third, etc., constituents respectively, the energy of the mixture is

$$U = n_1 \int \gamma_{v_1} dT + n_2 \int \gamma_{v_2} dT + n_3 \int \gamma_{v_3} dT + \dots \dots \dots \dots (4)$$

8. *Thermal Potential of a Gas Mixture.*—The thermal potential i of one mol is defined by the equation

$$i = u + Apv \dots \dots \dots \dots (5)$$

in which u denotes the energy and v the volume of one mol. For Apv may be substituted ART, or simply RT if R is taken as 1.985. Then

$$i = u + RT$$
$$di = du + RdT = \gamma_v dT + RdT$$
$$= (\gamma_v + R) \, dT = \gamma_p dT$$

Hence for one mol

$$i = \int \gamma_p dT$$

and for a mixture

$$I^* = n_1 \int \gamma_{p_1} dT + n_2 \int \gamma_{p_2} dT + n_3 \int \gamma_{p_3} dT + \dots \dots \dots \dots (6)$$

---

* The usual convention of small and capital letters is adopted. Thus u denotes the energy of 1 mol, U the energy of M mols, whence $U = Mu$; likewise $I = Mi$.

9. *Heat of Combustion.*—In the experimental determination of the heat of combustion the temperature of the products is brought back to the temperature of the original fuel mixture and the heat generated is absorbed by cold water. The usual energy equation may be applied to the process; thus

$$_1Q_2 = U_2 - U_1 + A \int_{V_1}^{V_2} p dV \quad \dots \dots \dots \dots \dots (7)$$

In this equation $_1Q_2$ denotes heat absorbed; therefore, since heat is rejected in the process, $_1Q_2$ is intrinsically negative. Hence, denoting by H the heat of combustion,

$$H = -_1Q_2 = U_1 - U_2 - A \int_{V_1}^{V_2} p dV$$

Two cases come under consideration: (a) If the volume is kept constant, the heat of combustion H_v is given by the equation

$$H_v = U_1 - U_2 \quad \dots \dots \dots \dots \dots \dots (8)$$

(b) If the pressure is kept constant, the heat of combustion is given by the equation

$$H_p = U_1 - U_2 - (ApV_2 - ApV_1).$$

Since by definition $I = U + ApV$, this equation becomes

$$H_p = I_1 - I_2 \quad \dots \dots \dots \dots \dots \dots (9)$$

For constant volume, the heat of combustion is the difference between the energy of the fuel mixture and the energy of the products mixture, both at the same temperature. Similarly, the difference between the thermal potentials of the two mixtures, at the same temperature, gives the heat of combustion at constant pressure.

A general expression for the heat of combustion at a given absolute temperature T is useful. This may be derived as follows: Assuming that the products of combustion with oxygen are CO_2 and H_2O, the reaction equation may be written

1 mol fuel $+ n_2$ mols $O_2 = n'$ mols $CO_2 + n''$ mols H_2O.
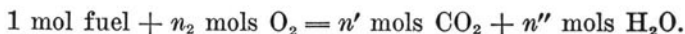
For example, in the combustion of H_2, $n_2 = \frac{1}{2}$, $n' = 0$, $n'' = 1$, in the combustion of CH_4, $n_2 = 2$, $n' = 1$, $n'' = 2$. Let the expressions for the four specific heats involved be:

$$\begin{aligned}
&\text{For the fuel} &\gamma_p &= \alpha_1 + \beta_1 T + \delta_1 T^2 \\
&\text{For the oxygen} &\gamma_p &= \alpha_2 + \beta_2 T + \delta_2 T^2 \\
&\text{For the } CO_2 &\gamma_p &= \alpha' + \beta' T + \delta' T^2 \\
&\text{For the } H_2O &\gamma_p &= \alpha'' + \beta'' T + \delta'' T^2
\end{aligned}$$

The thermal potential of the original mixture of fuel and oxygen is

$$I_1 = \int (\alpha_1 + \beta_1 T + \delta_1 T^2)\, dT + n_2 \int (\alpha_2 + \beta_2 T + \delta_2 T^2)\, dT$$

Likewise the thermal potential of the products mixture is

$$I_2 = n' \int (\alpha' + \beta' T + \delta' T^2) dT + n'' \int (\alpha'' + \beta'' T + \delta'' T^2)\, dT$$

Performing the integrations and substituting the results in equation (9), the result is

$$H_p = T\left[\alpha_1 + n_2\alpha_2 - n'\alpha' - n''\alpha''\right] + \tfrac{1}{2}T^2\left[\beta_1 + n_2\beta_2 - n'\beta' - n''\beta''\right]$$

$$+ \tfrac{1}{3}T^3\left[\delta_1 + n_2\delta_2 - n'\delta' - n''\delta''\right] + \left[i_{01} + n_2 i_{02} - n'i'_0 - n''i''_0\right] (10)$$

The first three terms in brackets are denoted by σ', σ'', σ''', respectively, and the last term by H_0. Therefore,

$$H_p = H_0 + T(\sigma' + \tfrac{1}{2}\sigma''T + \tfrac{1}{3}\sigma'''T^2) \ \ldots\ldots\ldots\ldots (11)$$

To get an expression for H_v, we take the specific heats at constant volume; namely,

$$\gamma_v = (\alpha_1 - R) + \beta_1 T + \delta_1 T^2, \text{ etc.}$$

and by integration obtain expressions for U_1 and U_2. The second and third terms in the second member of equation (10) will remain the same; the first term will be

$$T\left[(\alpha_1 - R) + n_2(\alpha_2 - R) - n'(\alpha' - R) - n''(\alpha'' - R)\right]$$

$$= T\left[\alpha_1 + n_2\alpha_2 - n'\alpha' - n''\alpha''\right] - RT\left[1 + n_2 - n' - n''\right]$$

and the last term will be

$$u_{01} + n_2 u_{02} - n'u'_0 - n''u''_0$$

Now u_0 is the energy of a constituent and i_0 is the corresponding thermal potential of the constituent when $T = 0$. Since

$$i = u + Apv = u + RT,$$

$i_0 = u_0$ when $T = 0$. Consequently the last terms are identical, and

$$H_v = H_0 + T(\sigma' + \tfrac{1}{2}\sigma''T + \tfrac{1}{3}\sigma'''T^2) - RT\left[1 + n_2 - n' - n''\right]$$

The expression $1 + n_2 - n' - n''$ gives the *decrease* in the molecular

volume incurred in the reaction, and this may be denoted by n. Thus, in the reaction $CO + \frac{1}{2}O_2 = CO_2$, $n = 1 + \frac{1}{2} - 1 = \frac{1}{2}$; in the reaction $CH_4 + 2O_2 = CO_2 + 2H_2O$, $n = 1 + 2 - 1 - 2 = 0$; and in the reaction $C_2H_6O + 3O_2 = 2CO_2 + 3H_2O$, $n = 1 + 3 - 2 - 3 = -1$. The expression for H_v is, therefore,

$$H_v = H_0 + T \left(\sigma' + \tfrac{1}{2}\sigma''T + \tfrac{1}{3}\sigma'''T^2\right) - nRT \quad \ldots\ldots\ldots (12)$$

and the difference between the two heats of combustion is

$$H_p - H_v = nRT \quad \ldots\ldots\ldots\ldots\ldots (13)$$

10. *Higher and Lower Heat of Combustion.*—In the experimental determination of the heat of combustion, the temperature of the products is usually reduced below the saturation temperature corresponding to the partial pressure of the H_2O constituent. Part of the water vapor is condensed and the latent heat released by such condensation is added to H_p, giving the so-called *higher* heat of combustion. A correction must be made to reduce the experimental higher value to the true *lower* value, which is the only one that is useful in the present discussion. The method used is given in Appendix II. Values of the heat of combustion for various reactions are given in Table 16, page 119.

11. *Entropy of a Gas Mixture.*—The expression for the entropy of unit weight (one pound) of a gas at pressure p and temperature T is deduced from the energy equation

$$dq = c_v dT + Apdv$$

From the characteristic equation $pv = BT$,

$$Apdv = ABdT - Avdp$$

Combining these equations, and taking $AB = c_p - c_v$, the result is

$$dq = c_p dT - Avdp$$

Then from the defining equation $ds = \dfrac{dq}{T}$

$$ds = c_p \frac{dT}{T} - \frac{Av}{T}dp$$

or, since

$$\frac{v}{T} = \frac{B}{p}$$

$$ds = c_p \frac{dT}{T} - AB \frac{dp}{p}.$$

This expression is applicable when the pound is the unit of weight; if the mol is taken as the unit, the expression becomes

$$ds = \gamma_p \frac{dT}{T} - R \frac{dp}{p} \quad \dots\dots\dots\dots\dots (14)$$

with the understanding that $R = 1.985$.

The entropy of 1 mol of a gas is therefore given by the expression

$$s = \int \gamma_p \frac{dT}{T} - R \log_e p + s_0 \dots\dots\dots\dots\dots (15)$$

In a mixture of gases each gas occupies the total volume V, and this being the case, the entropy of the mixture is the sum of the entropies of the individual constituents. If n_1, n_2, n_3, etc., denote the number of mols of the several constituents and p_1, p_2, p_3, etc., the corresponding partial pressures, the total entropy is

$$S = n_1 \int \gamma_{p_1} \frac{dT}{T} + n_2 \int \gamma_{p_2} \frac{dT}{T} + n_3 \int \gamma_{p_3} \frac{dT}{T} + \dots$$

$$- R \left(n_1 \log_e p_1 + n_2 \log_e p_2 + n_3 \log_e p_3 + \dots \right)$$

$$+ n_1 s_{01} + n_2 s_{02} + n_3 s_{03} + \dots\dots\dots\dots (16)$$

12. *Thermodynamic Potentials.*—Two important functions that will be required in the following chapter are the thermodynamic potentials at constant volume and at constant pressure, respectively. These are denoted by F_v and F_p, and they are defined by the following equations:

$$F_v = U - TS \quad \dots\dots\dots\dots\dots\dots (17)$$

$$F_p = U - TS + ApV = I - TS \quad \dots\dots\dots (18)$$

By a combination of the preceding equations a general expression for F_v or F_p of a mixture of gases may be readily derived; but such a procedure is unnecessary, as it is more convenient to operate with the individual terms, as U, I, and S, and ultimately combine the results.

III.   THERMODYNAMICS OF GAS REACTIONS.

13. *Chemical Equilibrium.*—In a mixture of gases in which chemical action is possible, for example, a mixture of CO, O_2, H_2, N_2, H_2O, reactions may proceed with an accompanying change of tempera-

ture; but at some definite state of the mixture, a state determined by the temperature and the partial pressures of the constituents of the mixture, chemical action ceases, and the mixture is said to be in equilibrium.

The determination of the conditions under which a gas mixture attains the equilibrium state is a fundamental problem in the investigation of temperatures and pressures due to combustion. The equations giving these conditions are deduced by various methods, all of which, however, are essentially identical with the analysis of Prof. J. Willard Gibbs, who first developed the general theory of chemical equilibrium. Haber first makes use of the entropy principle and afterwards deduces the fundamental equation with the aid of Van't Hoff's "equilibrium box." Nernst also uses the device of Van't Hoff. Planck makes use of the method of thermodynamic potentials, which is the original method of Gibbs.

In this section as much of the theory is presented as is necessary for solution of the problem proposed. The method of thermodynamic potentials is used because it is peculiarly applicable when several simultaneous equilibrium equations are to be established.

14. *Energy Changes in Chemical Reactions.*—When a system is subjected to any change, either physical or chemical, the intrinsic energy of the system will in general increase or decrease, the system will absorb heat from, or give heat to, the surroundings, and external work will be done by, or upon, the system. Let $- \Delta U$ denote the *decrease* of energy, $- \Delta Q$ the heat *given up* to the surroundings, and ΔW the work done *by* the system. Then the energy $- \Delta U$ liberated is partly expended in doing the work ΔW and the remainder is the heat $- \Delta Q$ rejected to external systems. This statement expressed symbolically gives the energy equation

$$- \Delta U = \Delta W - \Delta Q \quad \dots \dots \dots \dots \dots (19)$$

In a chemical reaction the decrease of energy $- \Delta U$ when 1 mol of the substance is combined is the heat of reaction H_v at constant volume. If $\Delta Q = 0$, the total energy given up is available for the performance of work; but in general, ΔQ is not equal to zero and the work attainable is not equal to the heat of reaction.

The work ΔW is in every case the product of two factors, one of which has the quality of a force. Thus the work done by an expanding gas is $\Delta W = p\Delta V$, in which the pressure p is the intensity factor or force; in a cell a quantity of electricity Δe is generated and the work is $\Delta W = E\Delta e$, and E is the electromotive force. Similarly, the work obtainable in a chemical reaction may be taken as proportional to the amount Δx of a constituent transformed; and if the expression for work is written

$$\Delta W = X\Delta x$$

the factor X may be regarded as a force. It is sometimes called the *driving force* of the reaction. If there are several fuel constituents in the gas mixture the work is given by the expression

$$\Delta W = X_1 \Delta x_1 + X_2 \Delta x_2 + X_3 \Delta x_3 +$$

and if there is a change in volume during the combustion the work $Ap\Delta V$ done against the external pressure must be added. Hence the energy equation takes the form

$$- \Delta U = X_1 \Delta x_1 + X_2 \Delta x_2 + X_3 \Delta x_3 + \ldots \ldots + Ap\Delta V - \Delta Q \quad (20)$$

15. *Introduction of Thermodynamic Potentials.*—The thermodynamic potential F_v is defined by the equation

$$F_v = U - TS$$

which upon differentiation gives

$$dF_v = dU - TdS - SdT$$

The general expression for entropy provided the process is reversible, is

$$dS = \frac{dQ}{T}$$

or

$$TdS = dQ$$

Substituting dQ for TdS in the preceding equation, the result is

$$dF_v = dU - dQ - SdT$$

The energy equation (19) in differential form is

$$- dU = dW - dQ$$

and a combination of the two equations gives

$$dF_v = - dW - SdT \ldots \ldots \ldots \ldots \ldots (21)$$

In the case of an irreversible process $TdS > dQ$, and equation (21) must be replaced by the inequality

$$dF_v < - dW - SdT \ldots \ldots \ldots \ldots (22)$$

For an isothermal process $dT = 0$, and equation (21) becomes

$$dW = - dF_v$$

Hence for a change of the system from state 1 to state 2,

$$_1W_2 = F_{v1} - F_{v2} \ldots \ldots \ldots \ldots \ldots (23)$$

For an isothermal change that is irreversible the inequality (22) gives

$$_1W_2 < F_{v1} - F_{v2} \ldots \ldots \ldots \ldots (24)$$

Hence the *maximum* work obtainable from an isothermal change of state is equal to the decrease of the potential function F_v.

Since

$$U = F_v + TS$$

$$U_1 - U_2 = F_{v1} - F_{v2} + T(S_1 - S_2) \ldots \ldots \ldots (25)$$

when T is constant. The total energy released is therefore made up of two parts: $F_{v1} - F_{v2}$, which is equal to the work obtainable and is therefore the available part; and $T(S_1 - S_2)$, which is the unavailable part. The first of these is the so-called "free energy," the second the "bound energy."

In the case of a chemical reaction,

$$dW = X_1 dx_1 + X_2 dx_2 + X_3 dx_3 + \ldots \ldots \ldots + Ap dV$$

If the temperature is kept constant $dW = -dF_v$; hence for $T = $ const.,

$$- dF_v = X_1 dx_1 + X_2 dx_2 + X_3 dx_3 + \ldots \ldots \ldots + Ap dV \ldots (26)$$

The coefficients X_1, X_2, etc., are the partial derivatives of F_v with respect to the variables x_1, x_2, etc. Thus

$$X_1 = -\frac{\partial F_v}{\partial x_1}, \ X_2 = -\frac{\partial F_v}{\partial x_2}, \ X_3 = -\frac{\partial F_v}{\partial x_3}, \ \ldots \ldots \ldots \ldots (27)$$

The second potential function F_p is defined by the equation

$$F_p = U - TS + Ap V$$

The result of differentiation is

$$dF_p = dU - TdS - SdT + Ap dV + AV dp$$
$$= dF_v + Ap dV + AV dp \ldots \ldots \ldots \ldots \ldots (28)$$

Combination of equations (26) and (28) gives the equation

$$- dF_p = X_1 dx_1 + X_2 dx_2 + X_3 dx_3 + \ldots \ldots + AV dp. \ (29)$$

which is valid for a reversible isothermal process.

The expressions (27) for X_1, X_2, etc. were obtained by taking the total volume V constant. If the pressure p is taken as constant, equation (29) gives

$$X_1 = -\frac{\partial F_p}{\partial x_1}, \ X_2 = -\frac{\partial F_p}{\partial x_2}, \ X_3 = -\frac{\partial F_p}{\partial x_3}, \ \ldots \ldots \ldots \ldots (30)$$

Since $F_p = I - TS$, the decrease of the thermal potential I for a change of state is

$$I_1 - I_2 = F_{p1} - F_{p2} + T(S_1 - S_2) \ldots \ldots \ldots \ldots \ldots (31)$$

an equation analogous to equation (25). In the case of an isothermal chemical combination $U_1 - U_2 = H_v$ and $I_1 - I_2 = H_p$; hence equations (25) and (31) may be written, respectively,

$$F_{v1} - F_{v2} = H_v - T(S_1 - S_2) \ldots \ldots \ldots \ldots \ldots (32)$$

$$F_{p1} - F_{p2} = H_p - T(S_1 - S_2) \ldots \ldots \ldots \ldots \ldots (33)$$

Equation (32) shows that the work obtainable from a reaction proceeding at constant temperature and volume is less than the heat of combustion by the amount $T(S_1 - S_2)$. For a reaction at constant pressure and temperature, equation (33) shows that the work obtainable is less than the heat of combustion H_p by the bound energy $T(S_1 - S_2)$.

16. *Conditions of Equilibrium.*—It is a well-established fact that in a chemical reaction the driving force changes continuously as the reaction proceeds, and that at some definite composition of the gas mixture, depending on the temperature, the driving force vanishes and the reaction halts. The mixture has then attained a state of equilibrium.
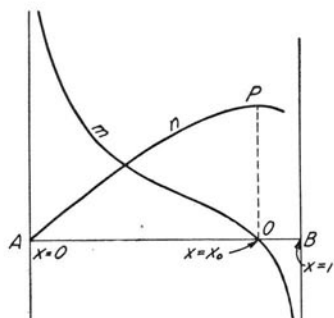
FIG. 1. DRIVING FORCE AND WORK OF   FIG. 2. TEMPERATURE CURVE FOR
CHEMICAL REACTION   CHEMICAL REACTION
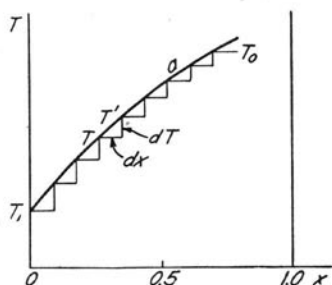
Consider, for example, the reaction $CO + \frac{1}{2}O_2 = CO_2$ and let x denote the fraction of CO transformed to CO_2. Values of x are given by the distances along the line AB, Fig. 1; at A, $x = 0$, at B, where the reaction is complete, $x = 1$. The magnitude of the driving force X is given by the ordinate of the curve m. The driving force is greatest when $x = 0$, and steadily decreases as x increases until for some value of x, as x_0, it becomes zero. For x greater than x_0 the driving force changes sign, which means that the reaction tends to proceed in the opposite direction; that is, for $x > x_0$, CO_2 dissociates into CO and O_2.

Curve n is the integral curve of curve m; that is, the ordinate of curve n represents the work

$$W_x = \int_0^x X dx \dots\dots\dots\dots\dots (34)$$

corresponding to the progress of the reaction from the beginning to the point indicated by the value of x. The maximum ordinate of curve n is OP corresponding to the value $x = x_0$.

The condition of equilibrium may now be established. The mixture of the three gases CO, O_2 and CO_2 is in a state of equilibrium when the driving force is zero, that is, when $x = x_0$. The condition is, therefore,

$$X = 0 \dots\dots\dots\dots\dots\dots (35)$$

If there are several fuel constituents, the corresponding conditions are

$$X_1 = 0, \ X_2 = 0, \ X_3 = 0, \ \dots\dots\dots (36)$$

If the reaction proceeds at constant temperature and the whole volume is kept constant, these conditions are equivalent to the conditions

$$\frac{\partial F_v}{\partial x_1} = 0, \ \frac{\partial F_v}{\partial x_2} = 0, \ \frac{\partial F_v}{\partial x_3} = 0, \ \dots\dots\dots\dots (37)$$

or if the pressure instead of the volume is constant, they are equivalent to the conditions

$$\frac{\partial F_p}{\partial x_1} = 0, \ \frac{\partial F_p}{\partial x_2} = 0, \ \frac{\partial F_p}{\partial x_3} = 0, \ \dots\dots\dots\dots (38)$$

In order to get these conditions in a useful form it is necessary to express the composition of the mixture in terms of the variable x, or in terms of the variables x_1, x_2, x_3, ... if there are several combustible constituents. An expression for F_v or F_p is then obtained, and by differentiation expressions for the driving forces X_1, X_2, etc., are found. Equating these to zero gives the required conditions of equilibrium. In the following paragraphs the equilibrium conditions are worked out in detail for several important cases.

17. *Case 1. The Reaction* $CO + \frac{1}{2}O_2 = CO_2$.—It is assumed that CO is burned in air and that an excess of air may be used; thus for 1 mol of CO let e mols of O_2 and f mols of N_2 be supplied. The initial composition is

$$\begin{aligned}
CO \ &= 1 \text{ mol} \\
O_2 \ &= e \text{ mols} \\
N_2 \ &= f \text{ mols} \\
\hline
\text{Total} \dots \ &1 + e + f = m_1 \text{ mols}
\end{aligned}$$

The composition of the mixture after the fraction x of CO has been converted to CO_2, is

$$\begin{aligned}
CO \ &= 1 - x \text{ mol} \\
CO_2 &= x \text{ mol} \\
O_2 &= e - \tfrac{1}{2}x \text{ mols} \\
N_2 &= f \text{ mols} \\
\hline
\text{Total} \dots 1 &+ e + f - \tfrac{1}{2}x = m = m_1 - \tfrac{1}{2}x
\end{aligned}$$

Let P denote the total pressure of this mixture; then the partial pressures of the constituents are, respectively,

$$p_{CO} = P\frac{1-x}{m_1 - \frac{1}{2}x}, \qquad p_{CO_2} = P\frac{x}{m_1 - \frac{1}{2}x}$$
$$p_{O_2} = P\frac{e - \frac{1}{2}x}{m_1 - \frac{1}{2}x}, \qquad p_{N_2} = P\frac{f}{m_1 - \frac{1}{2}x} \Bigg\} \quad \dots (39)$$

If the mixture is kept at constant volume during the reaction the total pressure P changes, but the partial pressures may be expressed in terms of P_1 the initial pressure. For the initial mixture,

$$P_1 V = m_1 RT$$

for the final mixture,

$$PV = (m_1 - \tfrac{1}{2}x) \cdot RT$$

Hence with T and V constant,

$$\frac{P}{m_1 - \frac{1}{2}x} = \frac{P_1}{m_1} \quad \dots\dots\dots\dots\dots (40)$$

and the expressions for the partial pressures are

$$p_{CO} = \frac{P_1}{m_1}(1-x), \qquad p_{CO_2} = \frac{P_1}{m_1}x,$$
$$p_{O_2} = \frac{P_1}{m_1}(e - \tfrac{1}{2}x), \qquad p_{N_2} = \frac{P_1}{m_1}f \Bigg\} \quad \dots\dots (41)$$

A certain function of the partial pressures will appear repeatedly in the following developments. For this reaction it is

$$\frac{p_{CO_2}}{p_{CO} \cdot p_{O_2}^{\frac{1}{2}}}$$

for the reaction $CH_4 + 2O_2 = CO_2 + 2H_2O$ it is

$$\frac{p_{CO_2} \cdot p^2_{H_2O}}{p_{CH_4} \cdot p^2_{O_2}}$$

The function is a fraction in the numerator of which appear the partial pressures of the products and in the denominator the partial pressures of the factors. Each partial pressure is given an exponent equal to the coefficient applied to the constituent in the reaction equation. Let this function be denoted by $K(p)$; then for the CO reaction under discussion

$$K(p) = \frac{p_{CO_2}}{p_{CO} \cdot p_{O_2}^{\frac{1}{2}}} = \frac{P\dfrac{x}{m_1 - \frac{1}{2}x}}{P\dfrac{1-x}{m_1 - \frac{1}{2}x}\left(P\dfrac{e - \frac{1}{2}x}{m_1 - \frac{1}{2}x}\right)^{\frac{1}{2}}}$$

or

$$K(p) = \frac{x}{1-x}\sqrt{\frac{m_1 - \frac{1}{2}x}{e - \frac{1}{2}x}} \cdot \frac{1}{\sqrt{P}} \quad\ldots\ldots\ldots\ldots\ldots (42)$$

If the volume is kept constant as well as the temperature,

$$K(p) = \frac{x}{1-x}\sqrt{\frac{m_1}{e - \frac{1}{2}x}} \cdot \frac{1}{\sqrt{P_1}} \quad\ldots\ldots\ldots (43)$$

In deriving the equation of equilibrium either the pressure or the volume may be taken as constant; the result is the same. The algebraic work is perhaps somewhat simpler when constant volume is assumed, and the potential F_v is used.

Taking the defining equation

$$F_v = U - TS,$$

the expression for the driving force X is

$$X = -\frac{\partial F_v}{\partial x} = -\frac{\partial U}{\partial x} + T\frac{\partial S}{\partial x} \quad\ldots\ldots\ldots\ldots (44)$$

The derivative $\dfrac{\partial U}{\partial x}$ is easily obtained. The energy of the final mixture is

$$U = (1-x)u_{CO} + xu_{CO_2} + (e - \tfrac{1}{2}x)u_{O_2} + fu_{N_2}$$

whence

$$-\frac{\partial U}{\partial x} = u_{CO} + \tfrac{1}{2}u_{O_2} - u_{CO_2}$$

The second member of this equation is the heat of combustion at constant volume, hence

$$-\frac{\partial U}{\partial x} = H_v \quad\ldots\ldots\ldots\ldots\ldots\ldots (45)$$

To evaluate the remaining term $T\dfrac{\partial S}{\partial x}$ we must obtain an expression for the total entropy S of the mixture, differentiate with respect to x, and multiply the result by T. To get the entropy S the entropy per mol of each constituent is multiplied by the weight of the constituent in mols, and the products are added.

The expression for the entropy of one mol of a gas is (Section 11)

$$s = \int \gamma_p \frac{dT}{T} - R\log_e p + s_0$$

For convenience, let $\quad h = \int \gamma_p \dfrac{dT}{T} + s_0$; then

$$s = h - R\log_e p$$

The expression for S will have two groups of terms; those contributed by the h functions and those contributed by the terms of the form

$$R\log_e p$$

The first group gives the sum

$$(1-x)h_{CO} + xh_{CO_2} + (e - \tfrac{1}{2}x)h_{O_2} + fh_{N_2}$$

Since for any constituent h is a function of the temperature only, the x derivative of this sum is simply

$$-(h_{CO} + \tfrac{1}{2}h_{O_2} - h_{CO_2}) = -\lambda$$

The expression for the specific heat of a gas is

$$\lambda_p = \alpha + \beta T + \delta T^2$$

The function h is, therefore,

$$h = \int \frac{\gamma_v dT}{T} + s_0 = \alpha \log_e T + \beta T + \tfrac{1}{2}\delta T^2 + s_0 \ldots \ldots \ldots \ldots (46)$$

Consequently, the expression for λ in the present reaction is

$$\lambda = h_{CO} + \tfrac{1}{2}h_{O_2} - h_{CO_2}$$
$$= \log_e T(\alpha_{CO} + \tfrac{1}{2}\alpha_{O_2} - \alpha_{CO_2}) + T(\beta_{CO} + \tfrac{1}{2}\beta_{O_2} - \beta_{CO_2})$$
$$+ \tfrac{1}{2}T^2(\delta_{CO} + \tfrac{1}{2}\delta_{O_2} - \delta_{CO_2}) + (s_{0CO} + \tfrac{1}{2}s_{0O_2} - s_{0CO_2})$$

The following symbols may be used for the terms in the parentheses:

$$\sigma' = \alpha_{CO} + \tfrac{1}{2}\alpha_{O_2} - \alpha_{CO_2} \qquad \sigma'' = \beta_{CO} + \tfrac{1}{2}\beta_{O_2} - \beta_{CO_2}$$
$$\sigma''' = \delta_{CO} + \tfrac{1}{2}\delta_{O_2} - \delta_{CO_2} \qquad k = s_{0CO} + \tfrac{1}{2}s_{0O_2} - s_{0CO_2}$$

Then

$$\lambda = \sigma'\log_e T + \sigma'' T + \tfrac{1}{2}\sigma''' T^2 + k \ldots \ldots \ldots (47)$$

The formation of the expressions for λ, σ', $\ldots \ldots k$ for any reaction is obvious. Thus for the reaction $CH_4 + 2O_2 = CO_2 + 2H_2O$,

$$\lambda = h_{CH_4} + 2h_{O_2} - h_{CO_2} - 2h_{H_2O}$$
$$\sigma' = \alpha_{CH_4} + 2\alpha_{O_2} - \alpha_{CO_2} - 2\alpha_{H_2O}$$
$$k = s_{0CH_4} + 2s_{0O_2} - s_{0CO_2} - 2s_{0H_2O}$$

The coefficients are those in the reaction equation; terms involving the factors are given the positive sign, those involving the products, the negative sign.

The group of terms involving the partial pressures must now receive attention. Each term has the form $m\,R\log_e p$, in which m denotes the number of mols of the constituent and p the partial pressure.

Thus for the CO constituent, $m = 1 - x$, and $p = P\dfrac{1-x}{m_1 - \frac{1}{2}x}$, or as the volume is considered constant, $p = P_1 \dfrac{1-x}{m_1}$. The sum of the terms in this group is

$$-R\left[(1-x)\log_e(1-x)\frac{P_1}{m_1} + x\log_e x\frac{P_1}{m_1} + (e-\tfrac{1}{2}x)\log_e(e-\tfrac{1}{2}x)\frac{P_1}{m_1} \right.$$
$$\left. + f\log_e f\frac{P_1}{m_1} \right]$$
$$= -R\left[(m_1 - \tfrac{1}{2}x)\log_e\frac{P_1}{m_1} + (1-x)\log_e(1-x) + x\log_e x \right.$$
$$\left. + (e-\tfrac{1}{2}x)\log_e(e-\tfrac{1}{2}x) + f\log_e f \right]$$

The x derivative of a term such as $(e - \tfrac{1}{2}x)\log_e(e - \tfrac{1}{2}x)$ is
$$-\tfrac{1}{2}\log_e(e - \tfrac{1}{2}x) - \tfrac{1}{2}$$
hence the x derivative of the preceding sum is

$$-R\left[-\tfrac{1}{2}\log_e\frac{P_1}{m_1} - \log_e(1-x) - 1 + \log_e x + 1 - \tfrac{1}{2}\log_e(e-\tfrac{1}{2}x) - \tfrac{1}{2} \right]$$
$$= \tfrac{1}{2}R - R\log_e\frac{x}{1-x}\sqrt{\frac{m_1}{e-\tfrac{1}{2}x}} \cdot \frac{1}{\sqrt{P_1}}$$
$$= \tfrac{1}{2}R - R\log_e K(p)$$

since $\qquad \dfrac{x}{1-x}\sqrt{\dfrac{m_1}{e-\tfrac{1}{2}x}} \cdot \dfrac{1}{\sqrt{P_1}} = K(p)$ (See page 27.)

Collecting the results, we have the following:

$$\frac{\partial S}{\partial x} = -\lambda + \tfrac{1}{2}R - R\log_e K(p)$$

$$T\frac{\partial S}{\partial x} = -\lambda T + \tfrac{1}{2}RT - RT\log_e K(p)$$

$$-\frac{\partial U}{\partial x} = H_v$$

$$X = -\frac{\partial U}{\partial x} + T\frac{\partial S}{\partial x} = H_v + \tfrac{1}{2}RT - \lambda T - RT\log_e K(p)$$

or, since $H_v + \frac{1}{2}RT = H_p$ in the case of the CO reaction,

$$X = H_p - \lambda T - RT \log_e K(p) \quad \ldots \ldots \ldots \ldots \ldots (48)$$

The heat of combustion H_p is a function of the temperature (page 17), that is

$$H_p = H_0 + \sigma'T + \tfrac{1}{2}\sigma''T^2 + \tfrac{1}{3}\sigma'''T^3$$

Also

$$\lambda T = \sigma'T\log_e T + \sigma''T^2 + \tfrac{1}{2}\sigma'''T^3 + kT$$

whence

$$H_p - \lambda T = H_0 - \sigma'T\log_e T - \tfrac{1}{2}\sigma''T^2 - \tfrac{1}{6}\sigma'''T^3 - (k - \sigma')T$$

Introducing this expression in equation (48), the result is

$$X = H_0 - \sigma'T\log_e T - \tfrac{1}{2}\sigma''T^2 - \tfrac{1}{6}\sigma'''T^3 - \\ (k - \sigma')\ T - RT\log_e K(p)$$

The condition of equilibrium is $X = 0$; hence denoting by K_p the value of the pressure function $K(p)$ when equilibrium exists, the equilibrium equation is

$$RT\log_e K_p = H_0 - \sigma'T\log_e T - \tfrac{1}{2}\sigma''T^2 - \tfrac{1}{6}\sigma'''T^3 - (k - \sigma')T,$$

or dividing both members by T,

$$R\log_e K_p = \frac{H_0}{T} - \sigma'\log_e T - \tfrac{1}{2}\sigma''T - \tfrac{1}{6}\sigma'''T^2 - (k - \sigma') \quad (49)$$

Denoting by primes the partial pressures in the equilibrium state, and by x_0, the value of x at equilibrium, we have

$$K_p = \frac{p'_{CO_2}}{p'_{CO}\ p'^{\frac{1}{2}}_{O_2}} = \frac{x_0}{1 - x_0}\sqrt{\frac{m_1 - \frac{1}{2}x_0}{e - \frac{1}{2}x_0}} \cdot \frac{1}{\sqrt{P}} \quad \ldots \ldots \ldots \ldots (50)$$

K_p is called the *equilibrium constant*. For any temperature T, the value of K_p may be calculated from equation (49); then from equation (50) the value of x_0 is found. The elimination of K_p between equations (49) and (50) gives the relation between T and x_0 that must exist when the mixture is in the equilibrium state.

It is evident that K_p is a function of the temperature T. The rate of change of K_p with the temperature is obtained by differentiating equation (49); thus

$$R\frac{\partial \log_e K_p}{\partial T} = -\frac{H_0}{T^2} - \frac{\sigma}{T} - \tfrac{1}{2}\sigma'' - \tfrac{1}{3}\sigma'''T$$

$$= -\frac{1}{T^2}(H_0 - \sigma'T + \tfrac{1}{2}\sigma''T^2 + \tfrac{1}{3}\sigma'''T^3) = -\frac{H_p}{T^2} \quad (51)$$

This result is entirely general and is important, though it has no bearing on the present investigation.

A convenient expression for the driving force X is obtained by combining equations (48) and (49), namely,

$$X = RT\left[\log_e K_p - \log_e K(p)\right]$$

or

$$X = RT\left[\log_e \frac{p'_{CO_2}}{p'_{CO} \cdot p'^{\frac{1}{2}}_{O_2}} - \log_e \frac{p_{CO_2}}{p_{CO} \cdot p^{\frac{1}{2}}_{O_2}}\right] \dots\dots\dots\dots (52)$$

While the equilibrium equation (49) was developed for a particular reaction, $CO + \frac{1}{2}O_2 = CO_2$, it is perfectly general. The same method applied to any other reaction will give an equation of the same form. The only question that demands attention is the expression of the equilibrium constant K_p (1) in terms of the partial pressures, (2) in terms of x_0.

For the reaction $H_2 + \frac{1}{2}O_2 = H_2O$, all the relations just developed for the CO reaction are immediately applicable merely by substituting H_2 for CO and H_2O for CO_2. Thus equation (50) gives the relation between K_p and x_0 equally for both reactions.

As another example we consider the reaction $CH_4 + 2O_2 = CO_2 + 2H_2O$. The composition of the mixture corresponding to the transformation of the fraction x is

$$CH_4\dots\dots 1 - x \text{ mol}$$
$$CO_2\dots\dots\dots x \text{ mol}$$
$$H_2O\dots\dots 2x \text{ mols}$$
$$O_2\dots\dots e - 2x \text{ mols}$$
$$N_2\dots\dots\dots f \text{ mols}$$
$$\overline{\text{Total}\dots\dots 1 + e + f = m_1}$$

The partial pressures are, respectively,

$$p_{CH_4} = P\frac{1-x}{m_1}; \quad p_{CO_2} = P\frac{x}{m_1}; \quad p_{H_2O} = P\frac{2x}{m_1}; \quad p_{O_2} = P\frac{e-2x}{m_1}; \quad p_{N_2} = P\frac{f}{m_1}.$$

The pressure function is

$$K(p) = \frac{p_{CO_2} \cdot p^2_{H_2O}}{p_{CH_4} \cdot p^2_{O_2}} \dots\dots\dots\dots\dots (53)$$

Hence the equilibrium constant is given by the expression

$$K_p = \frac{p'_{CO_2}(p'_{H_2O})^2}{p'_{CH_4}(p'_{O_2})^2} = \frac{x_0(2x_0)^2}{(1-x_0)(e-2x_0)^2} \dots\dots (54)$$

It will be observed that the pressure P does not appear in the expression for K_p given by (54); hence the same expression applies for constant pressure and for constant volume. Such is the case in all reactions in which there is no change in molecular volume.

If oxygen alone is supplied without any excess the expressions for K_p are as follows:

In the case of the CO and H_2 reactions, $e = \frac{1}{2}$, $f = 0$, $m_1 = \frac{3}{2}$, whence from equation (50)

$$K_p = \frac{x_0}{1-x_0}\sqrt{\frac{3-x_0}{1-x_0}}\cdot\frac{1}{\sqrt{P}} \dots\dots\dots\dots (55)$$

In the case of CH_4, $e = 2$, $f = 0$, and from equation (54)

$$K_p = \left(\frac{x_0}{1-x_0}\right)^3 \dots\dots\dots\dots\dots\dots (56)$$

18. *Case 2. Mixture of* CO, H_2, *and Air.*—Consider a mixture of a mols of CO, b mols of H_2, and an amount of air at least sufficient for combustion. The progress of the CO reaction may be denoted by x, that of the H_2 reaction by y. Then the original mixture and the mixture after combustion has progressed are given by the following schedules:

Original Mixture	Mixture during Combustion
CO...............a mols	CO......$a\,(1-x)$ mols
H_2...............b mols	H_2.......$b\,(1-y)$ mols
O_2...............e mols	CO_2......ax mols
N_2...............f mols	H_2O ......by mols
	O_2........$e - \frac{1}{2}(ax + by)$ mols
	N_2....... f mols
Total ......$a + b + e + f = m_1$	Total..........$m_1 - \frac{1}{2}(ax + by) = m$

Taking P as the total pressure of the mixture, the partial pressures are, respectively,

$$p_{CO} = \frac{P}{m}a(1-x)\ ,\quad p_{CO_2} = \frac{P}{m}ax\ ,\quad p_{O_2} = \frac{P}{m}\left[e - \tfrac{1}{2}(ax + by)\right]$$

$$p_{H_2} = \frac{P}{m}b(1-y)\ ,\quad p_{H_2O} = \frac{P}{m}by\ ,\quad p_{N_2} = \frac{P}{m}\cdot f$$

From these partial pressures the two pressure functions are given by the equations

$$\frac{p_{CO_2}}{p_{CO}\cdot p_{O_2}^{\frac{1}{2}}} = \frac{x}{1-x}\sqrt{\frac{m_1 - \frac{1}{2}(ax + by)}{e - \frac{1}{2}(ax + by)}}\cdot\frac{1}{\sqrt{P}} \dots\dots (57)$$

$$\frac{p_{H_2O}}{p_{H_2} \cdot p_{O_2}^{\frac{1}{2}}} = \frac{y}{1-y} \sqrt{\frac{m_1 - \frac{1}{2}(ax+by)}{e - \frac{1}{2}(ax+by)}} \cdot \frac{1}{\sqrt{P}} \quad \ldots \ldots (58)$$

A combination of (57) and (58) gives the relation

$$\frac{p_{H_2O} \cdot p_{CO}}{p_{H_2} \cdot p_{CO_2}} = \frac{y(1-x)}{x(1-y)} \quad \ldots \ldots \ldots \ldots (59)$$

which is the pressure function for the water-gas reaction

$$H_2 + CO_2 = H_2O + CO$$

In establishing the equations of equilibrium the method used in case 1 is followed in all details. The expression for the energy of the mixture is

$$U = a(1-x)u_{CO_2} + b(1-y)u_{H_2} + axu_{CO_2} + byu_{H_2O}$$
$$+ \left[e - \frac{1}{2}(ax+by) \right] u_{O_2} + fu_{N_2}$$

The x and y partial derivatives are, respectively,

$$-\frac{\partial U}{\partial x} = a\left[u_{CO} + \frac{1}{2}u_{O_2} - u_{CO_2} \right] = aH_{vCO}$$

$$-\frac{\partial U}{\partial y} = b\left[u_{H_2} + \frac{1}{2}u_{O_2} - u_{H_2O} \right] = bH_{vH_2}$$

Similarly, the sum of the h functions furnishes the derivatives

$$\frac{\partial}{\partial x}\sum h = -a(h_{CO} + \frac{1}{2}h_{O_2} - h_{CO_2}) = -a\lambda_{CO}$$

$$\frac{\partial}{\partial y}\sum h = -b(h_{H_2} + \frac{1}{2}h_{O_2} - h_{H_2O}) = -b\lambda_{H_2}$$

Taking the volume and the temperature as constant, the relation $\frac{P}{m} = \frac{P_1}{m_1}$ holds, and the sum of the group of terms in the entropy equation that involve the pressures is

$$-R\left\{ a(1-x)\log_e \frac{P_1}{m_1} a(1-x) + b(1-y)\log_e \frac{P_1}{m_1} b(1-y) + ax\log_e \frac{P_1}{m_1} ax \right.$$

$$\left. + by\log_e \frac{P_1}{m_1} by + \left[e - \frac{1}{2}(ax+by) \right]\log_e \frac{P_1}{m_1}\left[e - \frac{1}{2}(ax+by) \right] + f\log_e \frac{P_1}{m_1} f \right\}$$

After slight reduction the expression takes the form

$$-R\left\{\left[m_1-\tfrac{1}{2}(ax+by)\right]\log_e\frac{P_1}{m_1}+a(1-x)\log_e a(1-x)\right.$$
$$+b(1-y)\log_e b(1-y)+ax\log_e ax+by\log_e by$$
$$\left.+\left[e-\tfrac{1}{2}(ax+by)\right]\log_e\left[e-\tfrac{1}{2}(ax+by)\right]+f\log_e f\right\}$$

The x derivative of this expression is

$$-aR\left\{-\tfrac{1}{2}\log_e\frac{P_1}{m_1}-\log_e a(1-x)-1+\log_e ax\right.$$
$$\left.+1-\tfrac{1}{2}\log_e\left[e-\tfrac{1}{2}(ax+by)\right]-\tfrac{1}{2}\right\}$$

$$=\tfrac{1}{2}aR-aR\log_e\frac{x}{1-x}\sqrt{\frac{m_1}{e-\tfrac{1}{2}(ax+by)}}\cdot\frac{1}{\sqrt{P_1}}$$

or, making use of equation (57), the expression for the x derivative becomes

$$a\left[\tfrac{1}{2}R-R\log_e K(p)_{co}\right]$$

in which $K(p)_{co}$ denotes the pressure function $\dfrac{p_{co_2}}{p_{co}\cdot p_{o_2}^{\frac{1}{2}}}$.

Similarly, the y derivative is found to be

$$b\left[\tfrac{1}{2}R-R\log_e K(p)_{H_2}\right]$$

Collecting the results, the two driving forces X and Y are given by the expressions

$$\left.\begin{aligned}X&=a\left[H_{pco}-\lambda_{co}T-RT\log_e K(p)_{co}\right]\\[2mm]Y&=b\left[H_{pH_2}-\lambda_{H_2}T-RT\log_e K(p)_{H_2}\right]\end{aligned}\right\}\ \ \ldots\ldots\ (60)$$

The conditions of equilibrium are $X=0$, $Y=0$; inserting these values in equation (60), the resulting equations are precisely those that are obtained for the equilibrium of the two constituents when taken separately. It should be noted, however, that the equilibrium constant K_p is a function of both x_0 and y_0 when the two constituents are mixed.

19. *Case 3. Mixture Containing a Hydrocarbon Constitutent.*
—As a concrete example, let c mols of CH_4 be added to the mixture of
the preceding case, and let z denote the progress of the reaction
$CH_4 + 2O_2 = CO_2 + 2H_2O$. Then the original mixture and the mix-
ture after combustion has started are as follows:

Original Mixture	Mixture during Combustion
CO...............a mols	CO...$a (1 — x)$ mols
H_2................b mols	H_2...$b (1 — y)$ mols
CH_4................c mols	CH_4..$c (1 — z)$ mols
O_2................e mols	CO_2..$ax + cz$ mols
N_2.................f mols	H_2O .$by + 2cz$ mols
	O_2 ...$e — \frac{1}{2} (ax + by) — 2cz$ mols
	N_2...f mols
Total....$a + b + c + e + f = m_1$	Total...$m = m_1 — \frac{1}{2} (ax + by)$

If now the same process is followed as in case 2, the two equations
(60) will again be obtained; and in addition a third equation

$$Z = c\left[H_{pCH_4} - \lambda_{CH_4} T - RT \log_e K(p)_{CH_4} \right]$$

Putting $Z = 0$, for equilibrium, and K_p for $K(p)$,

$$R \log_e K_p = \frac{H_p}{T} - \lambda$$

The equilibrium equations for the CH_4 reaction are known approxi-
mately and K_p may be calculated for various assumed temperatures.
The equilibrium equations (see page 137) are:

For $T < 2900$ deg.

$$4.571 \log_{10} K_p = \frac{348\,330}{T} + 14.9462 \log_{10}T — 3.606 \cdot 10^{-3}T$$
$$+ 0.001 \cdot 10^{-6}T^2 — 47$$

For $T > 2900$ deg.

$$4.571 \log_{10} K_p = \frac{353\,210}{T} + 26.5651 \log_{10}T — 5.346 \cdot 10^{-3}T$$
$$+ 0.101 \cdot 10^{-6}T^2 — 84.7$$

From these equations the following results are calculated:

T =	1000	2000	3000	4000	5000
$\log_{10}K_p$ =	76.69	37.91	24.68	17.80	13.50
K_p =	5^{76}	8^{37}	4.8^{24}	6.3^{17}	3.2^{13}

That is, K_p is practically infinite, and $\dfrac{1}{K_p} = 0$.

Now, from the composition, the expression for K_p is

$$K_p = \frac{p_{CO_2} \cdot p^2{}_{H_2O}}{p_{CH_4} \cdot p^2{}_{O_2}} = \frac{(ax+cz)\,(by+2cz)^2}{c(1-z)\,(e-\frac{1}{2}ax-\frac{1}{2}by)^2}$$

It follows that z must be practically equal to 1 at all temperatures. In other words, at equilibrium there is no appreciable amount of CH_4 present.

Tizard and Pye* have pointed out the impossibility of the formation of methane at high temperature from the reaction

$$CO + 3H_2 = CH_4 + H_2O$$
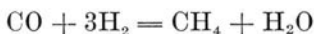
by using the following approximate equilibrium equation due to Nernst,

$$\log K_p = \log \frac{p_{CO} \cdot p^3{}_{H_2}}{p_{CH_4} \cdot p_{H_2O}} = -\frac{19\,000}{T} + 3.5 \log T + 2.2$$

in which T = deg. C. (abs.). From this formula K_p = about 10^{12} at 3000 deg. C. (abs.) and 10^8 at 2000 deg. C. (abs.). Methane, therefore, will not be formed from this reaction at the high explosion temperatures. However, at $T = 1000$ deg. C. (abs.) K_p = about 50 so that methane would be formed at low temperatures according to the above reaction if free CO and H_2 were present. This fact, according to Tizard and Pye, accounts for the presence of CH_4 in engine exhausts.

Tizard and Pye also show that the formation of formaldehyde according to the reaction $CO + H_2 = H.CHO$ can only occur at low temperatures. The equilibrium equation derived by the use of Nernst's heat theorem is

$$\log K = \log \frac{p_{CO} \cdot p_{H_2}}{p_{H \cdot CHO}} = -\frac{3700}{T} + 1.75 \log T + 2.1$$

in which T = deg C. (abs.).

The formation of methane and formaldehyde in engine exhausts will only be possible in case CO and H_2 are present in appreciable quantities. With sufficient oxygen in the mixture only very slight traces of CO and H_2 will exist, these traces being due to non-homogeneous combustion. With insufficient oxygen in the original mixture, appreciable quantities of free CO and H_2 are found in the cooled exhaust gas along with traces of methane and formaldehyde.

From the foregoing discussion it may be concluded that in the equilibrium state the products of combustion of a mixture of H_2, CO, and CH_4 with sufficient air will be CO_2, CO, H_2O, H_2, O_2, and N_2 only.

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* The Automobile Engineer, February, 1921, p. 59.

(See Section 33, on possibility of formation of NO.)   The equilibrium state for such a mixture is specified by equation (60) alone.

The question naturally arises as to the constitution of the mixture of gases in the equilibrium state resulting from the combustion of hydrocarbons other than methane with or without sufficient oxygen present for complete combustion.   In the case of insufficient oxygen the excess hydrocarbon may be unaffected by the high temperature, it may break down into simpler hydrocarbons, it may decompose into its elements, or any one of a number of phenomena might occur.   Experimental evidence, however, points rather directly to one result, namely, that the total hydrocarbon burns to CO and H_2 and that these two products burning in part to CO_2 and H_2O consume any remaining oxygen.   This was found to be the case by W. A. Bone[*] and others in explosions of CH_4, C_2H_2, C_2H_4, C_2H_6 with just sufficient oxygen present to burn the carbon to CO.   Only in the case of C_2H_6 was any carbon at all deposited.   Methane and aldehyde vapors were found in the products of combustion.

Further evidence is obtained from the analyses of exhaust gases obtained from engines running with insufficient air supplied to the mixture.   The following table of analyses is given by Dr. Watson[†] for dry exhaust gases from a petrol engine.   Traces of aldehyde were found in the condensed water obtained from the exhaust.

Ratio of Air to Petrol by Weight	Composition of Exhaust Gases					
	CO_2	O_2	CO	H_2	CH_4	N_2
9	6.7	0.0	12.0	4.3	1.4	75.6
10	8.2	0.0	9.6	3.5	1.2	77.5
11	9.6	0.0	7.3	2.6	0.9	79.6
12	11.1	0.0	5.0	1.8	0.6	81.5
13	12.5	0.0	2.6	0.9	0.3	82.7
14	13.5	0.4	0.4	0.1	0.0	85.6

From the evidence given in this table, from the experiments of Bone, with the satisfactory explanation of the presence of methane and aldehyde in the cooled products of combustion, and also from the known general instability of hydrocarbons at high temperature, it may be safely assumed that the mixture of gases in the equilibrium state resulting from the combustion of any hydrocarbon will consist

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* Jour. Chem. Soc., V. 71, pp. 26-41.—Phil. Trans. Roy. Soc., Ser. A. V. 215, (1915), pp. 278-318.

† Proc. Inst. of Auto. Engrs., 1909.

Also, A. W. Judge, "Automobile and Aircraft Engines," (1921), p. 23.

only of CO_2, CO, H_2O, H_2, O_2, and N_2. The only condition is that sufficient oxygen be present to burn all the carbon to CO.

20. *The General Case.*—The mixture contains CO, H_2, one or more hydrocarbons, as CH_4, C_2H_4, and possibly CO_2 and H_2O. When equilibrium is attained the mixture will have the six constituents CO, CO_2, H_2, H_2O, O_2, and N_2. The relative proportions of these constituents will determine the two variables x_0 and y_0; thus

$$\frac{CO_2}{CO} = \frac{x_0}{1 - x_0} \quad , \quad \frac{H_2O}{H_2} = \frac{y_0}{1 - y_0}$$

The first step in the application of the equilibrium equations is the determination of the composition of the mixture in the equilibrium state in terms of x_0 and y_0. For this purpose it is convenient to assume (a) that all the reactions are completed, and (b) that products CO_2 and H_2O in this mixture are then partially dissociated. The following example illustrates the procedure.

The 15 per cent mixture of coal gas and air used in David's experiments (see page 60) had the following composition:

Carbon monoxide	CO	0.060
Hydrogen	H_2	0.480
Methane	CH_4	0.335
Ethylene	C_2H_4	0.035
Benzene	C_6H_6	0.010
Carbon dioxide	CO_2	0.020
Water vapor	H_2O	0.033
Oxygen	O_2	1.179
Nitrogen	N_2	4.515
	Total	6.667

Complete combustion of the fuel constituents gives the mixture

$$CO_2 = 0.545$$
$$H_2O = 1.283$$
$$O_2 = 0.059$$
$$N_2 = 4.515$$
$$\text{Total} \quad 6.402$$

The equilibrium mixture is now obtained from this hypothetical mixture by the dissociation of the fraction $1 - x_0$ of CO_2 and the fraction $1 - y_0$ of H_2O. These dissociations produce

$$\tfrac{1}{2} \cdot 0.545 \, (1 - x_0) + \tfrac{1}{2} \cdot 1.283 \, (1 - y_0) \text{ mols of } O_2;$$

hence in the equilibrium mixture the oxygen present is

$$0.059 + \tfrac{1}{2}(0.545 + 1.283) - 0.2725x_0 - 0.6415y_0$$

The desired composition in the equilibrium state is, therefore,

$$
\begin{aligned}
&CO \ldots 0.545\,(1 - x_0) \\
&CO_2 \ldots 0.545\,x_0 \\
&H_2 \ldots 1.283\,(1 - y_0) \\
&H_2O \ldots 1.283\,y_0 \\
&O_2 \ldots 0.973 - 0.2725x_0 - 0.6415y_0 = e_0 \\
&N_2 \ldots 4.515
\end{aligned}
$$

$$\text{Total} \ldots 7.316 - 0.2725x_0 - 0.6415y_0 = m_0$$

From this composition the following expressions for K_p are obtained:

$$
K_{p(CO)} = \frac{p'_{CO_2}}{p'_{CO} \cdot p'^{\frac{1}{2}}_{O_2}} = \frac{0.545x_0\,\dfrac{P}{m_0}}{0.545(1 - x_0)\,\dfrac{P}{m_0}\left(e_0\,\dfrac{P}{m_0}\right)^{\frac{1}{2}}}
$$

$$
= \frac{x_0}{1 - x_0}\sqrt{\frac{m_0}{e_0}}\,\frac{1}{\sqrt{P}} \quad\ldots\ldots\ldots\ldots (61)
$$

$$
K_{p(H_2)} = \frac{y_0}{1 - y_0}\sqrt{\frac{m_0}{e_0}}\cdot\frac{1}{\sqrt{P}} \quad\ldots\ldots\ldots\ldots (62)
$$

The formulas (61) and (62) are perfectly general. Provided there is sufficient oxygen supplied for complete combustion, the mixture of products, assuming complete combustion, will contain n_1 mols of CO_2, n_2 mols of H_2O, excess oxygen, and nitrogen. Then the composition of the mixture at equilibrium must be

$$
\begin{aligned}
&\hspace{2.2cm}\text{mols} \\
&CO \ldots n_1\,(1 - x_0) \\
&CO_2 \ldots n_1 x_0 \\
&H_2 \ldots n_2\,(1 - y_0) \\
&H_2O \ldots n_2 y_0 \\
&O_2 \ldots e_0 \\
&N_2 \ldots f
\end{aligned}
$$

$$\text{Total} \ldots n_1 + n_2 + e_0 + f = m_0$$

From this composition follow the expressions for K_p given by equations (61) and (62).

A possible modification of the equilibrium composition should be mentioned. If the temperature at equilibrium is sufficiently high the endothermic reaction

$$N_2 + O_2 = 2\,NO$$
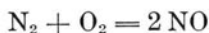
may be present, and the mixture may contain NO along with the other constituents. In this case the equilibrium equation for the reaction in addition to equations (61) and (62) is required. It will be shown subsequently that under most conditions the amount of NO formed is so small as to be negligible.

21. *Reactions with Increasing Temperature.*—In the discussion of Section 16 the equilibrium conditions expressed by equations (37) and (38) were based on the assumption of constant temperature; and this same assumption is involved in the derivation of equations (48), (49), and (50). In combustion reactions the temperature does not remain constant but rises rapidly. It might be inferred, therefore, that the relations that have been deduced are not applicable in such reactions with varying temperature.

The assumption of constant temperature does not mean that the temperature is necessarily the same throughout the whole course of the reaction. Consider, for example, the reaction $CO + \frac{1}{2}O_2 = CO_2$ in a closed space. The increase of temperature T with the weight x transformed is represented by some such curve as a, Fig. 2. For the purpose of the analysis the actual continuous process may be regarded as made up of a series of steps, as indicated by the broken line. First, the combustion proceeds at constant temperature T while the amount dx is transformed; secondly, the heat developed by the combustion is used to raise the temperature of the mixture from T to $T + dT = T'$; and so on. For each of the constant temperature transformations the driving force X is given correctly by equation (48) when the proper values of P, T, and x are introduced. The final constant temperature transformation will be at the equilibrium temperature T_0, and for this transformation $X = 0$, and $K(p) = K_p$. Equation (50) correctly expresses K_p as a function of x_0 provided $P = P_0$, the pressure of the mixture in the equilibrium state.

In the same way equations (61) and (62) are applicable in the general case. The pressure P in these equations must be taken as P_0, the pressure in the equilibrium state; and the temperature T in equation (49), which expresses K_p as a function of T, must be the temperature T_0 of the mixture in equilibrium.

The equations deduced for the equilibrium condition are, therefore, valid under all conditions. Whether equilibrium is attained at constant temperature or varying temperature, at constant volume or with a changing volume, such equations as (49), (61), and (62) will be applicable in the equilibrium state.

When the combustion is at constant pressure equations (61) and (62) are immediately applicable, since $P = $ const. When the combustion is at constant volume, the pressure is continuously changing and it is convenient to replace the variable P by the variable T. The change is really made through the characteristic equation of the gas mixture. In the initial state there are m_1 mols at pressure P_1 and temperature T_1; in the equilibrium state m_0 mols at pressure P_0 and temperature T_0. Hence with the volume constant

$$P_1 V = m_1 R T_1, \qquad P_0 V = m_0 R T_0,$$

$$\frac{1}{P_0} = \frac{1}{P_1} \cdot \frac{m_1 T_1}{m_0 T_0}.$$

Substituting this expression in (61) and (62),

$$K_{p(CO)} = \frac{x_0}{1 - x_0} \sqrt{\frac{m_1}{e_0}} \cdot \frac{1}{P_1^{\frac{1}{2}}} \cdot \left(\frac{T_1}{T_0}\right)^{\frac{1}{2}} \quad \ldots \ldots \text{(61a)}$$

$$K_{p(H_2)} = \frac{y_0}{1 - y_0} \sqrt{\frac{m_1}{e_0}} \cdot \frac{1}{P_1^{\frac{1}{2}}} \cdot \left(\frac{T_1}{T_0}\right)^{\frac{1}{2}} \quad \ldots \ldots \text{(62a)}$$

A more convenient form of equation (61a) is

$$\log K_{p(CO)} + \tfrac{1}{2}\log T_0 = \log x_0 - \log(1 - x_0) + \tfrac{1}{2}\log m_1 - \tfrac{1}{2}\log e_0$$
$$+ \tfrac{1}{2}\log T_1 - \tfrac{1}{2}\log P_1 \ldots \ldots \ldots \ldots \text{(61b)}$$

In this equation the first member is a function of the equilibrium temperature T_0 alone, and the second member is a function of x_0 and y_0.

22. *The Water-Gas Equilibrium.*—The two equations (61) and (62) may be combined into the single equation

$$\frac{K_{p H_2}}{K_{p CO}} = \frac{y_0(1 - x_0)}{x_0(1 - y_0)}$$

Introducing the partial pressures,

$$\frac{K_{p H_2}}{K_{p CO}} = \frac{p'_{H_2O}}{p'_{H_2} \cdot p'^{\frac{1}{2}}_{O2}} \cdot \frac{p'_{CO} \; p'^{\frac{1}{2}}_{O2}}{p'_{CO_2}} = \frac{p'_{CO} \cdot p'_{H_2O}}{p'_{CO_2} \cdot p'_{H_2}}.$$

The ratio K_{pH2}/K_{pCO} is therefore the equilibrium constant of the reaction

$$H_2 + CO_2 = H_2O + CO$$
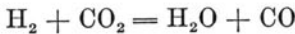
the water-gas reaction. Hence

$$K_p \text{ (w.g.)} = \frac{y_0(1 - x_0)}{x_0(1 - y_0)}. \quad \ldots \ldots \ldots \ldots \text{(63)}$$

The composition of the mixture at equilibrium must be such that the water-gas equilibrium expressed by equation (63) is satisfied. This equation (63) may replace either (61) or (62) in the specification of the equilibrium state.

The value of the constant K_p (w.g.) at a temperature T gives an indication of the relative values of x_0 and y_0. For example, at the maximum temperature attained in the internal combustion engine the value of this constant is about 7; hence

$$\frac{1 - x_0}{1 - y_0} = \frac{7x_0}{y_0}$$

or the dissociation of CO_2 is from 6 to 7 times the dissociation of H_2O when x is 0.8 or greater.

23. *Constants in the Equilibrium Equations.*—The general form of the equilibrium equation is

$$R \log_e K_p = \frac{H_0}{T} - \sigma' \log_e T - \tfrac{1}{2}\sigma'' T - \tfrac{1}{6}\sigma''' T^2 - (k - \sigma') \dots (49)$$

The constant H_0 is determined from the heat of combustion; the constants σ', σ'', σ''' from the specific heats of the components involved in the reaction. These constants for the two principal equilibrium equations are here given.

(a) **The Reaction** $H_2 + \tfrac{1}{2}O_2 = H_2O$. The constant $H_0 = 102\ 820$. From the expressions for the specific heats of the three constituents, we obtain:

For H_2 $\qquad \gamma_p = 6.00\ + 0.6667 \cdot 10^{-3} T$
For $\tfrac{1}{2}O_2$ $\qquad \tfrac{1}{2}\gamma_p = 3.465 \qquad\qquad\qquad + 0.06\ \cdot 10^{-6} T^2$
$\qquad\qquad$ Sum... $\overline{9.465 + 0.6667 \cdot 10^{-3} T + 0.06\ \cdot 10^{-6} T^2}$
For H_2O $\qquad \gamma_p = 8.33\ - 0.276\ \cdot 10^{-3} T + 0.423 \cdot 10^{-6} T^2$
$\qquad$ Difference... $\overline{1.135 + 0.9427 \cdot 10^{-3} T - 0.363 \cdot 10^{-6} T^2}$

Hence

$$\sigma' = 1.135, \quad \sigma'' = 0.9427 \cdot 10^{-3}, \quad \sigma''' = -0.363\ \cdot 10^{-6}$$
$$2.3026\,\sigma' = 2.6135, \tfrac{1}{2}\sigma'' = 0.4713 \cdot 10^{-3}, \tfrac{1}{6}\sigma''' = -0.0605 \cdot 10^{-6}$$

The constant k is determined by experiments on the chemical composition of the mixture in the equilibrium state. An account of such experiments is given in Appendix III. For the reaction under consideration, the experiments indicate the following:

$$k - \sigma' = 2.3, \quad k = 3.435$$

The first member of the equilibrium equation (49) may be transformed as follows:

$$R \log_e K_p = 2.3026 \ R \log_{10} K_p = 2.3026 \times 1.985 \log_{10} K_p$$
$$= 4.571 \log_{10} K_p$$

The final equilibrium equation is therefore

$$4.571 \log_{10} K_p = \frac{102 \ 820}{T} - 2.6135 \log_{10} T - 0.4713 \cdot 10^{-3}T$$
$$+ 0.0605 \cdot 10^{-6}T^2 - 2.3 \ \ldots\ldots\ldots\ldots\ldots\ldots\ldots (64)$$

(b) **The Reaction** $CO + \frac{1}{2}O_2 = CO_2$. The constant H_0 is 120 930. For temperatures below 2900 deg. F. (abs.) the following schedule of specific heats applies:

For CO $\qquad\qquad \gamma_p = 6.93 \qquad\qquad\quad + 0.12 \cdot 10^{-6}T^2$
For $\frac{1}{2}O_2 \qquad\qquad \frac{1}{2}\gamma_p = 3.465 \qquad\qquad\quad + 0.06 \cdot 10^{-6}T^2$
$\qquad\qquad\qquad$ Sum...$\overline{10.395 \qquad\qquad\quad + 0.18 \cdot 10^{-6}T^2}$
For $CO_2 \qquad\qquad\qquad 7.15 \ \ + 3.9 \cdot 10^{-3}T - 0.60 \cdot 10^{-6}T^2$
$\qquad\qquad$ Difference...$\overline{3.245 - 3.9 \cdot 10^{-3}T + 0.78 \cdot 10^{-6}T^2}$

Hence

$$\sigma' = 3.245, \quad \sigma'' = -3.9 \ \cdot 10^{-3}, \quad \sigma''' = 0.78 \cdot 10^{-6}$$
$$2.3026 \ \sigma' = 7.4719, \ \tfrac{1}{2}\sigma'' = -1.95 \cdot 10^{-3}, \ \tfrac{1}{6}\sigma''' = 0.13 \cdot 10^{-6}$$

From Appendix III,

$$k - \sigma' = -0.6, \ k = 2.645.$$

With $T < 2900$, the final equation is

$$4.571 \ \log_{10} K_p = \frac{120 \ 930}{T} - 7.4719 \ \log_{10} T + 1.95 \cdot 10^{-3}T$$
$$- 0.13 \cdot 10^{-6}T^2 + 0.6 \ \ldots\ldots\ldots\ldots\ldots\ldots \ \ldots (65)$$

For temperatures exceeding 2900 deg. the equilibrium equation must be modified to conform with the different expression for γ_p of CO_2. The details of the transformation need not be repeated. The final equation $(T > 2900)$ is

$$4.571 \ \log_{10} T = \frac{125 \ 810}{T} + 4.147 \ \log_{10} T + 0.21 \cdot 10^{-3}T$$
$$- 0.03 \cdot 10^{-6}T^2 - 37.107 \ \ldots\ldots\ldots\ldots\ldots (66)$$

(c) **The Water-gas Reaction** $H_2 + CO_2 = H_2O + CO$. The equilibrium equation for the water-gas reaction is obtained by subtracting the equations for the H_2 and CO reactions, respectively. Thus for $T < 2900$, equation (65) is subtracted from equation (64) giving

$$4.571 \log_{10} K_p(\text{w.g.}) = \frac{-18 \ 110}{T} + 4.8584 \log_{10} T$$
$$-2.4213 \cdot 10^{-3}T + 0.1905 \cdot 10^{-6}T^2 - 2.9 \ \ldots\ldots\ldots\ldots (67)$$

Similarly, for $T > 2900$, equation (66) is subtracted from equation (64).

In Table 30, page 144, the values of $\log_{10}K_p$ for the CO reaction are given for 10-deg. intervals from $T = 3000$ deg. to $T = 7000$ deg. F. (abs.). Similar values for the H_2 reaction are given in Table 31, page 146. Subtraction of these values gives the logarithm of K_p for the water-gas reaction in accordance with the equation

$$\log_{10}K_p(\text{w.g.}) = \log_{10}K_{pH_2} - \log_{10}K_{pCO}.$$

Thus, for $T = 4000$,

$$\log_{10}K_p(_{H_2}) = 2.86015, \ \log_{10}K_{pCO} = 2.10965$$

whence

$$\log_{10}K_p(\text{w.g.}) = 2.86015 - 2.10965 = 0.75050, \text{ and } K_p(\text{w.g.}) = 5.63.$$

Table 32, page 148, gives values of K_p for the water-gas reaction.

The expression for K_p in terms of x_0, y_0 will, in general, contain some power of the pressure P. Thus in equations (50), (61), and (62) the factor $P^{-\frac{1}{2}}$ appears. Only when there is no change in molecular volume, as in the CH_4 reaction or the water-gas reaction is K_p independent of the pressure. When K_p involves the pressure, as in the CO and H_2 reactions, the pressure unit employed must be in some way bound up in the equilibrium equation. It is evident that the constant k is the only one that can be affected. Since most of the experiments in equilibrium were made under a pressure of one atmosphere, it is convenient to use the atmosphere as the unit of pressure. The constants –2.3, and 0.6 in equations (64) and (65) are based on this unit.

IV. CALCULATION OF MAXIMUM TEMPERATURES.

24. *The Energy Equation.*—It is *assumed* in the first instance that the maximum temperature is reached when the products mixture attains the equilibrium state and the reactions halt. This assumption is perhaps justified when the combustion is extremely rapid as in the explosion of rich mixtures; it may not be justified in the case of the relatively slow combustion of a weak mixture. The calculation of the maximum temperature involves also the determination of the composition of the products mixture in the equilibrium state, that is, the determination of the unknown values of x_0 and y_0. There are, consequently, three unknown quantities, T_0, x_0, and y_0, and there must be three independent equations from which to determine them. Two of these are the equilibrium equations for the CO and H_2 reactions, respectively; the third is obtained by applying the energy equation to the combustion process.

It is assumed that the combustion is at constant volume. Then the energy equation applied to the process may be expressed as

follows: Heat absorbed = energy of products in equilibrium state — energy of original mixture. The mixture of products in equilibrium at the end of the process has the unknown higher temperature T_0; the original mixture has the temperature T_1. Let subscripts e and m be used to denote these two mixtures, and let a prime and double prime be associated with the temperatures T_1 and T_0, respectively; then U''_e denotes the energy of the mixture of products at T_0 and U'_m the energy of the original mixture at T_1. Also let Q_r denote the heat *lost* during the process by radiation and conduction. Then the energy equation may be written

$$- Q_r = U_e'' - U_m'$$

The U's in the second member of this equation are determined uniquely by the fixed initial and final states, hence Q_r must be the same whatever series of changes is traversed in passing from one state to the other. We are at liberty, therefore, to replace the actual combustion process by any hypothetical process that leads from the initial gas mixture to the final mixture in equilibrium. The following assumed changes lead directly to the desired result: (a) Let the mixture be completely burned at the constant initial temperature T_1; (b) let the products CO_2 and H_2O dissociate at the same temperature T_1 until the composition of the mixture is the same as that in the final state of equilibrium; (c) finally, let the mixture at temperature T_1 be heated without change of composition until the final temperature T_0 is attained. Constant volume is assumed in each of these changes. The heat absorbed and rejected in the three changes may now be considered. In the first change heat Q_1 is rejected; evidently Q_1 is simply the heat of combustion of the mixture at temperature T_1. For the dissociations in the second change, heat Q_2 must be supplied. Denoting by n_1, n_2 the number of mols of CO_2 and H_2O, respectively, and by H'_{vCO} and H'_{vH_2} the heat of combustion per mol of CO and H_2, respectively, at temperature T_1 we have

$$Q_2 = n_1(1-x_0) H'_{vCO} + n_2(1-y_0) H'_{vH_2}$$

In the third change heat Q_3 is supplied to raise the temperature of the products mixture from T_1 to T_2; hence

$$Q_3 = U_e'' - U_e'.$$

If the sum of Q_2 and Q_3 be subtracted from Q_1 the result is the net heat rejected by the system during the three changes, and this is equal to Q_r, the heat rejected in the actual combustion process. Thus

$$Q_r = Q_1 - (Q_2 + Q_3).$$

The heat Q_1, the heat of combustion of the initial mixture at the temperature T_1, may be denoted by H'_m; and the heat rejected Q_r by

fH'_m, where f is a proper fraction. Then the energy equation takes the form

$$(1-f) H'_m = n_1 (1-x_0) H'_{vCO} + n_2 (1-y_0) H'_{vH_2} + U''_e - U'_e \quad (68)$$

This equation is of the first degree in x_0 and y_0 and may ultimately be thrown into the form

$$y_0 = b - ax_0. \quad \ldots\ldots\ldots\ldots\ldots\ldots (69)$$

To show the application of the energy equation (68), the combustion of the Cambridge coal gas (see page 38) is taken. The following schedule shows the calculation of H_m:

Constituent	Mols	H_v per mol at 60° F.	Product B.t.u.
CO	0.06	121 600	7 296
H_2	0.48	103 000	49 440
CH_4	0.335	345 930	115 887
C_2H_4	0.035	575 400	20 139
C_6H_6	0.010	1 360 000	13 600
		$H'_m =$	206 362

David's experiments showed a loss of heat equal to 8.9 per cent of the heat of combustion; hence

$$(1 - f) H'_m = (1 - 0.089) \cdot 206\ 362 = 187\ 996$$

From the products composition at equilibrium (page 39),

$$n_1 = 0.545, \ n_2 = 1.283;$$
$$\text{also for } T_1 = 520, \ H'_{vCO} = 121\ 600, \ H'_{vH2} = 103\ 000.$$

These values are substituted in equation (68) and the result is the equation

$$U''_e - U'_e = 187\ 996 - 0.545 (1 - x_0)\ 121\ 600$$
$$- 1.283 (1 - y_0)\ 103\ 000$$

or

$$U''_e - U'_e = 66\ 272\ x_0 + 132\ 150\ y_0 - 10\ 425$$

The initial temperature T_1 is known, hence an expression for the initial energy U'_e of the equilibrium mixture is readily obtained. The final temperature T_0 is, of course, unknown. David's experiments indicated a value of T_0 in the vicinity of 4500 deg. F., hence we assume values of T_0 such as 4450, 4500, 4550 and work out the energy equation for each temperature.

In Tables 24 to 29 are given the energies per mol of the various constituents at different temperatures. From these tables the following values are obtained:

Gas	Energy per mol, B. t. u.				Increase of Energy from 520 deg. to T_0		
	$T_1 = 520$	$T_0 = 4450$	$T_0 = 4500$	$T_0 = 4550$	520–4450	520–4500	520–4550
CO_2	3186	44 719	45 324	45 929	41 533	42 138	42 743
H_2O	3282	37 927	38 606	39 294	34 645	35 324	36 012
H_2	2178	24 468	24 818	25 169	22 290	22 640	22 991
CO, O_2, N_2	2577	25 529	25 897	26 267	22 952	23 320	23 690

In the equilibrium composition the sum of the diatomic constituents CO, O_2, and N_2 is $6.033 - 0.8175x_0 - 0.6415y_0$. The CO_2 is $0.545x_0$ mols, the H_2O, $1.283y_0$ mols, and the H_2, $1.283(1 - y_0)$ mols. For each of the assumed temperatures the change of energy per mol given in the preceding table is multiplied by the number of mols and the products are added. Thus for $T_0 = 4450$,

$$U_e'' - U_e' = 41\ 533 \times 0.545x_0 + 34\ 645 \times 1.283y_0 + 22\ 290$$

$$\times 1.283(1 - y_0) + 22\ 952\ (6.033 - 0.8175x_0 - 0.6415y_0)$$

$$= 167\ 066 + 3872x_0 + 1128y_0.$$

Introducing this expression for the first member of the preceding equation, the result is the equation

$$62\ 400x_0 + 131\ 022y_0 = 177\ 491,$$

or

$$y_0 = 1.3547 - 0.4763x_0.$$

For $T = 4500$, the corresponding equation is

$$y_0 = 1.3770 - 0.4768x_0$$

and for $T = 4550$, it is

$$y_0 = 1.3996 - 0.4772x_0.$$

The preceding discussion has been based on the assumption that the combustion proceeds at constant volume. A slight modification fits the analysis to the case of combustion at constant pressure. All that is necessary is to replace H_v by H_p and the energy U by the thermal potential I.

25. *Other Expressions for the Energy Equation.*—A second method of arriving at the energy equation is sometimes convenient. The following series of changes in passing from the initial state to the

equilibrium state is assumed: (a) let the temperature of the initial mixture be raised from T_1 to T_0 at constant volume; (b) let the mixture be completely burned at the temperature T_0; (c) let the products CO_2 and H_2O be dissociated until the equilibrium state characterized by the variables x_0, y_0 is reached. In the first operation heat $Q' = U''_m - U'_m$ is absorbed; in the second process heat Q'' is rejected, and this heat is H''_m, the heat of combustion of the mixture at temperature T_0; in the third process heat Q''' is absorbed, and the expression for Q''' is

$$Q''' = n_1(1-x_0)H''_{v\text{CO}} + n_2(1-y_0)H''_{v\text{H}_2}$$

Denoting again by Q_r the heat lost by radiation and conduction,

$$Q_r = Q'' - (Q' + Q''')$$

or

$$Q'' - Q_r = Q' + Q'''$$

Inserting the proper expressions,

$$H''_m - Q_r = U''_m - U'_m + n_1(1-x_0)H''_{v\text{CO}} + n_2(1-y_0)H''_{v\text{H}_2} \quad (70)$$

It will be observed that the expression (68) contains the heats of combustion at the initial temperature T_1 and the increase of energy of the products of combustion; while expression (70) contains the heats of combustion at the equilibrium temperature T_0 and the increase of energy of the initial mixture.

A third expression for the energy equation is derived from equation (68) by algebraic manipulation. The composition of the mixture at equilibrium is

$$
\begin{aligned}
&\text{mols}\\
\text{CO} \;&= n_1(1-x_0)\\
\text{CO}_2 \;&= n_1 x_0\\
\text{H}_2 \;&= n_2(1-y_0)\\
\text{H}_2\text{O} \;&= n_2 x_0\\
\text{O}_2 \;&= e_1 - \tfrac{1}{2}n_1 x_0 - \tfrac{1}{2}n_2 y_0\\
\text{N}_2 \;&= f
\end{aligned}
$$

Let the three diatomic gases having the same specific heat be combined; thus,

$$\text{CO} + \text{O}_2 + \text{N}_2 = n_1 + e_1 + f - \tfrac{3}{2}n_1 x_0 - \tfrac{1}{2}n_2 y_0$$
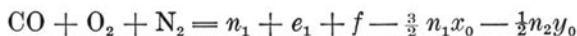
and let u'_D, u''_D denote the energy per mol of these gases at temperatures T_1 and T_0 respectively. Then the expression for the increase of energy of the whole mixture is

$$U''_c - U'_c = (u''_D - u'_D)(n_1 + e_1 + f - \tfrac{3}{2}n_1 x_0 - \tfrac{1}{2}n_2 y_0)$$
$$+ (u''_{\text{H}_2} - u'_{\text{H}_2})n_2(1-y_0) + (u''_{\text{CO}_2} - u'_{\text{CO}_2})n_1 x_0 + (u''_{\text{H}_2\text{O}} - u'_{\text{H}_2\text{O}})n_2 y_2$$

Inserting this expression in equation (68), the following equation is obtained:

$$n_1 x_0 \left[H'_{vCO} + \tfrac{3}{2}(u''_D - u'_D) - (u''_{CO_2} - u'_{CO_2}) \right]$$

$$+ n_2 y_0 \left[H'_{vH} + \tfrac{1}{2}(u''_D - u'_D) + (u''_{H_2} - u'_{H_2}) - (u''_{H_2O} - u'_{H_2O}) \right]$$

$$= (n_1 + e_1 + f)(u''_D - u'_D) + n_2(u''_H - u'_{H_2}) - (1-f)H'_m$$

$$+ n_1 H'_{vCO} + n_2 H'_{vH_2} \quad \dots \dots \dots \dots (71)$$

The terms in the brackets are simply the heats of combustion at the final temperature T_0. The proof of this statement has the same basis as the derivation of equation (10) (see page 18). For the temperature T_1 the expression for the heat of combustion H_v is

$$H'_v = H_0 + \int_0^{T_1} \gamma_{v(factors)} dT - \int_0^{T_1} \gamma_{v(products)} dT$$

or

$$H'_v = H_0 + U'_{(factors)} - U''_{(products)}$$

and likewise for the temperature T_0

$$H''_v = H_0 + U''_{(factors)} - U''_{(products)}$$

Combining these expressions,

$$H''_v = H'_v + (U'' - U')_{(factors)} - (U'' - U')_{(products)}$$

Now for the reaction $CO + \tfrac{1}{2}O_2 = CO_2$, the factors CO and O_2 are diatomic gases having the same energy per mol; hence

$$U''_{(factors)} = u''_{CO} + \tfrac{1}{2}u''_{O_2} = \tfrac{3}{2}u''_D$$

and $U''_{(products)} = U''_{CO_2}$. Therefore the expression in the first bracket gives H''_{vCO} and likewise that in the second bracket gives H''_{vH_2}.

The expression $n_1 H'_{vCO} + n_2 H'_{vH_2} - (1-f)H'_m$ is independent of T_0, x_0, y_0, and in any given problem is a constant. Let it be denoted by Q_0. Equation (71) may now be written

$$n_2 y_0 H''_{vH_2} = Q_o + (n_1 + e_1 + f)(u''_D - u'_D) + n_2(u''_{H_2} - u'_{H_2})$$

$$- n_1 x_0 H''_{vCO} \dots \dots \dots \dots (72)$$

In this form of the energy equation, it will be observed that the energy of the products CO_2 and H_2O does not appear; but heats of combus-

tion at both temperatures T_1 and T_2 are required. Necessarily the three equations (68), (70), and (72) give the same expression when reduced to the form $y_0 = b - ax_0$.

26. *System of Two Equations; Combustion of* CO.—In the case of the combustion of a single constituent, either CO or H_2, there are two unknown quantities to determine, namely T_0 and x_0, and there are two independent equations for the purpose, the equilibrium equation and the energy equation. Four cases will be considered:

    (a)   Adiabatic combustion at constant volume with oxygen.

    (b)   Adiabatic combustion at constant volume with air.

    (c)   Adiabatic combustion at constant pressure of one atmosphere with oxygen.

    (d)   Combustion at constant pressure of one atmosphere with loss of heat due to conduction and radiation.

Case (a)   The mixtures involved in the problem are

Initial State mols		Equilibrium State mols	
		CO	$1 - x_0$
CO	1	CO_2	x_0
O_2	0.5	O_2	$0.5 - 0.5x_0$
$m_1 = 1.5$		$m_0 =$	$1.5 - 0.5x_0$

The energy equation may be obtained from either equation (68) or equation (70). If (68) is used, put $f = 0$, $n_1 = 1$, $n_2 = 0$; then the equation becomes

$$x_0 H'_v = U''_e - U'_e$$

$$= 1.5(1 - x_0)\,(u''_D - u'_D) + x_0(u''_{CO_2} - u'_{CO_2})$$

If (70) is used with $Q_r = 0$, $n_2 = 0$, the resulting equation is

$$x_0 H''_v = U''_m - U'_m$$

$$= 1.5\,(u''_D - u'_D)$$

Let the temperature and pressure of the mixture initially be $T_1 = 520$, $P_1 = 1$ atmosphere. Then taking values of H_v and U from the appropriate tables the following results are obtained:

$T =$	1500	2000	2500	3000	3500	4000	4500	5000	5500	6000	6500
$x_0 =$	0.061	0.096	0.132	0.171	0.212	0.258	0.305	0.357	0.411	0.468	0.530

These results plotted give the curve *a*, Fig. 3.

The equilibrium equation for this case is equation (61b). Taking $m_1 = 1.5$, $e_0 = 0.5\,(1 - x_0)$, $P_1 = 1$, $T_1 = 520$, the equation becomes

$$\log K_{pCO} + \tfrac{1}{2} \log T_0 = \log \frac{x_0}{1 - x_0} + \tfrac{1}{2} \log \frac{3}{1 - x_0} + 1.358$$

With values of K_p taken from Table 30, the following results are found:

$x_0 =$	0.3	0.4	0.5	0.6	0.7	0.8	0.9	0.95
$T_0 =$	6850	6450	6100	5780	5460	5080	4620	4250

The curve b, Fig. 3, is determined from these results, and represents equation (61b). The intersection P of the two curves gives the re-
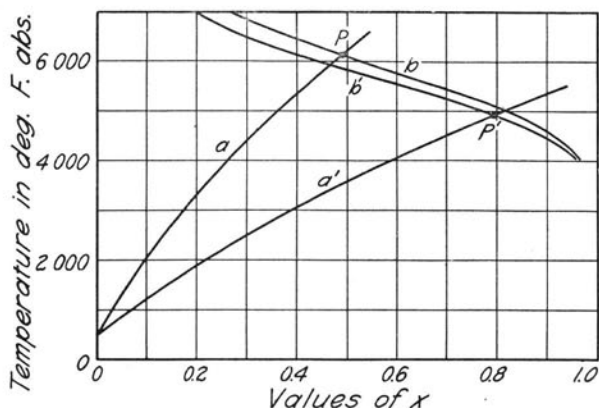
Fig. 3. Combustion of Carbon Monoxide at Constant Volume

quired values of T_0 and x_0. Apparently T_0 lies between 6100 and 6200. To determine T_0 accurately, we assume tentatively three temperatures, 6100, 6150, and 6200, and calculate the two members of the preceding equation for each temperature. The details of the computation are as follows:

	$T = 6100$	6150	6200
$1.5\,(u''_D - u'_D) =$	54980	55688	56402
$H''_v =$	114570	114640	114710
$x_0 =$	0.4799	0.4858	0.4917
$1 - x_0 =$	0.5201	0.5142	0.5083
Second member	1.70356	1.71629	1.72908
$\log K_p =$	−0.13562	−0.17080	−0.20547
$\tfrac{1}{2} \log T =$	1.89267	1.89444	1.89620
First member......	1.75705	1.72364	1.69073

The two sets of values are plotted against T, and the intersection of the two lines gives $T_0 = 6158$, $x_0 = 0.487$.

Case (b) With the theoretical weight of air supplied the two compositions become

Initial State		Equilibrium State	
	mols		mols
		CO	$1 - x_0$
CO	1	CO_2	x_0
O_2	0.5	O_2	$0.5 - 0.5x_0$
N_2	1.89	N_2	1.89
$m_1 = 3.39$		$m_0 =$	$3.39 - 0.5x_0$

The energy equation now becomes

$$x_0 H''_v = 3.39 \ (u''_D - u'_D)$$

that is, the values of x are those obtained in case (a) multiplied by $3.39/1.5$. The resulting curve representing this energy equation is curve a', Fig. 3.

Since in this case $m_1 = 3.39$, the quotient $\dfrac{m_1}{e_0}$ becomes $\dfrac{6.78}{1 - x_0}$, and thus replaces $\dfrac{3}{1 - x_0}$ in equation (73). The result is a shifting of the equilibrium curve to the position b', Fig. 3. The values of T_0 and x_0 determined by the intersection P' are

$$T_0 = 4950, \ x_0 = 0.795$$

Case (c) Adiabatic combustion at constant pressure of one atmosphere.

The energy equation is in this case

$$xH''_p = \tfrac{3}{2}(i''_D - i'_D),$$

in which $i_D = u_D + 1.985T$.

The equilibrium equation for constant pressure is simply

$$\log K_p = \log \frac{x_0}{1 - x_0} + \tfrac{1}{2}\log \frac{3 - x_0}{1 - x_0} - \tfrac{1}{2}\log P$$

Taking $P = 1$ atmosphere, the last term becomes zero. The curve a, Fig. 4, represents the simultaneous values of x and T from the energy equation, the curve b, values of x and T from the equilibrium equation. The intersection P gives

$$T_0 = 5456, \ x_0 = 0.511.$$
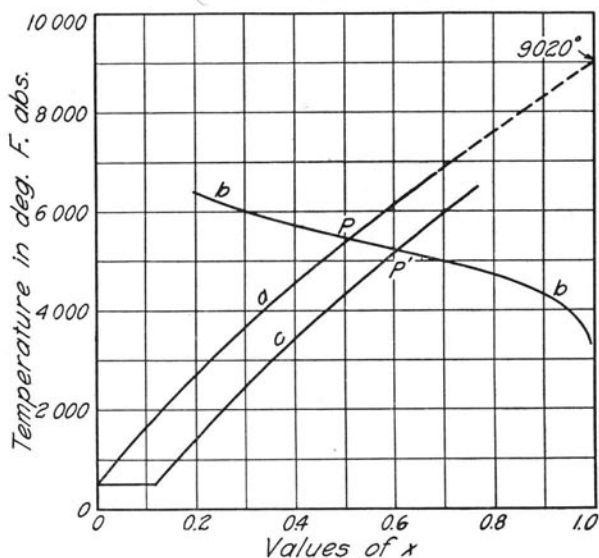
FIG. 4. COMBUSTION OF CARBON MONOXIDE AT CONSTANT PRESSURE

Case (d)   Combustion at constant pressure of one atmosphere, but with a loss of heat equal to 15 000 B. t. u. per mol of CO, that is, about one-eighth of H_p.

For the energy equation in this case, we choose equation (68), which becomes for constant pressure

$$x_o H'_p - 15\,000 = x_o(i''_{CO_2} - i'_{CO_2}) + 1.5(1 - x_o)(i''_D - i'_D)$$

whence

$$x_o = \frac{1.5(i''_D - i'_D) + 15\,000}{H'_p + 1.5(i''_D - i'_D) - (i''_{CO_2} - i'_{CO_2})}$$

Various values of T are chosen and values of x_0 are calculated. The simultaneous values when plotted give the curve c, Fig. 4. The equilibrium curve is the same as in case (c); and the intersection P' gives the results $T_0 = 5225$, $x_0 = 0.608$.

These examples show clearly the marked effect of dissociation in limiting the maximum temperatures attainable. If the curve a, Fig. 3, were continued it would meet the line $x = 1$ at the point $T = 10\,450$; and curve a, Fig. 4, for the constant pressure case, would meet it at the point $T = 9020$. These are the temperatures that would be deduced from the energy equation alone for complete combustion. The dissociation of the products reduces these apparent maximum temperatures about 40 per cent.

It will be observed also that in cases (a) and (c) the value of x_0 is approximately 0.50; that is, the reaction halts when about one-half of the CO is consumed. As soon as the temperature falls, however, the equilibrium is disturbed and more CO will be burned in the effort to re-establish equilibrium. Ultimately, when the temperature has dropped to 2000 deg. F. or 2500 deg. F., the equilibrium curve b practically merges into the line $x = 1$, which means that the combustion is complete. The point representing the coincident values of T and x moves along the curve a until the point P is reached, and then along the equilibrium curve b.

From the form of the equilibrium curve b, it is evident that a reduction in temperature for any reason results in a larger value of x_0, that is, smaller dissociation. Thus, comparing cases (a) and (b) the introduction of nitrogen results in a lower temperature throughout as shown by the curve a'. As a consequence, x_0 is increased to nearly 0.8. In case (d), the assumed loss of heat by conduction and radiation reduces the temperature, and the result is an increase of x_0.

27. *System of Three Equations; General Case.*—For the determination of the three unknowns x_0, y_0, T_0 there are three independent equations:

(a)   The energy equation, having the form

$$y_0 = b - ax_0$$

(b)   The equation of the water-gas equilibrium. Denoting the equilibrium constant by c, this is

$$\frac{y_0(1 - x_0)}{x_0(1 - y_0)} = c$$

(c)   The equilibrium equation for the CO reaction (or if preferred, that of the H_2 reaction). For a reaction at constant volume equation (61b) is applicable:

$$\log K_{pCO} + \tfrac{1}{2} \log T = \log x_0 - \log (1 - x_0) + \tfrac{1}{2} \log m_1 - \tfrac{1}{2}\log e_0$$
$$+ \tfrac{1}{2} \log T_1 - \tfrac{1}{2} \log P_1$$

If the reaction is at constant pressure, equation (61) is used in the form

(c′) $\log K_{pCO} = \log x_0 - \log (1 - x_0) + \tfrac{1}{2} \log m_0 - \tfrac{1}{2} \log e_0$
$- \tfrac{1}{2}\log P$

The elimination of y_0 between equations (a) and (b) gives the quadratic equation

(d) $a(c-1)x^2_o + \left[a + b - c(b-1) \right] x_o - b = 0$

For various assumed values of T the constants a, b, c are determined and corresponding values of x_0 are obtained from the quadratic equation (d). It will be observed that the first (or left hand) member of the equilibrium equations (c) or (c') is a function of the temperature T only; therefore, let it be denoted by $L(T)$. The second (right hand) member is a function of x_0 and y_0 and may be denoted by $R(x_0,y_0)$. For each assumed value of T simultaneous values of x_0 and y_0 have been found from equation (c). The value of T substituted in the first member of equation (c) gives a value of $L(T)$; and the corresponding values of x_0 and y_0 substituted in the second member give a value of $R(x_0,y_0)$. If now these two functions are plotted against T as abscissa, the intersection of the two curves gives the desired values of T, x_0, y_0 that satisfy all three of the independent equations.

As an example we continue the calculation for the Cambridge coal gas. The constants a and b for the assumed temperatures have already been determined (see page 47). Values of the constant c, the equilibrium constant for the water-gas reaction, are found in Table 32. Then the following results are obtained:

	T = 4450	4500	4550
a =	0.47 630	0.47 680	0.47 720
b =	1.35 470	1.37 700	1.39 960
c =	6.56 770	6.67 100	6.77 440
x_0 =	0.81 490	0.84 630	0.87 910
y_0 =	0.96 660	0.97 350	0.98 010
$\log T$ =	3.64 738	3.65 321	3.65 801
$\frac{1}{2}\log T$ =	1.82 369	1.82 661	1.82 901
$\log K_p$ =	1.45 154	1.38 659	1.32 307
$L(T)$ =	3.27 523	3.21 320	3.15 208

To determine $R(x_0,y_0)$, we have $e_0 = 0.973 - 0.2725\, x_0 - 0.6415\, y_0$, and $m_1 = 6.667$; $P_1 = 1$, $\log P_1 = 0$; $T_1 = 520$, $\frac{1}{2}(\log T_1 + \log m_1) = 1.76\,827$.

The calculation proceeds as follows:

	T = 4450	4500	4550
$\log x_0$ =	$\bar{1}.91$ 110	$\bar{1}.92$ 752	$\bar{1}.94$ 404
$\frac{1}{2}(\log m_1 + \log T_1)$ =	1.76 827	1.76 827	1.76 827
Sum of + terms.......	1.67 937	1.69 579	1.71 231
e_0 =	0.13 080	0.11 790	0.10 470
$1 - x_0$ =	0.18 510	0.15 370	0.12 090
$\frac{1}{2}\log e_0$ =	$\bar{1}.55$ 831	$\bar{1}.53$ 576	$\bar{1}.50$ 997
$\log (1 - x_0)$ =	$\bar{1}.26$ 741	$\bar{1}.18$ 667	$\bar{1}.08$ 243
Sum of − terms......	$\bar{2}.82$ 572	$\bar{2}.72$ 243	$\bar{2}.59$ 240
$R(x_0,y_0)$ =	2.85 365	2.97 336	3.11 991

The values of $L(T)$ and $R(x_0,y_0)$ are plotted and give the curves shown in Fig. 5. The intersection of the curves shows that $T_2 = 4557$;
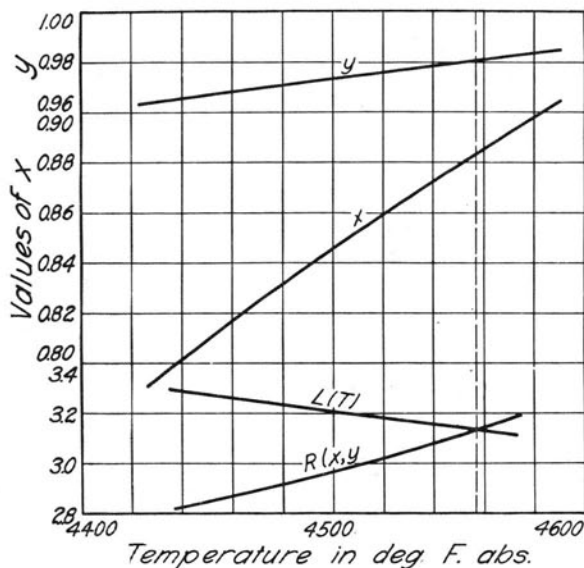
FIG. 5. GRAPHICAL SOLUTION; GENERAL CASE

and for this temperature the values of x_0, y_0 from the x_0 curve and the y_0 curve are approximately

$$x_0 = 0.884 \qquad y_0 = 0.981$$

By interpolation the more accurate value $x_0 = 0.8838$ is found. As a check these values of x_0 and y_0 may be substituted in equation (64); thus

$$c = \frac{0.981 \times 0.1162}{0.8838 \times 0.019} = 6.789$$

From Table 32 the value of c, that is, the value of K_p for the water-gas reaction, for $T = 4557$ is 6.7899; therefore the system of values satisfies the three equations.

28. *Equilibrium and Maximum Temperature.*—In the preceding analysis the assumption has been made that the gas mixture has attained equilibrium when the maximum temperature is reached; this assumption requires examination.

Consider a combustion reaction proceeding at constant volume. During an element of time dt the heat generated by the combustion is $H_v dx$, the heat lost by conduction and radiation is dQ_r, and the in-

crease of thermal energy of the gas mixture is du. The energy equation applied to the process is

$$H_v dx - dQ_r = du \ \ldots\ldots\ldots\ldots\ldots\ldots (73)$$

The magnitude of the term dQ_r depends upon the temperature of the mixture and upon the time; that is,

$$dQ_r = kf(T)dt$$

The exact form of the function $f(T)$ is not essential at present. The magnitude of the coefficient k depends on the character of the fuel and the nature of the containing vessel.

Introducing the expression for dQ_r in equation (73), the result is the equation

$$H_v dx - kf(T)dt = du,$$

or

$$H_v \frac{dx}{dt} - kf(T) = \frac{du}{dx}\frac{dx}{dt}$$

whence

$$\frac{dx}{dt} = \frac{kf(T)}{H_v - \dfrac{du}{dx}} \ \ldots\ldots\ldots\ldots\ldots (74)$$

The significance of this equation will be understood by reference to Fig. 6, in which the curves a, b, c are reproduced from Fig. 4. The
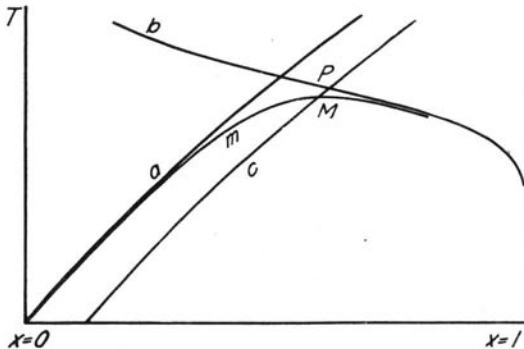
FIG. 6.   APPROACH OF ACTUAL COMBUSTION TO EQUILIBRIUM

curve c is merely a hypothetical locus obtained by assuming that for any value of x the loss of heat is a fixed amount; thus, if 20 per cent of CO is burned and 15 000 B. t. u. are lost, one point on the curve is found; if it is assumed that 40 per cent of CO is burned and during

the process the same amount, 15 000 B. t. u., is lost, a second point is found; and so on. The curve a represents the relation between T and x when the combustion is adiabatic. With a constantly increasing loss of heat, aggregating Q_r when maximum temperature is reached, the actual curve m giving the relation between T and x will lie below the curve a and will intersect the curve c at a point M. Now curve c is the locus corresponding to a constant heat loss Q_r and by hypothesis Q_r is the aggregate heat loss when maximum temperature is attained; therefore, the intersection M must be the maximum point on the curve m. At this point M, $\dfrac{dT}{dx} = 0$, and since the energy u and potential i are functions of T alone, we must have also at M, $\dfrac{du}{dx} = 0$, $\dfrac{di}{dx} = 0$.

Putting $\dfrac{du}{dx} = 0$ in equation (74), we have

$$\frac{dx}{dt} = \frac{kf(T)}{H_v} \dots\dots\dots\dots\dots\dots (75)$$

which shows that the reaction is still progressing, and that equilibrium has not been reached when the maximum temperature is attained. After the point M is passed the temperature is decreasing and therefore $\dfrac{du}{dx}$ is negative; hence the reaction velocity $\dfrac{dx}{dt}$ continues to decrease. The equation shows, however, that this velocity cannot vanish until $\dfrac{du}{dx}$ becomes infinite. In other words, equilibrium is not attained until the combustion is complete. The curve m approaches the equilibrium curve b and both curves approach the line $x = 1$ as an asymptote.

In the case of the combustion of CO, the curve b is practically coincident with $x = 1$ when T is reduced to about 2500 deg. F.; hence at this same temperature, the mixture is practically in the equilibrium state.

The assumption that equilibrium exists when maximum temperature is attained requires that point M coincide with point P on the equilibrium curve. The assumption is evidently untenable, because at point P, as at all points on the equilibrium curve, the reaction velocity is zero, while at point M it has the positive value given by equation (75). The segment MP measures, in a way, the deviation of the state of the gas mixture from the equilibrium state. As the curve m approaches more closely to the equilibrium curve b the mixture approaches the condition of equilibrium.

The preceding calculation of maximum temperatures by the solution of the energy equation and equilibrium equation gives the temperature at the point P, a temperature that must be somewhat greater than the actual maximum temperature indicated by point M. The calculated temperature must be regarded, therefore, as an upper limit which will be attained in the actual combustion only when the combustion is adiabatic. With rapid explosions of rich mixtures the loss of heat is relatively small and the calculated temperature may be a good approximation to the maximum temperature. If the mixture burns slowly, so that the loss of heat is large, the segment MP is correspondingly large, and the calculated temperature must necessarily exceed the actual maximum temperature by a considerable amount.

As will be shown by the experiments to be described in the following chapter, the time occupied by an explosion is only a fraction of a second; consequently, the reaction velocity must be very high. It is a question whether at such high velocities equilibrium can even be approached. Again, in the actual explosion, there must be a variation of temperature throughout the mass of burning gas, and therefore the temperature deduced from the observed pressure must in a certain sense be a mean temperature. It is not to be expected, therefore, that the temperature calculated from an analysis of ideal equilibrium conditions will coincide accurately with observed experimental temperatures. The fairly good agreement between theory and experiment to be described in the following chapter indicates that the mixture *does* approach a condition of equilibrium.

V.   Explosion Experiments of David and of Bone and Haward

29. *Experimental Data Available.*—A large amount of experimental work has been done along the line of gaseous explosions in closed vessels. A complete bibliography is contained in Bulletin No. 133 of the Engineering Experiment Station, University of Illinois, entitled "A Study of Explosion of Gaseous Mixtures," by A. P. Kratz and C. Z. Rosecrans. With one exception the experimental results published to date do not lend themselves readily to the verification of a theoretical analysis because no attempt has been made to measure the heat losses during the combustion period and the subsequent cooling period. The one exception is the recent work of Dr. W. T. David* on "The Internal Energy of Inflammable Mixtures of Coal Gas and Air after Explosion," in which explosion tempera-

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* Proc. Roy. Soc., V. 98A, p. 303, 1921.

tures and total heat losses are given for various points on the explosion curve. The results of Bone and Haward[*] on the explosions of hydrogen-air and carbon-monoxide-air mixtures at high initial pressures are also useful in the verification of the theory.

30. *Experimental Methods.*—David used a cylindrical explosion vessel of 0.788 cu. ft. capacity. Ignition was obtained by a spark placed in the center of the explosion vessel. Pressures were measured by a Hopkinson optical indicator. The spot of light was reflected from the indicator to a photographic film mounted on a rotating drum. Radiation measurements were made with a bolometer receiving the heat radiated through a small window in the explosion vessel. Values of the heat losses by conduction were obtained by measuring the rise in temperature of a thin polished silver plate mounted on a backing of linoleum and placed upon the inside surface of one of the end covers of the explosion vessel. Various mixtures of Cambridge coal gas and air were exploded from atmospheric pressure and room temperature.

Bone and Haward used a spherical explosion vessel 3 inches in internal diameter equipped with a Petavel optical indicator. An initial pressure of 50 atmospheres was used with room temperatures. Various mixtures of hydrogen, carbon monoxide, and air were used in the series of experiments which is of particular interest here.

31. *Experimental Results.*—The experimental results of David are given in Table 2. The temperatures given by David were calculated from the recorded pressures by means of the equation $PV = RT$, making the proper correction for the change of molecular volume upon combustion.

The experimental results of Bone and Haward are given in Table 3.

32. *Chemical Analysis of Cambridge Coal Gas used by David.*— In the absence of any exact analysis of the Cambridge coal gas used by David the following is taken as being a typical analysis:

	Percent. by Vol.
Hydrogen H_2	48.0
Methane CH_4	33.5
Ethylene C_2H_4	3.5
Benzene C_6H_6	1.0
Carbon Monoxide CO	6.0
Nitrogen N_2	5.5
Carbon-dioxide CO_2	2.0
Water Vapor H_2O	0.5
Total	100.0

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[*] Proc. Roy. Soc., V. 100A, p. 65. 1921.

Analyses of the products of combustion resulting from the explosions of the various mixtures of gas and air are given by David, and the lower heat of combustion is also stated. An analysis of Cambridge coal gas for a period previous to 1914 was obtained and a few minor shifts were made so as to duplicate as nearly as possible the data given by David. The preceding analysis is the result. A humidity of 30 per cent at 60 deg. F. is assumed. The analyses of the products of combustion given by David are contained in Table 1. The values in parentheses are those resulting from the foregoing analysis.

<p align="center">TABLE 1</p>

<p align="center">COMPARISON OF PRODUCTS OF COMBUSTION OBTAINED FROM CAMBRIDGE
COAL GAS ANALYSIS WITH THE EXPERIMENTAL VALUES OF DAVID</p>

Percentage of Gas in Mixture....................		15.0	12.4	9.7
Products of Combustion, Percentage by Volume	H_2O	20.0 (20.0)	16.4 (16.5)	12.9 (13.0)
	CO_2	8.5 (8.5)	7.0 (7.0)	5.5 (5.4)
	N_2+O_2	71.5 (71.5)	76.6 (76.5)	81.6 (81.6)

The lower heat of combustion given by David is 145 000 calories per cu. ft. (0 deg. C. and 760 mm.) or 206 394 B. t. u. per mol. The lower heat of combustion at constant volume calculated from the preceding analysis is 206 362 B. t. u. per mol. The products of combustion and the heat of combustion are the only factors resulting from the gas analysis that enter into the computation of the explosion temperature; hence the calculated results will be the same even if the assumed gas analysis does not duplicate precisely the actual analysis.

33. *Calculation of Temperatures.*—The maximum temperature for the 15 per cent mixture with 8.9 per cent loss of heat has been given as an illustrative example in the preceding section. By the same method the theoretical maximum temperatures for the other mixtures are obtained, and also the temperatures subsequent to the explosion when the mixture is cooling. The results are given in Table 2 and Fig. 7.

As suggested before, it is possible that at the highest temperatures the reaction $\frac{1}{2}N_2 + \frac{1}{2}O_2 = NO$ may require consideration. This being an endothermic reaction, the result would be a decrease in the maximum temperature. The equilibrium equation given by Haber is

$$R \log_e K_p = -\frac{38\ 700}{T} + 2.45$$
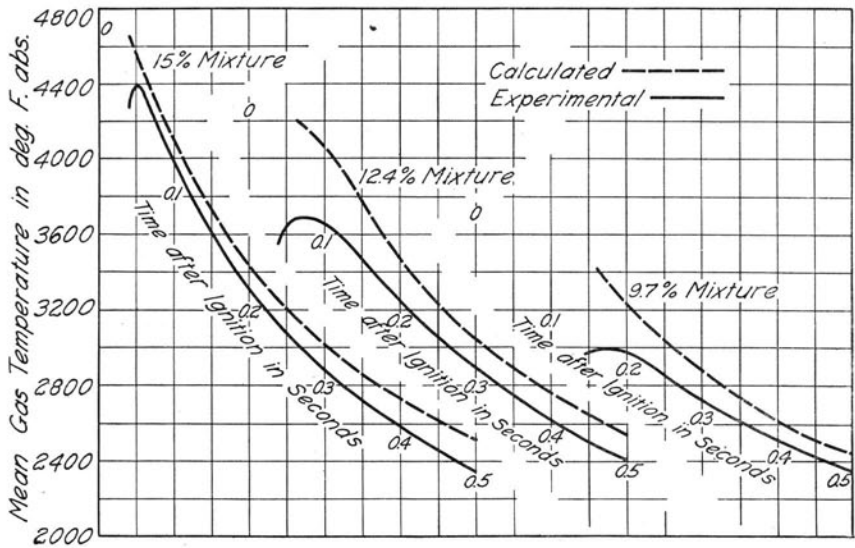
FIG. 7. EXPERIMENTAL AND CALCULATED EXPLOSION TEMPERATURE CURVES
FOR CAMBRIDGE COAL GAS AND AIR MIXTURES

in which

$$K_p = \frac{p_{NO}}{\sqrt{p_{N_2} \cdot p_{O_2}}}$$

Assuming that the values of x_0 and y_0 are but little changed by the formation of NO the expression for K_p is approximately

$$K_p = \frac{9.03z}{\sqrt{(0.104 - 4.515z)} \cdot \sqrt{4.515(1-z)}}$$

in which z denotes the part of the N_2 present that is used in the formation of NO. This equation applies to the 15 per cent mixture. For a temperature in the vicinity of 4500 deg. F. (abs.) the value of z is found to be about 0.003. Therefore the heat absorbed in this reaction is $38\,700 \times 9.03 \times 0.003 = 1050$ B. t. u. Taking this amount of heat into consideration, and revising the original calculation, the maximum temperature is found to be approximately 4530 instead of 4557. The method of calculation is not at all exact, but the result is sufficiently accurate to show that the effect of the NO reaction is negligible.

34. *Comparison of Experimental and Calculated Temperatures.* —A comparison of the maximum temperatures shows the following differences:

Mixture	15 per cent	12.4 per cent	9.7 per cent
T calc.	4557	4141	3327
T exp.	4390	3690	3000
Diff., per cent.	3.8	12.2	10.9

The difference of 3.8 per cent for the richer mixture is about what might be expected. The theoretical temperature, 4557 deg. F., is based on the assumption of an equilibrium that does not exist, and the actual temperature must be slightly lower. In the case of the slower burning 9.7 per cent mixture the gas at maximum temperature is still further from equilibrium, and the difference between calculated and experimental temperatures is greater, as it should be. The intermediate 12.4 per cent mixture, however, shows a divergence that is difficult to explain. With only 10 per cent heat loss compared with 18 per cent for the weaker mixture, and with 0.08 second as the time of explosion compared with 0.18 second for the weaker mixture, the difference between calculated and experimental temperatures should certainly be less for the 12.4 per cent mixture than for the 9.7 per cent mixture. David,[*] in his discussion of these experiments, divides the heat of combustion into three parts: (a) the increase of internal energy of the mixture; (b) the available chemical energy remaining when maximum temperature is attained; and (c) the heat loss by conduction and radiation. The following results are deduced:

Mixture per cent	Heat of Combustion	Internal Energy	Available Chemical Energy	Heat Loss
15	100	81	10	9
12.4	100	78	12	10
9.7	100	72.5	9.5	18

Here again the 12.4 per cent mixture is not in line with the other two. There is no conceivable reason why this mixture should retain a greater amount of available chemical energy than either the richer or the weaker mixture. Apparently there must be some error in the experimental results.

A comparison of the successive temperature differences for each of the experiments is important:

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[*] Proc. Roy. Soc., Ser. A, V. 98, p. 316.

15 per cent Mixture

T calc.	4557	4092	3721	3442	3204	3017	2719	2505
T exp.	4390	4000	3640	3310	3080	2880	2570	2340
Diff., per cent	3.8	2.3	2.25	4.0	4.03	4.76	5.8	7.06

12.4 per cent Mixture

T calc.	4141	4064	3763	3483	3233	3051	2750	2534
T exp.	3690	3650	3460	3240	3060	2900	2630	2390
Diff., per cent	12.2	11.6	8.75	7.5	5.6	5.2	4.6	6.0

9.7 per cent Mixture

T calc.	3327	3237	3039	2877	2600	2441	......	......
T exp.	3000	2970	2840	2740	2500	2360	......	......
Diff., per cent	10.9	5.0	7.0	5.0	4.0	3.4	......	......

After the maximum temperature is passed the gas mixture should be approaching nearer to the equilibrium state, and consequently the difference between calculated and experimental temperatures should be growing smaller. Such is the case in the two weaker mixtures, but the 15 per cent mixture shows an opposite tendency. Several explanations may be advanced for the apparent conflict of theory and experiment:

(a)   The calculated values of T may be too large because of inaccuracy of the formulas for the specific heats used. However, a very large increase in the specific heat of diatomic gases would be required to bring the two sets of temperatures into reasonable agreement.

(b)   The magnitude of the heat losses might have been underestimated. A slight increase of the values given in column 6, Table 2, would reduce the calculated temperatures appreciably.

(c)   Accurate measurements of pressure are difficult to attain even with the best instrumental methods. It is possible that all the measured pressures were slightly low, and consequently the temperatures deduced from them are likewise low.

After taking account of all the discrepancies herein noted, it must be concluded that David's experiments, on the whole, furnish a thoroughly satisfactory verification of the theoretical analysis.

35.   *Experiments of Bone and Haward.*—Various mixtures of H_2 and CO along with O_2 and N_2 were exploded. Table 3 gives the composition of the initial mixture and the maximum pressure attained. The initial pressure in each case was 50 atmospheres. The proportions of CO and H_2 were varied, but the sum CO $+$ H_2 was kept approxi-

mately constant. The volume of N_2 was approximately four times the volume of O_2.

The heat losses during the explosion were not determined; hence a direct comparison between calculated and experimental temperatures is not possible. It is possible, however, to estimate the heat loss that will bring the calculated temperature into coincidence with the experimental temperature, assuming that maximum temperature and equilibrium are attained together.

This calculation is performed as follows: Assuming heat losses of 0, 5, 10, and 15 per cent, the equilibrium state is calculated for each case, that is, P, T, x_0, and y_0 are obtained; a curve is plotted using the calculated explosion pressures as ordinates and the assumed heat losses as abscissæ; from this curve the heat loss is obtained corresponding to the experimental maximum pressure obtained from the explosion of the given mixture; the required values of T, x_0, and y_0 consistent with the experimental explosion pressure are obtained from curves plotted with heat loss as abscissæ. The results of the calculation are the figures given in column 3 of Table 3.

For experiments II, X, and XI, the calculated heat losses are apparently too high, considering the short time interval occupied by the explosion. It will be noted, however, that in these experiments the H_2 content of the mixture is high, and it was thought possible that slight dissociation of H_2 into atomic hydrogen (see Section 45) would account for the discrepancy. Calculation showed that the high maximum pressure reduced the dissociation of H_2 practically to zero, so that no error is introduced by neglecting this dissociation. The only other explanation which presents itself is the possibility that the Petavel indicator used was too slow to record accurately the maximum pressures of the extremely rapid explosions. In the remaining experiments the figures for the heat loss are reasonable, and the variations are no more than might be expected considering the nature of the experiments.

It should be noted that the figures given for the heat loss are based on the assumption that equilibrium exists at the point of maximum pressure. For these rapid explosions it is probable that the mixture is very near equilibrium at maximum pressure. However, the calculated temperature, with a known heat loss, must slightly exceed the actual temperature; consequently, the calculated values for the heat loss are greater than the actual values.

The application of the system of calculation to the experiments of Bone and Haward gives a satisfactory correlation. From the comparisons made in this section it seems evident that the maximum temperatures resulting from the combustion of rich mixtures with high reaction velocities may be calculated with a good degree of accuracy from the equations deduced in the preceding chapters.

TABLE 2

EXPERIMENTAL AND CALCULATED RESULTS FOR EXPLOSIONS OF
MIXTURES OF CAMBRIDGE COAL GAS AND AIR

Experimental Data by David								
Time after Ignition	Mean Gas Temperature		Heat Loss Expressed as a Percentage of the Heat of Combustion of the Coal Gas			Calculated Values using Heat Losses given in col. 6.		
sec.	deg. C. (abs.)	deg. F. (abs.)	Radiation	Conduction	Total	T deg. F. (abs.)	x	y
15 per cent Mixture of Coal Gas and Air								
0.05	2440	4390	5.1	3.8	8.9	4557	0.884	0.981
0.10	2220	4000	14.4	10.4	24.8	4092	0.965	0.994
0.15	2020	3640	20.3	15.0	35.3	3721	0.990	0.998
0.20	1840	3310	24.5	17.9	42.4	3442	0.998	1.000
0.25	1710	3080	27.7	20.3	48.0	3204	1.000	1.000
0.30	1600	2880	30.0	22.2	52.2	3017	1.000	1.000
0.40	1430	2570	34.4	24.3	58.7	2719	1.000	1.000
0.50	1300	2340	37.6	25.6	63.2	2505	1.000	1.000
12.4 per cent Mixture of Coal Gas and Air								
0.08	2050	3690	5.5	4.5	10.0	4141	0.978	0.996
0.10	2030	3650	6.8	5.8	12.6	4064	0.983	0.997
0.15	1920	3460	12.5	9.7	22.2	3763	0.995	1.000
0.20	1800	3240	17.4	13.0	30.4	3483	1.000	1.000
0.25	1700	3060	21.7	15.6	37.3	3233	1.000	1.000
0.30	1610	2900	25.0	17.2	42.2	3051	1.000	1.000
0.40	1460	2630	30.2	19.8	50.0	2750	1.000	1.000
0.50	1330	2390	34.0	21.4	55.4	2534	1.000	1.000
9.7 per cent Mixture of Coal Gas and Air								
0.18	1660	3000	11.0	7.0	18.0	3327	1.000	1.000
0.20	1650	2970	12.8	8.3	21.1	3237	1.000	1.000
0.25	1580	2840	16.5	11.2	27.7	3039	1.000	1.000
0.30	1520	2740	19.4	13.6	33.0	2877	1.000	1.000
0.40	1390	2500	24.4	17.4	41.8	2600	1.000	1.000
0.50	1310	2360	27.7	19.0	46.7	2441	1.000	1.000

TABLE 3

EXPERIMENTAL AND CALCULATED RESULTS FOR HIGH PRESSURE EXPLOSIONS

Expt. No.	Experimental Maximum Press. atm.	Calculated				Percentage Composition of Original Mixture				Initial Temp. deg. F.	Initial Press. atm.	Time between Ignition and Max. Press. sec.
		Heat Loss % H_{7520}	T	x	y	CO	H_2	O_2	N_2			
II	391	11.2	4760	.....	0.993	nil	28.20	14.50	57.30	63.5	50	0.005
X	399	9.6	4870	0.961	0.995	14.50	13.00	15.10	57.40	68.9	50	0.015
XI	390	12.7	4760	0.969	0.995	13.65	13.85	14.90	57.60	68.7	50	0.015
XII	410	4.3	4985	0.951	0.993	19.90	6.70	14.55	58.85	70.7	50	0.015
XIII	409	7.4	4920	0.959	0.994	21.95	3.55	14.20	60.30	68.0	50	0.025
XIV	418	2.4	5045	0.943	0.994	22.90	3.60	14.30	59.20	68.0	50	0.025
IXV	427	3.4	5035	0.938	0.992	24.60	2.20	14.00	59.20	55.4	50	0.025 to 0.030
XVI	425	3.4	5025	0.936	0.991	24.80	2.00	13.80	59.40	57.2	50	0.025 to 0.030
XVII	417	7.0	4951	0.945	0.992	25.60	1.45	14.05	58.90	58.1	50	0.030
XVIII	425	4.3	5020	0.946	0.994	25.50	1.10	14.30	59.10	55.4	50	0.030
VIII	421	8.2	5108	0.946	.....	28.60	nil	16.00	55.40	64.8	50	0.180

NOTE.—T given in deg. F. (abs.).

VI. Effect of Varying Conditions in the Combustion of Gaseous Fuels

36. *Problems Investigated.*—With a system of calculation available, certain important problems connected with the combustion of gaseous fuels may be attacked. In this chapter, therefore, attention is given to the following topics:

(a)   The effect of the initial pressure of the gas mixture.

(b)   The effect of the initial temperature of the mixture.

(c)   The effect of excess air; also the effect of the loss of heat during combustion.

(d)   A comparison of several well-known fuel gases.

In all the cases considered, explosion at constant volume has been assumed.

As has been stated, the calculated results are more accurate for rich mixtures that burn rapidly and thus more nearly attain chemical equilibrium at the point of maximum temperature. The absolute values calculated for weaker and slower burning mixtures are undoubtedly too high; still the results are of value in making a study of the effects of various initial conditions on the explosion temperatures and pressures. A more complete study of the gaseous fuels has been made than of the vapors of liquid fuels, because the chemical and physical constants for the gases are more accurately known; and the gas fuels have a more definite chemical composition.

37. *Effect of Initial Pressure.*—The 15 per cent mixture of Cambridge coal gas and air is used as an example. The initial temperature is taken as 60 deg. F. and a heat loss of 10 per cent of the heat of combustion at 60 deg. F. is assumed. Initial pressures up to five atmospheres are used. The calculated results are given in Table 4 and Fig. 8.

TABLE 4
EFFECT OF INITIAL PRESSURE

Initial Press., atm.	0.25	0.50	1.00	2.00	3.00	4.00	5.00
Max. Explosion Temp., deg. F. (abs.)	4456	4494	4528	4558	4572	4583	4590
Max. Press., atm.	2.076	4.182	8.416	16.921	25.443	33.995	42.539
x_0	0.844	0.868	0.891	0.911	0.921	0.928	0.933
y_0	0.973	0.978	0.982	0.986	0.987	0.989	0.990
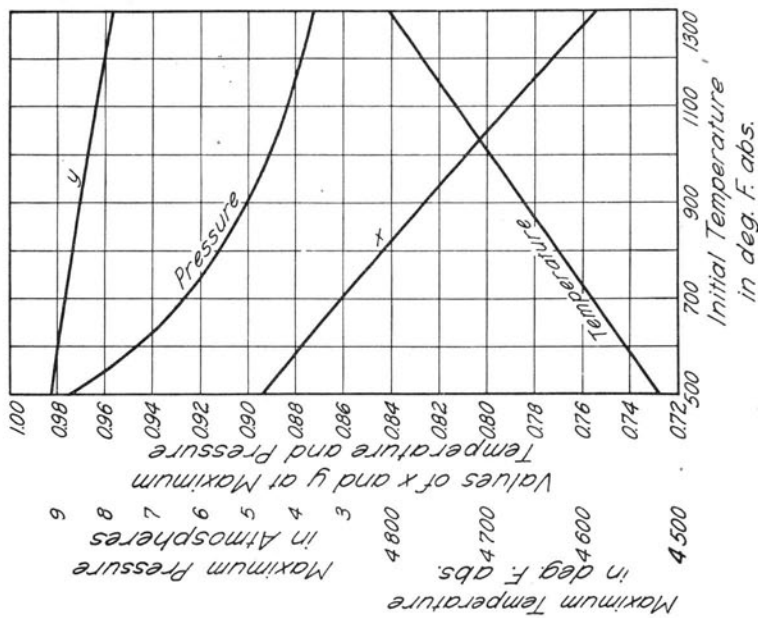
FIG. 9. EFFECT OF INITIAL TEMPERATURE
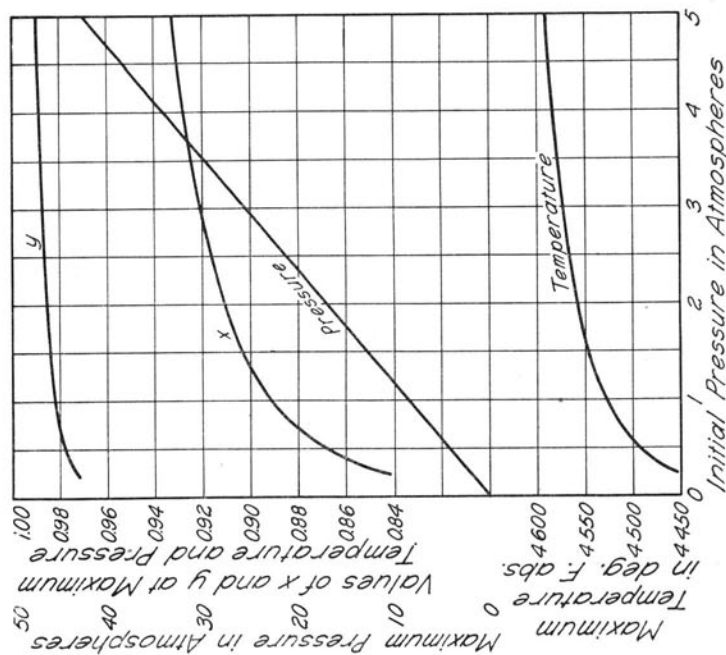
FIG. 8. EFFECT OF INITIAL PRESSURE

The linear relation between the initial and the maximum pressures has been verified experimentally by Bairstow and Alexander[*] for mixtures of coal gas and air.

38. *Effect of Initial Temperature.*—The same 15 per cent mixture of Cambridge coal gas and air is taken. The initial pressure is one atmosphere and a heat loss of 10 per cent during the period of attainment of maximum temperature is assumed. Initial temperatures from 500 to 1300 deg. F. (abs.) are used. The results are given in Table 5 and Fig. 9.

A linear relation is found to exist between the initial temperature and the maximum temperature. The general effect of an increase in initial temperature at a constant initial pressure is an increase of the maximum temperature and a decrease in the maximum pressure with a consequent increase of the dissociation of the products of combustion. The falling off of the maximum pressure is due to the decrease in the ratio of the maximum temperature to the initial temperature.

TABLE 5

EFFECT OF INITIAL TEMPERATURE

Initial Temp., deg. F. (abs.)	520	700	900	1100	1300
Max. Temp.. deg. F. (abs.)........	4528	4591	4662	4732	4804
Max. Press., atm.	8.41	6.35	5.03	4.18	3.60
x_0............................	0.891	0.861	0.826	0.791	0.754
y_0............................	0.982	0.977	0.971	0.964	0.957

39. *Effect of Excess Air and Heat Loss.*—Curves of maximum temperature and dissociation for various mixtures of Cambridge coal gas and air, hydrogen and air, and carbon monoxide and air, with various percentages of heat loss up to the time of attainment of maximum temperature, are shown in Figs. 10, 11, and 12. The results are given in Table 6. The initial temperature taken is 60 deg. F. and initial pressure one atmosphere.

An increase either in the amount of air present or in the heat loss tends to decrease the maximum temperature and makes the reactions go nearer to completion.

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[*] Proc. Roy. Soc., V. 76A, p. 345.
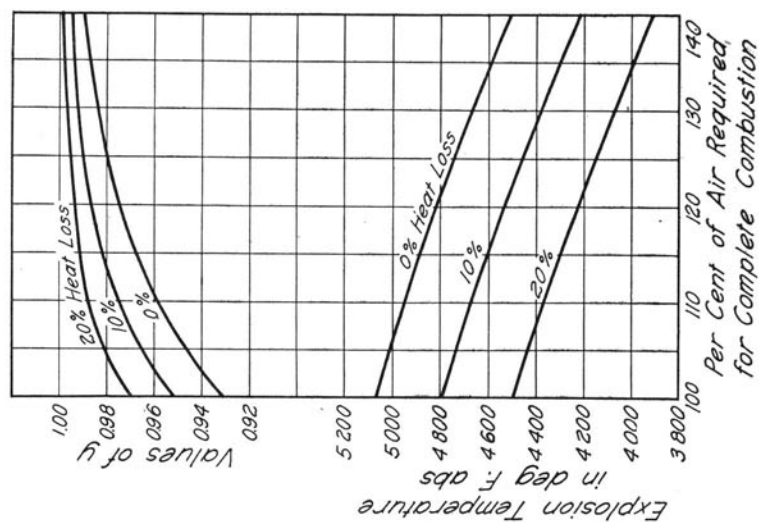
FIG. 11. CALCULATED EXPLOSION CURVES FOR MIXTURES OF HYDROGEN AND AIR
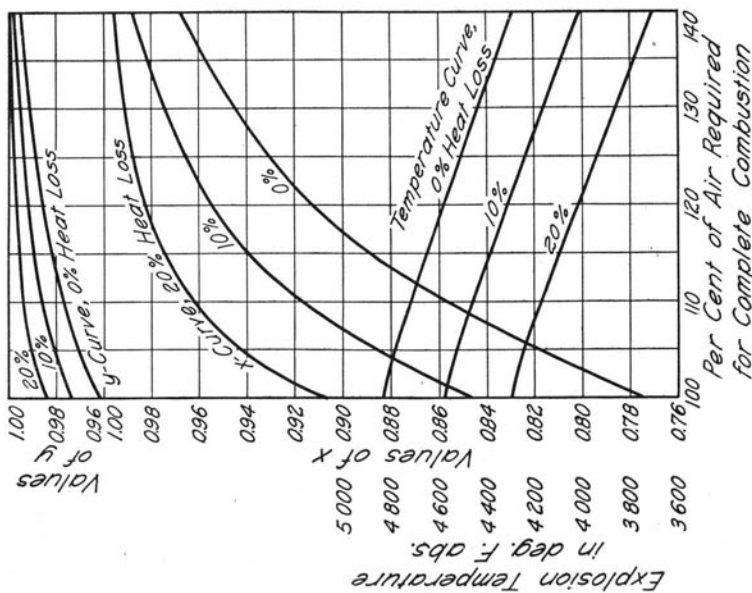
FIG. 10. CALCULATED EXPLOSION CURVES FOR MIXTURES OF CAMBRIDGE COAL GAS AND AIR

TABLE 6

CALCULATED EXPLOSION DATA FOR THREE GAS-AIR MIXTURES

Initial Temp. = 520 deg. F. (abs.).   Initial Pressure = One Atmosphere

Heat Loss, Percentage of Heat of Combustion		Percentage of Air Required for Complete Combustion				
		100	110	120	130	140
Cambridge Coal Gas						
0	T	4830	4720	4580	4430	4290
	x_0	0.775	0.856	0.913	0.945	0.968
	y_0	0.962	0.977	0.986	0.991	0.995
10	T	4580	4460	4310	4160	4010
	x_0	0.847	0.917	0.955	0.975	0.988
	y_0	0.974	0.986	0.992	0.995	0.998
20	T	4300	4170	4010	3860	3700
	x_0	0.907	0.962	0.983	0.991	0.996
	y_0	0.984	0.994	0.997	0.999	1.000
Hydrogen						
0	T	5072	4954	4810	4670	4509
	y_0	0.931	0.959	0.975	0.984	0.990
10	T	4798	4676	4526	4390	4220
	y_0	0.952	0.976	0.987	0.992	0.995
20	T	4498	4370	4212	4080	3908
	y_0	0.970	0.988	0.994	0.997	0.999
Carbon Monoxide						
0	T	4950	4844	4806	4720	4626
	x_0	0.795	0.883	0.868	0.897	0.922
10	T	4732	4668	4582	4488	4382
	x_0	0.850	0.885	0.916	0.939	0.958
20	T	4486	4415	4324	4215	4092
	x_0	0.900	0.933	0.956	0.971	0.982

NOTE.—T given in deg. F. (abs.).

40. *Comparison of Various Gas-Air Mixtures.*—Explosion temperatures have been calculated for various fuel gases using the analyses given in Table 7.

TABLE 7

GAS ANALYSES

Gas	Constituents—Percentage by Volume					
	H_2	CO	CH_4	C_2H_4	CO_2	N_2
Carburetted Water Gas	22.0	28.0	31.0	13.0	4.0	2.0
Natural Gas	2.0	1.0	94.0	....	....	3.0
Producer Gas	14.0	20.0	3.0	....	9.0	54.0
Blast Furnace Gas	3.0	28.0	....	....	10 0	59 0

An initial temperature of 60 deg. F. is used with an initial pressure of one atmosphere. A heat loss of 10 per cent of the heat of combustion is assumed to take place during the period of attainment of maximum temperature. The calculated results are given in Table 8 and Fig. 13.

The explosion temperatures attained depend primarily on the heat of combustion per unit volume of the fuel mixture including the required air. For the gases CO and H_2, respectively, one volume of the gas requires $\frac{1}{2}(1 + 3.78) = 2.39$ volumes of air for combustion, giving a total of 3.39. Taking the cubic foot as the unit, the heat of combustion per unit volume is 271 B. t. u. for H_2 and 320 B. t. u. for CO (Table 16, page 119). Hence the heat of combustion per cubic foot of mixture is: for H_2, $271 \div 3.39 = 79.9$ B. t. u.; and for CO, $320 \div 3.39 = 94.4$ B. t. u. A similar computation gives for the other gases the following numbers:

Carburetted water gas. .91.1   Natural gas. 86.0
Cambridge coal gas. . . . .85.3   Producer gas 61.6
                                       Blast furnace gas. 56.1

It will be noted that the temperature curves follow these numbers in a general way.

The location of a temperature curve is influenced, however, by the character of the products mixture. Since the dissociation of CO_2 is greater than that of H_2O, the presence of a large per cent of CO_2 in the products has the effect of reducing the maximum temperature. Thus the curves for CO and H_2 are nearly coincident, notwithstanding the higher heat of combustion of CO.

A study of Fig. 13 shows that the effect of weakening the mixture is the same for all the gases. The greater the excess of air, the lower is the explosion temperature and the more complete the combustion.

TABLE 8

CALCULATED EXPLOSION DATA FOR VARIOUS GAS-AIR MIXTURES
10 Per Cent Heat Loss

No.	Gas		Percentage of Air Required for Complete Combustion				
			100	110	120	130	140
1	Hydrogen	T	4798	4676	4526	4385	4220
		y_0	0.952	0.976	0.987	0.992	0.995
2	Carbon Monoxide	T	4732	4668	4582	4488	4382
		x_0	0.850	0.885	0.916	0.939	0.958
3	Carburetted Water Gas	T	4632	4528	4388	4240	4097
		x_0	0.842	0.908	0.948	0.970	0.983
		y_0	0.974	0.985	0.991	0.996	0.998
4	Cambridge Coal Gas	T	4580	4460	4310	4160	4010
		x_0	0.847	0.917	0.955	0.975	0.988
		y_0	0.974	0.986	0.992	0.995	0.998
5	Natural Gas	T	4516	4398	4240	4080	3920
		x_0	0.864	0.933	0.996	0.981	0.989
		y_0	0.977	0.989	0.994	0.997	1.000
6	Producer Gas	T	3858	3780	3674	3575	3470
		x_0	0.969	0.989	0.995	0.998	1.000
		y_0	0.994	0.998	0.999	1.000	1.000
7	Blast Furnace Gas	T	3600	3538	3459	3375	3288
		x_0	0.985	0.996	1.000	1.000	1.000
		y_0	0.997	1.000	1.000	1.000	1.000

NOTE.—T given in deg. F. (abs.)
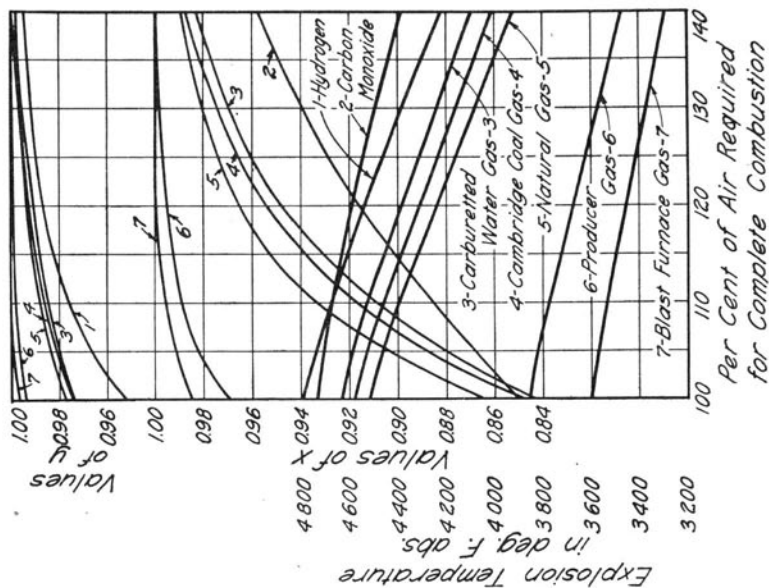
FIG. 13.   CALCULATED EXPLOSION CURVES FOR VARIOUS
GAS-AIR MIXTURES
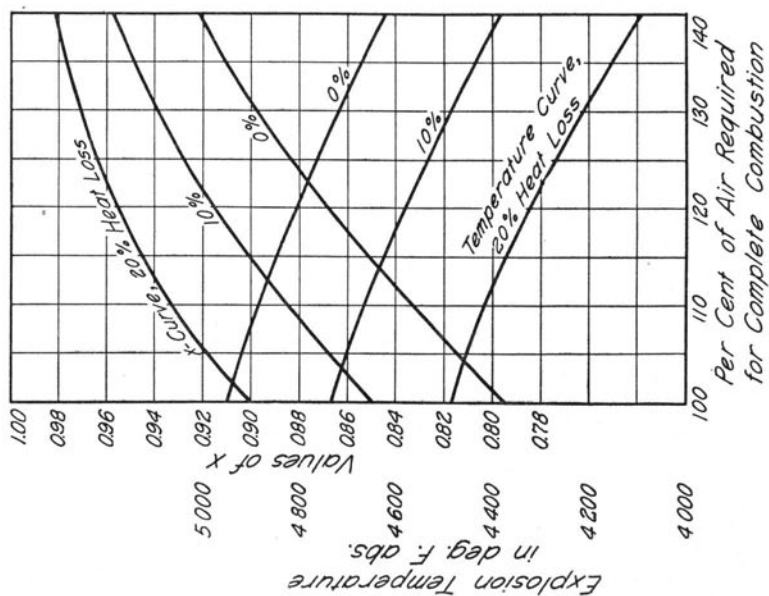
FIG. 12.   CALCULATED EXPLOSION CURVES FOR MIXTURES OF
CARBON MONOXIDE AND AIR

VII. Liquid Fuels

41. *Method of Tizard and Pye.*—In a paper entitled "The Character of Various Fuels for Internal Combustion Engines,"[*] Tizard and Pye present a method of calculating maximum explosion temperatures for mixtures of various fuel vapors and air. Their method is briefly described in the following:

It is assumed that the products of combustion consist only of CO_2, CO, H_2O, H_2, O_2, and N_2.

For purposes of illustration, the case of a mixture of benzene vapor (C_6H_6) with the theoretical amount of air required for combustion is taken. Explosion at constant volume without heat loss is assumed, in an engine having a compression ratio of 5. The temperature at the end of the suction stroke is taken as 100 deg. C. or 672 deg. F. (abs.). The corresponding pressure taken is one atmosphere.

The initial and intermediate mixtures are:

Initial Mixture	mols	Intermediate	Mixture mols
C_6H_6	2.0	CO_2	A
O_2	15.0	CO	B
N_2	56.4	H_2O	C
		H_2	D
		O_2	E
		N_2	56.4

Since the number of atoms of a given element remain unchanged by the combustion, the following equation can be set up:

$$A + B = 12 \text{ carbon atoms}$$

$$2A + B + C + 2E = 30 \text{ oxygen atoms}$$

$$2C + 2D = 12 \text{ hydrogen atoms}$$

Two additional equations for the determination of A, B, C, D, and E are obtained from the equilibrium expressions

$$\frac{(p_{CO})^2 \cdot p_{O_2}}{(p_{CO_2})^2} = K_1 = \frac{B^2 E}{A^2}$$

$$\frac{p_{CO} \cdot p_{H_2O}}{p_{CO_2} \cdot r_{H_2}} = K = \frac{B}{A} \cdot \frac{C}{D}$$

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[*] The Automobile Engineer, I, Feb., 1921, p. 55, II. March, 1921, p. 98, III, April, 1921, p. 134.

The equilibrium equations are assumed to have the form

$$\log K_1 = \alpha' - \frac{\beta'}{T}$$

$$\log K = \alpha - \frac{\beta}{T}$$

The constants α', β', α, and β are determined for temperature ranges of 2000 to 2500 and 2500 to 3000 deg. C. (abs.), from tables of values given by Nernst.

To effect a solution a maximum temperature is assumed, thus determining K_1 and K. From the five equations given above, the quantities A, B, C, D, and E are then determined. From these values the heat liberated on combustion and the specific heat of the products of combustion are calculated. From the heat of combustion and the specific heat of the products a maximum explosion temperature is calculated. When the assumed maximum temperature is found to agree with the final calculated temperature a solution has been effected.

The following general expression for initial mixture strength is used by Tizard and Pye:

$$2(1 + \alpha)\,C_6H_6 + 15O_2 + 56.4\,N_2$$

In their computations α, the degree of richness, was varied from $+0.5$ to -0.5. The results for benzene vapor are given in Table 9.

42. *Recalculation of Tizard and Pye's Values.*—With the method here used it is more convenient to express mixture strength in terms of the amount of air required for complete combustion of the fuel to CO_2 and H_2O. This amount is designated as 100 per cent of the required air.

Taking the case of benzene vapor and air mixtures calculated by Tizard and Pye, the percentages of required air corresponding to the various values of α are as follows:

$\alpha =$	$+0.5$	$+0.2$	$+0.1$	0.0	-0.2	-0.5
Per cent of required air....	66.7	83.3	90.9	100	125	200

The following subscripts are used: s for the state at the end of the suction stroke, c for the state at the end of the compression stroke, and e for the state existing at the instant of maximum explosion temperature.

In the adiabatic compression process the work done is equal to the increase of thermal energy of the gas mixture being compressed. From this consideration the following equation is established for the determination of T_c:

$$F(T_c) - F(T_s) = \frac{m_s \cdot 1.985}{a} \cdot \log_{10} \frac{V_s}{V_c}$$

where

$$F(T) = \log_{10} T + \frac{b}{2.3026a} T + \frac{f}{2 \cdot 2.3026a} \cdot T^2$$

a, b, and f are constants in the constant volume instantaneous specific heat equation for the total initial mixture. This equation is

$$\gamma_v = a + bT + fT^2$$

m_s = total mols of gas mixture being compressed. The pressure P_c is given by the equation

$$P_c = \frac{V_s}{V_c} \frac{T_c}{T_s} \cdot P_s$$

The results for T_c and P_c using $T_s = 672$ deg. F. (abs.) and $\frac{V_s}{V_c} = 5$ are given in Table 9.

As pointed out in Section 19, the constituents of the products of combustion of a hydrocarbon-air mixture containing insufficient oxygen are taken to be the usual six gases, namely, CO_2, CO, H_2O, H_2, O_2, and N_2. The determination of the composition of the intermediate mixture for a given case is facilitated by first assuming a primary combination of C_6H_6 with O_2 to form CO and H_2. Then the composition of the intermediate mixture is easily determined. For the combustion of benzene with n mols of oxygen supplied by the air per mol of benzene the initial mixture and that resulting from an assumed primary combination are, respectively,

Initial Mixture mols		Mixture Resulting from Primary Combination mols	
C_6H_6	1.00		
O_2	n	CO	6.00
N_2	$3.78n$	H_2	3.00
		O_2	$n - 3$
$m' = 1 + 4.78n$		N_2	$3.78n$

TABLE 9

CALCULATED RESULTS FOR BENZENE-AIR MIXTURES COMPARED WITH THE RESULTS OF TIZARD AND PYE

Mixtures Exploded in an Engine with a Compression Ratio of 5

| Mixture | | Explosion Temperatures Calculated by Tizard and Pye | | T_e | x_0 | y_0 | Explosion Pressure | | Compression | | |
Percentage of Required Air	Degree of Richness = x	deg. C.	deg. F. (abs.)	deg. F. (abs.)			atm.	lb. per sq. in. (abs.)	Temp. T_c deg. F. (abs.)	atm.	lb. per sq. in. (abs.)
66.7	+0.5	2561	5101	5113	0.285	0.760	42.63	627	1140	8.482	125
83.3	+0.2	2701	5353	5410	0.564	0.918	42.77	629	1159	8.624	127
90.9	+0.1	2690	5333	5405	0.656	0.943	42.15	620	1166	8.676	128
100.0	0.0	2655	5270	5337	0.739	0.960	41.16	605	1173	8.728	129
125.0	−0.2	2470	4937	5044	0.887	0.984	38.24	562	1190	8.854	130
200.0	−0.5	1994	4081	4098	0.994	1.000	30.71	451	1213	9.025	133

The intermediate or equilibrium composition is then easily written down as follows: •

Intermediate Mixture

mols

CO_2	$6x_0$
CO	$6(1-x_0)$
H_2O	$3y_0$
H_2	$3(1-y_0)$
O_2	$(n-3)-3x_0-1.5y_0$
N_2	$3.78n$

$$m'' = (m'+5)-3x_0-1.5y_0$$

The energy equation reduces to

$$y_0\left[3H''_{rH_2}\right] = \left[E+3u''_{H_2}+(2+m')u''_D\right]-x_0\left[6H''_{vCO}\right]$$

where

$$E = -H'_{vC_6H_6}+6H'_{vCO}+3H'_{rH_2}-3u'_{H_2}-(2+m')u'_D$$

Single primes are used for the state at the end of compression and double primes for the state at maximum explosion temperature.

The equilibrium equation becomes, with the proper values substituted,

$$\log K_{pCO}+\tfrac{1}{2}\log T = \log x_0+\tfrac{1}{2}\log\frac{m_c T_c}{P_c}-\log(1-x_0)$$

$$-\tfrac{1}{2}\log\left[(n-3)-3x_0-1.5y_0\right]$$

$$\frac{m_c T_c}{P_c} = \frac{m_s T_s}{P_s}\cdot\frac{V_c}{V_s} = 134.4m_s$$

The third equation, namely, the quadratic used for the determination of x, has the usual form.

The calculated results for the adiabatic constant volume explosions of benzene vapor and air mixture are given in Table 9 with those of Tizard and Pye, and also in Fig. 14.

It can be seen from Fig. 14 that the agreement of the results produced by the two methods of procedure is remarkably good. The maximum variation is about 2.5 per cent, the values of Tizard and Pye being the lower. The method of Tizard and Pye is undoubtedly the more laborious and indirect. The many approximations used greatly increase the probability of error in any wide application of their method.
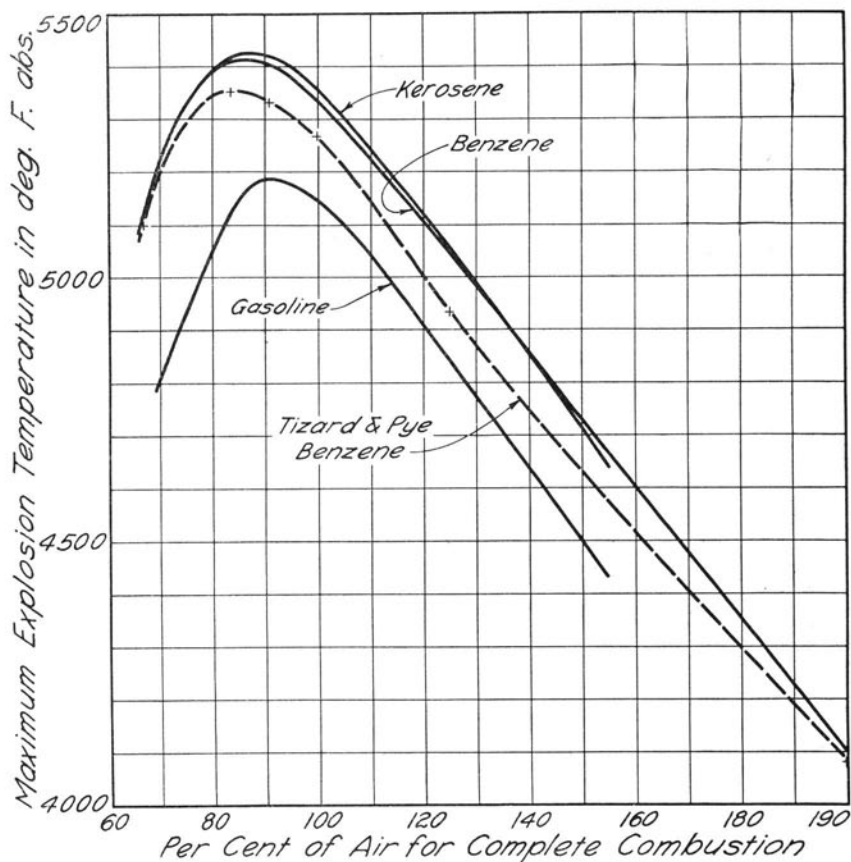
FIG. 14. CALCULATED EXPLOSION TEMPERATURE CURVES FOR MIXTURES OF LIQUID
FUEL VAPORS AND AIR WHEN EXPLODED ADIABATICALLY IN AN ENGINE
HAVING A COMPRESSION RATIO OF 5

43. *Mixtures of Gasoline and Kerosene Vapors and Air.*—The
mixtures of gasoline vapor and air are assumed to be exploded adia-
batically at constant volume in an engine having a compression ratio
of 5.

$$T_s = 672 \text{ deg. F. (abs.)}, \; P_s = 1 \text{ atmosphere.}$$

The gasoline is assumed to have the molecular formula C_8H_{18}.*

The calculated results are given in Table 10 and Fig. 14.

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* Wilson and Barnard, Jour. S. A. E., V. 9, p. 313, 1921.

For kerosene vapor the same conditions are assumed as for the gasoline vapor mixtures. The kerosene is assumed to have the molecular formula $C_{12}H_{26}$.[*]

The calculated results are given in Table 10 and Fig. 14.

TABLE 10

CALCULATED EXPLOSION DATA FOR MIXTURES OF GASOLINE VAPOR AND AIR
AND KEROSENE VAPOR AND AIR

Mixtures Exploded in an Engine with a Compression Ratio of 5

Percentage of Air Required for Complete Combustion	Explosion Temperature deg. F.(abs.)	x_0	y_0	Explosion Pressure		Compression		
							Pressure	
				atm.	lb. per sq. in.(abs.)	Temp. deg. F.(abs.)	atm.	lb. per sq. in.(abs.)
Gasoline ($C_8 H_{18}$)								
70	4808	0.317	0.773	41.833	615	1096	8.154	120
80	5049	0.495	0.885	42.215	621	1108	8.244	121
90	5187	0.670	0.943	42.170	620	1121	8.340	123
100	5149	0.784	0.967	41.155	605	1131	8.415	124
125	4847	0.923	0.989	37.902	557	1152	8.572	126
150	4502	0.974	0.996	34.836	477	1166	8.676	128
Kerosene ($C_{12} H_{26}$)								
70	5222	0.306	0.784	45.691	672	1090	8.110	119
80	5394	0.473	0.886	45.394	667	1105	8.222	121
90	5425	0.620	0.934	44.476	654	1118	8.318	122
100	5359	0.726	0.958	43.179	635	1129	8.400	123
125	5058	0.883	0.983	39.764	584	1150	8.557	126
150	4718	0.952	0.993	36.635	538	1166	8.676	128

44. *Water Injection.*—The advantage of water injection has often been urged in connection with the operation of internal combustion engines. The effect of adding water to the fuel mixture may readily be determined by an extension of the analytical method developed in the preceding sections.

It is assumed that water in varying amounts is injected into the fuel mixture at the end of the compression stroke. The fuel chosen is gasoline, the theoretical amount of air is taken, and all processes are assumed to be adiabatic.

The method used to determine the compression temperature and pressure after the water has been injected is as follows:

The compression volume is determined from the perfect gas law, the pressure, temperature, and the number of mols present being

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[*] Wilson and Barnard, Jour. S. A. E., V. 9, p. 313, 1921.

known. The compression volume is equal to the total volume of steam resulting from the water injected. The volume per pound of steam is then known. From the steam tables the saturation temperature and the energy required to transform one pound of water from water at the temperature of injection to saturated steam are obtained. The energy tables for water vapor (Appendix IV) are used for the superheat range. The heat given up by the compressed gases is easily computed by the use of the energy tables, and is equal to the heat absorbed by the water in being transformed to superheated steam. The compression temperature after water injection is therefore determined. The values are given in Table 11.

TABLE 11

EFFECT OF WATER INJECTION ON GASOLINE-AIR COMBUSTION

Pounds of Water Injected per Pound of Gasoline	Compression			Explosion			Values at Explosion Temp.	
	Temp. deg. F. (abs.)	Pressure		Temp. deg. F. (abs.)	Pressure		x_0	y_0
		atm.	lb. per sq. in. (abs.)		atm.	lb. per sq. in. (abs.)		
0.0	1131	8.415	123.7	5149	41.155	605.0	0.784	0.967
0.2	1059	8.044	118.2	5059	41.163	605.1	0.809	0.970
0.4	991	7.681	112.9	4971	41.164	605.1	0.830	0.974
0.6	925	7.313	107.5	4884	41.155	605.0	0.850	0.976
1.0	798	6.556	96.4	4718	41.128	604.6	0.886	0.982

Let $n' = $ the number of mols of water injected per mol of gasoline; then the mixture compositions are as follows:

Initial Mixture
mols

C_8H_{18}	1.00
O_2	12.50
N_2	47.25
H_2O	n'
$m' = $	$\overline{60.75 + n'}$

Intermediate Mixture
mols

CO_2	$8x_0$
CO	$8(1-x_0)$
H_2O	$(n'+9)y_0$
H_2	$(n'+9)(1-y_0)$
O_2	$8.5 + \dfrac{n'}{2} - 4x_0 - \frac{1}{2}(n'+9)y_0$
N_2	47.25
	$(72.75 + \frac{3}{2}n') - 4x_0 - \frac{1}{2}(n'-9)y_0$

The energy equation takes the form

$$y_0\left[(n'+9)H''_{vH_2}\right] = \left[E + (n'+9)u''_{H_2} + \left(63.75 + \frac{n'}{2}\right)u''_D\right]$$
$$-x_0\left[8H''_{vCO}\right]$$

where

$$E = -H'_{vC_8H_{18}} + 8H'_{vCO} + (n' + 9)H'_{rH_2}$$

$$- (n' + 9)u'_{H_2} - \left(63.75 + \frac{n'}{2}\right)u'_D$$

The equilibrium equation becomes

$$\log K_{pCO} + \tfrac{1}{2}\log T = \log x_0 + \tfrac{1}{2}\log\left(\frac{m_s T_s V_c}{P_s \cdot V_s}\right) - \log(1 - x_0)$$

$$- \tfrac{1}{2}\log\left[8.5 + \frac{n'}{2} - 4x_0 - \tfrac{1}{2}(n' + 9)y_0\right]$$

These two equations with the usual quadratic give the solutions found in Table 11. The results are also represented by the curves of Fig. 15.
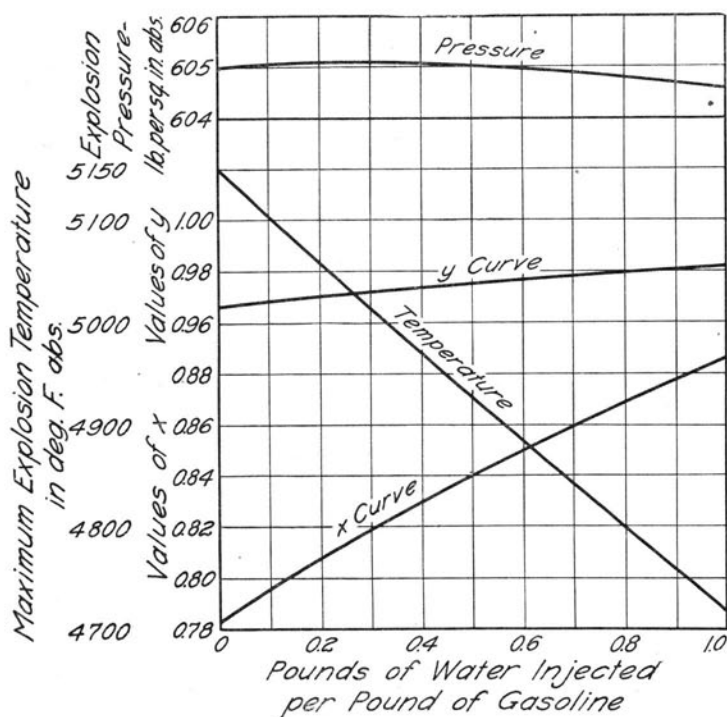
FIG. 15.   EFFECT OF WATER INJECTION

The outstanding result shown in Fig. 15 is the constancy of the explosion pressure with variation in the amount of water injected. With a water injection of one pound per pound of fuel vapor present the compression pressure is lowered 22 per cent, but due to the additional weight of charge and the more complete combustion the explosion pressure is unaffected. With injection of the water into the intake manifold a reduction in the work of compression is probably effected, but this saving is more than likely offset by a slowing down of the combustion process. V. W. Brinkerhoff* found that for a class B U. S. Army truck engine with a compression ratio of 3.71 no change in power or efficiency was obtained when water up to 0.6 pound per pound of gasoline was injected into the intake manifold. For amounts above 0.6 pound there was a decided decrease in power.

VIII. Welding Flames

By George T. Felbeck

45. *Dissociation of Hydrogen into Atoms.*—In oxy-hydrogen and oxy-acetylene flames as ordinarily used in commercial practice the partial pressures of the various gas constituents in the flame are very low, the total pressure being one atmosphere. The low partial pressure of the hydrogen coupled with the high temperature causes an appreciable dissociation of the molecular hydrogen into atomic hydrogen. A quantitative determination of the extent of this dissociation has been made by Dr. Irving Langmuir.† An equation for the equilibrium constant for the reaction $H_2 = H + H$ has been derived from the data given by Langmuir. (See Appendix III.)

46. *Possibilities of Error in Flame Temperature Calculations.*— The conditions which tend to invalidate the calculated temperatures for the oxy-hydrogen and oxy-acetylene flames may be briefly stated as follows:

(a) The specific heat equations have been extended past the range of experimental verification.

(b) The specific heat equation used for molecular hydrogen may include some of the heat of dissociation of molecular hydrogen into atomic hydrogen at the higher temperatures. This error is probably small, since the specific heat equation is a linear relation, and also, since the explosion method was used in determining the specific heats, the dissociation was materially decreased by the high pressure.

(c) There is a possibility of the dissociation of the molecular oxygen into atoms.

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* Report No. 45, Nat. Adv. Com. for Aeronautics.
† Jour. Am. Chem. Soc., V. 37, p. 417, 1915.

(d)   The value used for the heat of dissociation of molecular hydrogen into atomic hydrogen has a rather weak experimental foundation.

(e)   Experimental values for the equilibrium constant for the reaction $H_2 = H + H$ have not been verified.

Because of the uncertainty of the data concerning the dissociation of hydrogen into atoms, flame temperatures have been calculated both with and without taking this dissociation into consideration.

47.   *Oxy-hydrogen Flame Temperatures.*—The gases previous to combustion are assumed to be at 60 deg. F.; the combustion takes place at a pressure of one atmosphere; the combustion is assumed to be adiabatic; the calculated temperatures are therefore the maximum attainable.

Taking n mols of oxygen per mol of hydrogen, the mixtures given are for the case where dissociation of hydrogen into atoms does not occur.

Initial Mixture mols		Intermediate Mixture mols	
		H_2O	y
H_2	1	H_2	$1 - y$
O_2	n	O_2	$n - \tfrac{1}{2}y$
$m' = 1 + n$		$m'' = m' - \tfrac{1}{2}y$	

The equations for the determination of the maximum temperature and extent of combustion become

$$y = \frac{i''_{H_2} + ni''_{O_2} - i'_{H_2} - ni'_{O_2}}{H''_{pH_2}}$$

$$\log K_{pH_2} = \log y + \tfrac{1}{2}\log(m' - \tfrac{1}{2}y) - \log(1 - y) - \tfrac{1}{2}\log(n - \tfrac{1}{2}y)$$

For the oxy-hydrogen flame temperature with dissociation of hydrogen into atoms, the procedure is as follows: Of the initial hydrogen a portion equal to y burns to H_2O. Of the remaining hydrogen equal to $(1 - y)$ a portion z exists as molecular hydrogen.

Let the subscript a indicate the atomic state. The initial and intermediate mixtures are:

Initial Mixture mols		Intermediate Mixture mols	
		H_2O	y
H_2	1	H_2	$z(1 - y)$
O_2	n	H_a	$2(1 - z)\ (1 - y)$
$m' = 1 + n$		O_2	$n - \tfrac{1}{2}y$
		$m'' = 0.5 + n + (\tfrac{3}{2} - z)(1 - y)$	

Following the usual procedure the equations established are:

$$(1-z) = \frac{yH''_{p_{H_2}} - i''_{H_2} - ni''_{O_2} + i'_{H_2} + ni'_{O_2}}{(1-y)H''_{p_{Ha}}} \quad \ldots \text{(A)}$$

$$\log K_{p_{Ha}} = \log\left[\frac{4(1-z)^2}{z} \cdot \frac{(1-y)}{0.5+n+(\frac{3}{2}-z)(1-y)}\right] \ldots \text{(B)}$$

$$\log K_{p_{H_2}} = \log\left[\frac{y\left[0.5+n-(\frac{3}{2}-z)(1-y)\right]^{\frac{1}{2}}}{z(1-y)(n-\frac{1}{2}y)^{\frac{1}{2}}}\right] \ldots \text{(C)}$$

The solutions of the three equations given above were obtained as follows: Several probable values of y were assumed and equations (A) and (B) solved by trial for values of z and T corresponding to each value of y. Values of the right-hand member of equation (C) were obtained upon substitution of each set of values of y, z, and T. The intersection of the curve of the right-hand member of equation (C) with the curve of the values of $\log K_{p_{H_2}}$ obtained from the tables gives the solution.

The calculated temperatures for the oxy-hydrogen flame are given in Table 12 and Fig. 16. The third curve gives the percentage of oxygen present in the flame for the case with dissociation of hydrogen into atoms. The dissociation of the hydrogen reduces the maximum attainable temperature about 11 per cent. For welding purposes a non-oxidizing flame is required. From the oxygen curve, Fig. 16, it is seen that the oxygen content is inappreciable in the flames resulting from mixtures having an oxygen to hydrogen ratio of 1 to 4 or less.

TABLE 12

OXY-HYDROGEN FLAME TEMPERATURES

Vols. Oxygen per vol. Hydrogen	No Dissociation of Hydrogen into Atoms		With Dissociation of Hydrogen into Atoms			
	T deg. F. (abs.)	y	T deg. F. (abs.)	y	z	Percentage Oxygen in Flame
0.15	4195	0.300	4096	0.300	0.992	0.00
0.25	5552	0.493	5074	0.499	0.919	0.096
0.375	6100	0.638	5648	0.686	0.770	2.90
0.50	6169	0.712	5727	0.752	0.712	12.40
0.70	6085	0.790	5713	0.818	0.661	21.50
1.00	5844	0.869	5535	0.872	0.646	35.10

In commercial work this ratio of 1 to 4 for the oxygen to hydrogen in the mixture is found to give a non-oxidizing flame, and is therefore used. The temperature for the welding flame having this ratio is 5074 deg. F. (abs.), or say 4600 deg. F. This is slightly higher than the usually accepted value of 4100 deg. F. which has been calculated by previous investigators. For cutting purposes where the oxygen content can be increased, the maximum temperature may be taken as 5000 deg. F.

48. *Chemical Reactions Occurring in Oxy-acetylene Flame.*— The following statements are taken from a report of an experimental investigation by W. A. Bone and J. C. Cain:[*]

> (1) When acetylene is exploded with less than its own volume of oxygen, carbon monoxide and hydrogen are finally obtained in accordance with the equation $C_2H_2 + O_2 = 2CO + H_2$.
>
> (2) The excess of acetylene was for the greater part resolved into its elements by the shock of the explosion wave. A small quantity (as much as 1 per cent in some cases) is, however, found in the products of combustion. This may be due to acetylene which has escaped decomposition altogether, or possibly to a recombination of H_2 and C in the rear of the explosion wave.
>
> (3) No methane was formed.
>
> (4) Possibly small amounts of CO_2 present.
>
> (5) Carbon was deposited. In the cases of C_2H_2 mixed with three-fourths of its own volume of oxygen a thick deposit of carbon was formed, but when mixtures contained a larger proportion of oxygen much less carbon was formed.

The primary phase in the flame may therefore be represented by the reaction

$$C_2H_2 + O_2 = 2CO + H_2$$
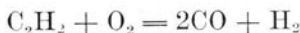
Any excess oxygen that may be present enters into a secondary phase, namely, the formation of CO_2 and H_2O.

At the high temperature attained in the flame there is possibility of the dissociation of hydrogen into atoms, the dissociation of oxygen into atoms, and the dissociation of carbon monoxide into carbon and oxygen. The dissociation of hydrogen into atoms has been discussed. There being no evidence available as to the dissociation of oxygen into atoms, such dissociation is assumed not to occur. An equilibrium equation for the reaction $C + \frac{1}{2}O_2 = CO$ can be obtained by a combination of the equilibrium equations for the reactions $CO + \frac{1}{2}O_2 = CO_2$ and $C + CO_2 = 2CO$. From an equilibrium equation so established it has been determined that if carbon monoxide alone were heated up to 8000 deg. F. (abs.) no dissociation whatever would occur.

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[*] Jour. Chem. Soc., V. 71, pp. 26-41, 1897.
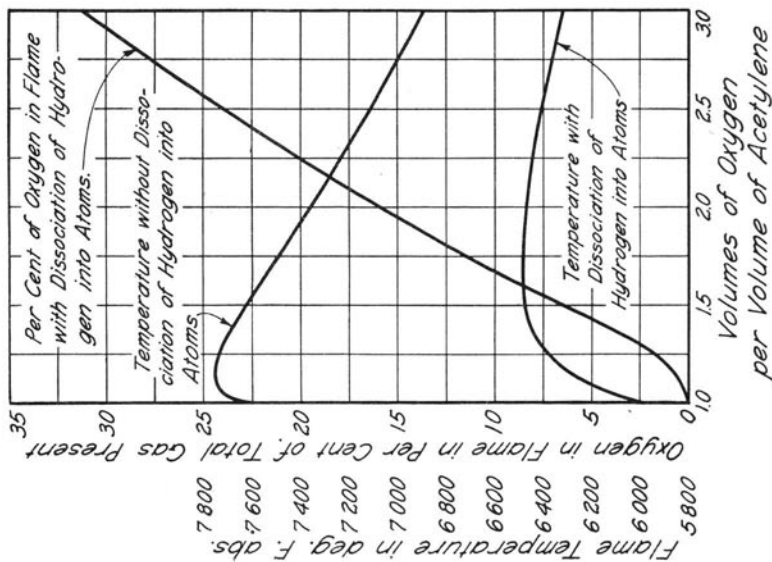
FIG. 17.   CALCULATED MAXIMUM TEMPERATURE CURVES
FOR OXY-ACETYLENE FLAMES
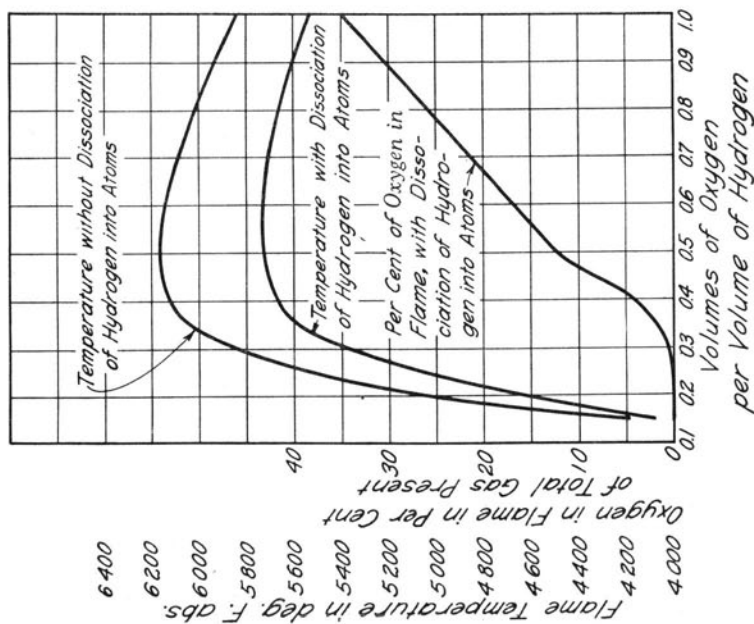
FIG. 16.   CALCULATED MAXIMUM TEMPERATURE CURVES
FOR OXY-HYDROGEN FLAMES

49. *Oxy-acetylene Flame Temperatures.*—The initial temperature is taken as 60 deg. F. and total pressure one atmosphere. The combustion is assumed to be adiabatic.

For the case without dissociation of hydrogen into atoms, the initial and intermediate mixtures and resulting equations are:

Initial Mixture		Intermediate Mixture	
	mols		mols
C_2H_2	1	CO_2	$2x$
O_2	n	CO	$2(1-x)$
m'	$= \overline{1+n}$	H_2O	y
		H_2	$1-y$
		O_2	$(n-1) - x - \frac{1}{2}y$
		$m'' =$	$\overline{(n+2) - x - \frac{1}{2}y}$

$$y\left[H''_{pH_2}\right] = \left[-H'_{pC_2H_2} + 2H'_{pCO} + H'_{pH_2} + (n+1)i''_D + i''_{H_2}\right.$$

$$\left. -(n+1)i'_D - i'_{H_2}\right] - x\left[2H''_{pCO}\right]$$

$$x = \frac{\left[c(b-1)-(a+b)\right] + \sqrt{\left[c(b-1)-(a+b)\right]^2 + 4ba(c-1)}}{2a(c-1)}$$

$$\log K_{pCO} = \log x + \tfrac{1}{2}\log\left[(n+2) - x - \tfrac{1}{2}y\right] - \log(1-x)$$

$$-\tfrac{1}{2}\log\left[(n-1) - x - \tfrac{1}{2}y\right]$$

For the case with dissociation of hydrogen into atoms, the mixtures and resulting equations are:

Initial Mixture		Intermediate Mixture	
	mols		mols
C_2H_2	1	CO_2	$2x$
O_2	n	CO	$2(1-x)$
m'	$= \overline{1+n}$	H_2O	y
		H_2	$z(1-y)$
		H_a	$2(1-z)(1-y)$
		O_2	$(n-1) - x - 0.5y$
		$m'' =$	$\overline{(1.5+n) + (\frac{3}{2}-z)(1-y) - x}$

$$y\left[H''_{pH_2} + (1-z)H''_{pH_a}\right]$$

$$=\left[-H'_{pC_2H_2} + 2H'_{pCO} + H'_{pH} + (n+1)i''_D + i''_{H_2} - (n+1)i'_D - i'_{H_2}\right]$$

$$-x\left[2H''_{pCO}\right]$$

$$x=\frac{\left[cz(b-1)-(a+b)\right]-\sqrt{\left[cz(b-1)-(a+b)\right]^2+4ba(cz-1)}}{2a(cz-1)}$$

$$\log K_{pCO}=\log x + \tfrac{1}{2}\log\left[(1.5+n)+(\tfrac{3}{2}-z)(1-y)-x\right]-\log(1-x)$$

$$-\tfrac{1}{2}\log\left[(n-1)-x-\tfrac{1}{2}y\right]$$

$$\log K_{pH_a}=\log\left[\frac{4(1-z)^2}{z}\right]+\log(1-y)$$

$$-\log\left[(1.5+n)+(\tfrac{3}{2}-z)(1-y)-x\right]$$

The solution of the four equations for the four unknowns x, y, z, and T is obtained as follows: Assume a probable value of $z = z_1$. The first three equations then are solved in the usual way. These values of z_1, x_1, y_1 are substituted in the right-hand member of the fourth equation. For the value of T_1 obtained a value of $\log K_{pHa}$ is obtained from the equation (see Appendix III)

$$\log K_{pH_a}=\frac{1}{4.571}\left[\frac{-168\,550}{T}+9.0262\log_{10}T-\tfrac{1}{3}\cdot10^{-3}\,T-7.2\right]$$

After several values of v have been assumed and the corresponding values of x, y, and T found, curves for the right- and left-hand members of the fourth equation can be established. The intersection of these curves gives the desired solution.

The calculated data for the oxy-acetylene flame are given in Table 13 and Fig. 17.

TABLE 13

OXY-ACETYLENE FLAME TEMPERATURES

Vols. Oxygen per vol. Acetylene	No Dissociation of Hydrogen into Atoms			With Dissociation of Hydrogen into Atoms				
	T deg. F. (abs.)	x	y	T deg. F. (abs.)	x	y	z	Percentage Oxygen in Flame
1.0	7587	0.000	0.000	5960	0.000	0.000	0.680	0.0
1.1	7746	0.009	0.131	....	.....	.....	.....	....
1.2	7750	0.014	0.198	6338	0.050	0.227	0.500	1.1
1.5	7630	0.028	0.329	6477	0.095	0.336	0.414	6.5
1.7	7525	0.038	0.392	6484	0.116	0.376	0.394	10.5
2.0	7360	0.054	0.466	6462	0.143	0.422	0.376	16.1 *
2.5	7112	0.084	0.564	....	.....	.....	.....	....
3.0	6896	0.118	0.640	6320	0.225	0.540	0.364	31.4

The temperatures calculated, taking into consideration the dissociation of hydrogen, are accepted as being the more nearly correct. Judging from Fig. 17, the proportion of oxygen to acetylene should not be over 1.2 for a non-oxidizing flame. This is a little lower than the proportions recommended by various handbooks and manufacturers' catalogs, which vary from 1.3 to 1.7. Whittemore* found that a proportion of 1.38 gave satisfactory results. Assuming this proportion of 1.4 vols. of oxygen to 1 volume of acetylene to be correct, the calculated temperature of the oxy-acetylene welding flame is 6460 deg. F. (abs.) or 6000 deg. F. This is somewhat lower than the calculated temperature of 6300 which is usually quoted. Unfortunately, no method has been developed whereby these calculated temperatures could be checked up experimentally.

* Eng. Exp. Sta., Univ. of Ill., Bul. No. 45, p. 58.

APPENDIX I

SPECIFIC HEATS OF GASES*

1. *Methods of Measurement.*—Two principal methods have been used in the determination of the specific heat of gases:

(a) The constant pressure method, in which the gas is made to flow at constant pressure (usually atmospheric pressure) through a heater and then through a calorimeter where it is cooled. A comparison of the change of temperature with the heat rejected gives the specific heat.

(b) Explosion experiments, in which a known mixture of gases is heated by internal combustion in a vessel of constant volume.

In a third method used by Dugald Clerk the gas was alternately compressed and expanded, the change of temperature was calculated from the change of pressure measured from the indicator diagram, and the specific heat was estimated by comparing the change of temperature with the work done.

The constant pressure measurements are applicable at relatively low temperatures. The method has been used by Regnault, Wiedemann, Holborn and Austin, Holborn and Henning, and by Swann. For high temperatures the explosion method has been used by Mallard and Le Chatelier, Langen, Pier, and Bjerrum.

2. *Results of Experiments.*—Some of the specific heat measurements are now known to be of little or no value. Thus no reliance can be placed on the results obtained from the explosion experiments of Mallard and Le Chatelier, and Langen. For high temperatures, the results given by Pier as recalculated by Bjerrum and Bjerrum's own results may be accepted as fairly accurate. At low temperatures great weight should be given to Swann's figures. Holborn and Henning's values should receive consideration, but they are doubtless too low in some cases.

The most reliable of the experimental results are presented on the following page.

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* For an exhaustive discussion of this subject, the reader is referred to an article by David R. Pye in Glazebrook's Dictionary of Applied Physics, V. 1.

Swann's Results

INSTANTANEOUS SPECIFIC HEAT PER MOL AT TEMPERATURE t DEG. C.

Air		CO_2	
$t= 0°$ $\gamma_p = 6.96$	$100°$ 6.99	$t = 20°$ $\gamma_p = 8.92$	$100°$ 9.74

Holborn and Henning's Results

MEAN SPECIFIC HEAT PER MOL AT CONSTANT VOLUME

Nitrogen		CO_2		H_2O	
Temp.Range	γ_v(mean)	Temp.Range	γ_v(mean)	Temp. Range	γ_v(mean)
0–200° C.	4.73	0–200° C.	7.48	110°–620° C.	6.51
0–630° C.	4.91	0–630° C.	8.60	110°–1000°C.	6.95
0–1000° C.	5.25	0–1000° C.	9.33	110°–1327°C.	7.40
0–1347° C.	5.31	0–1364° C.	9.84		

Pier's Results, Recalculated by Bjerrum

MEAN SPECIFIC HEAT PER MOL AT CONSTANT VOLUME

Nitrogen		CO_2^*		H_2O	
Temp. Range	γ_v(mean)	Temp. Range	γ_v(mean)	Temp. Range	γ_v(mean)
18°–1519° C.	5.43	0–1611° C.	9.98	18°–1811° C.	7.92
18°–1783° C.	5.58	0–1839° C.	10.28	18°–2110° C.	8.54
18°–1951° C.	5.79	0–2110° C.	10.47	18°–2377° C.	9.37
18°–2182° C.	5.87				
18°–2367° C.	5.90				

* In the case of CO_2, Bjerrum found that Pier's results needed no correction.

Bjerrum's Results

MEAN SPECIFIC HEAT PER MOL AT CONSTANT VOLUME

Hydrogen		CO_2		H_2O	
Temp. Range	γ_v(mean)	Temp. Range	γ_v(mean)	Temp. Range	γ_v(mean)
18°–1461° C.	5.23	18°–2714° C.	10.9	18°–2663° C.	10.00
18°–1810° C.	5.44			18°–2908° C.	10.50
18°–2158° C.	5.68			18°–3064° C.	10.90
18°–2374° C.	5.76				

3. *Diatomic Gases.*—The diatomic gases that are of importance in the present investigation are air, CO, N_2, O_2, and H_2. Most of the experiments have been made on nitrogen and air, and from these the specific heat of oxygen has been deduced. The experiments of Holborn and Austin indicate that the specific heat per mol of oxygen is slightly higher than that of nitrogen; however, the usual practice of taking the specific heats per mol of air, CO, N_2, and O_2 as identical is fairly well justified. The specific heat of hydrogen seems to be somewhat lower.

The equations for the specific heat of the diatomic gases have usually been given the linear form $\gamma = a + bT$. It is probable, however, that the rate of increase of specific heat with temperature is not constant but increases somewhat with rise of temperature. Thus comparing Bjerrum's measurements at temperatures ranging from 1500 deg. to 2300 deg. C. with the measurements of Swann at 20 deg. and 100 deg. C., it is found that the rate of increase at 2000 deg. C. is more than three times the rate of increase at 100 deg. C. Apparently, therefore, an equation of the second degree at least is required.

The experiments of Swann on the specific heat of air at low temperatures are beyond question the most accurate for the range 0 deg. to 100 deg. C. These are represented by the equation

$$c_p = 0.2413 \ (1 + 0.00\,005t)$$

or, taking molecular specific heat,

$$\gamma_p = 6.96 \ (1 + 0.00\,005t)$$

At high temperature the measurements of Pier and Bjerrum furnish the only fairly reliable experimental evidence.

The values of γ_p (mean) for nitrogen as given by Bjerrum are plotted in Fig. 18. A straight line would represent the points fairly well, but for $t = 0$ would give a value of γ_p considerably smaller than Swann's value 6.96. To reconcile Swann's measurements with the Bjerrum points, a second degree equation is assumed with the first term 6.96; thus

$$\gamma_p(\text{mean}) = 6.96 + at + bt^2;$$

then the coefficients a and b are determined by the method of least squares from Bjerrum's values. The values of a and b thus obtained are: $a = 0.1069 \cdot 10^{-3}$, $b = 0.1296 \cdot 10^{-6}$. The equation for the instantaneous specific heat is, therefore,

$$\gamma_p = 6.96 + 0.2138 \cdot 10^{-3}t + 0.3888 \cdot 10^{-6}t^2$$

With absolute temperatures, centigrade, the equation becomes

$$\gamma_p = 6.9306 + 0.00\,157 \cdot 10^{-3}T + 0.3888 \cdot 10^{-6}\,T^2$$

The coefficient of T is negligible; hence the equation may be written

$$\gamma_p = 6.93 + 0.3888 \times 10^{-6}\,T^2;$$

or using absolute temperatures on the Fahrenheit scale

$$\gamma_p = 6.93 + 0.1200 \times 10^{-6}T^2$$
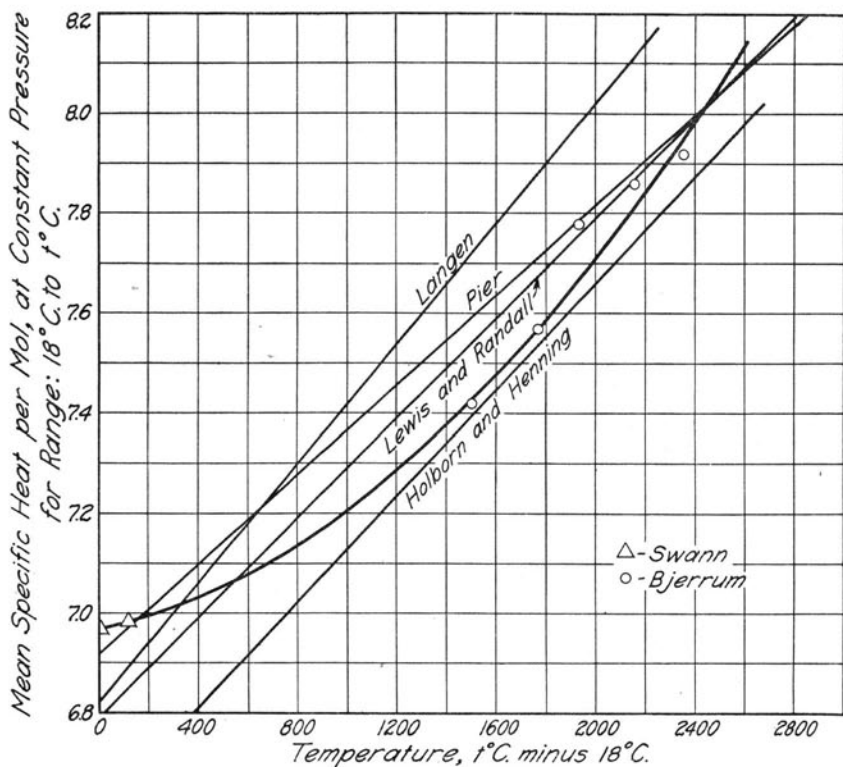
FIG. 18. SPECIFIC HEAT OF DIATOMIC GASES O_2, N_2, CO

In Fig. 18 the curve represents the mean specific heat given by the preceding formula. The various straight lines represent the equations proposed by Langen, Pier, Holborn and Henning, and Lewis and Randall.

Bjerrum's measurements of the specific heat of hydrogen are represented accurately by the linear formula γ_p (mean) $= 6.35 +$

$0.6 \times 10^{-3}(t - 18)$. The corresponding formula for instantaneous specific heat at constant pressure with the Fahrenheit absolute scale is

$$\gamma_p = 6.00 + 0.667 \times 10^{-3}T$$

4. *Carbon Dioxide.*—The experiments on the specific heat of carbon dioxide may be summarized as follows:

(a) The earlier experiments of Regnault and Wiedemann at low temperatures.

(b) The experiment of Joly and Swann, also at low temperatures.

(c) The experiments of Holborn and Austin extending to about 800 deg. C., and the subsequent experiments of Holborn and Henning, which covered the range 0 deg. to 1400 deg. C.

(d) The explosion experiments; of these, the experiments of Pier and Bjerrum are beyond question the most reliable.

The following are some of the formulas that have been proposed for the mean specific heat of CO_2 from 0 deg. to t deg. C.:

Holborn and Austin

$$\gamma_{p_m} = 8.923 + 3.045 \times 10^{-3}\,t - 0.735 \times 10^{-6}\,t^2$$

Holborn and Henning

$$\gamma_{p_m} = 8.84 + 3.267 \times 10^{-3}t - 0.792 \times 10^{-6}t^2$$

Langen

$$\gamma_{p_m} = 8.7 + 0.0026\,t$$

Pier

$$\gamma_{p_m} = 8.79 + 3.3 \cdot 10^{-3}t - 0.95 \cdot 10^{-6}t^2 + 0.1 \cdot 10^{-9}t^3$$

The various experiments show conclusively that the rate of increase of specific heat is rapid at low temperatures, but becomes smaller as the temperature increases. Hence Langen's linear formula is not even a close approximation for temperatures above 2000 deg. C. The second-degree formulas are likewise defective, as they give a maximum at about 2000 deg. C., and the experiments show that such a maximum does not exist. Pier's third-degree formula represents quite accurately the experiments at the low temperatures and also through the high temperature range. A slight modification makes the formula fit more closely Swann's results at 0 deg. and 100 deg. and also Bjerrum's measurement at 2714 deg. The modified formula is

$$\gamma_{p_m} = 8.75 + 3.527 \cdot 10^{-3}\,t - 1.175 \cdot 10^{-6}\,t^2 + 0.1583 \cdot 10^{-9}t^3 \quad \text{(B)}$$

or the instantaneous specific heat in degrees Fahrenheit absolute is

$$\gamma_p = 6.4587 + 5.0668 \cdot 10^{-3}T - 1.2480 \cdot 10^{-6}T^2 + 0.1086 \cdot 10^{-9}T^3$$

A third-degree equation for the specific heat has, however, the objection that the additional term appears in the equilibrium equations, and all computations are thereby rendered more tedious. To obviate this objection the following expedient is used: A second-degree equation is used to represent the instantaneous specific heat from 0 deg. to some intermediate temperature; then for the higher temperatures a linear relation is assumed. The equations thus determined are

$$\left.\begin{array}{l} \gamma_p = 7.15 + 3.9 \cdot 10^{-3}T - 0.6 \cdot 10^{-6}T^2, \quad T < 2900 \text{ deg. F. (abs.)} \\ \gamma_p = 12.196 + 0.42 \cdot 10^{-3}T. \quad T > 2900 \text{ deg. F. (abs.)} \end{array}\right\} \text{(C)}$$

The following table gives a comparison of mean specific heats from 0 deg. to t deg. C. obtained from the three formulas:

$t =$	0	500	1000	1500	2000	2500	3000
Eq. (C)	8.922	10.249	11.253	11.935	12.382	12.727	13.019
Eq. (B)	8.750	10.239	11.260	11.931	12.370	12.696	13.030
Pier	8.790	10.215	11.240	11.940	12.390	12.665	12.840

It appears that equations (C) give results practically identical with equation (B).
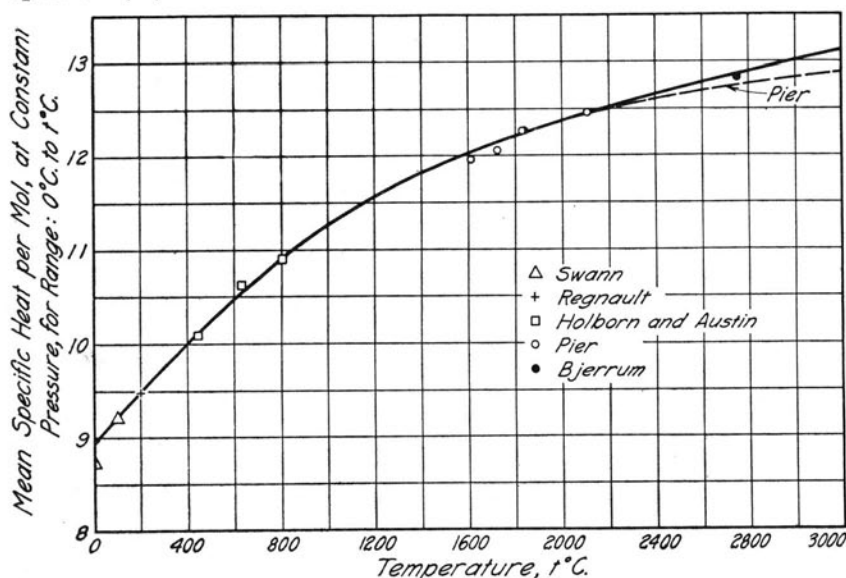
FIG. 19.   SPECIFIC HEAT OF CARBON DIOXIDE

In Fig. 19 the curve represents values derived from equations (C), the points show the experimental results obtained by various observers. Except for Swann's point at 0 deg., the agreement is satisfactory.

5. *Water Vapor.*—For the high temperature range the experiments of Pier and Bjerrum are accepted. The values of γ_p (mean) for the range 18 deg. to t deg. C. are plotted in Fig. 20. Again the problem is to pass a satisfactory curve through these points and at the same time make the curve represent fairly the available experimental data at low temperatures.

Holborn and Henning's equation when applied to a range 18 deg. to t deg. C. gives the curve shown in the figure. This curve might be accepted as conclusive if it were not for the experiments of Knoblauch and Jakob. These had reference to superheated steam at various pressures, and, as is well known, gave different curves for different pressures. Since the water vapor in a gas mixture has usually a low pressure, it is sufficient to take a single curve for a pressure of 1 or 2 lb. per sq. in. The Knoblauch and Jakob values reduced to mean specific heat from 18 deg. to t deg. C. give the curve shown in the figure. The two curves show a decidedly different trend; the *H-H* curve prolonged could be made to pass through the Bjerrum points, but the *K-J* curve if prolonged would pass above them.

The curve chosen is a compromise between these two curves at the low-temperature end, and is made to give the best possible agree-
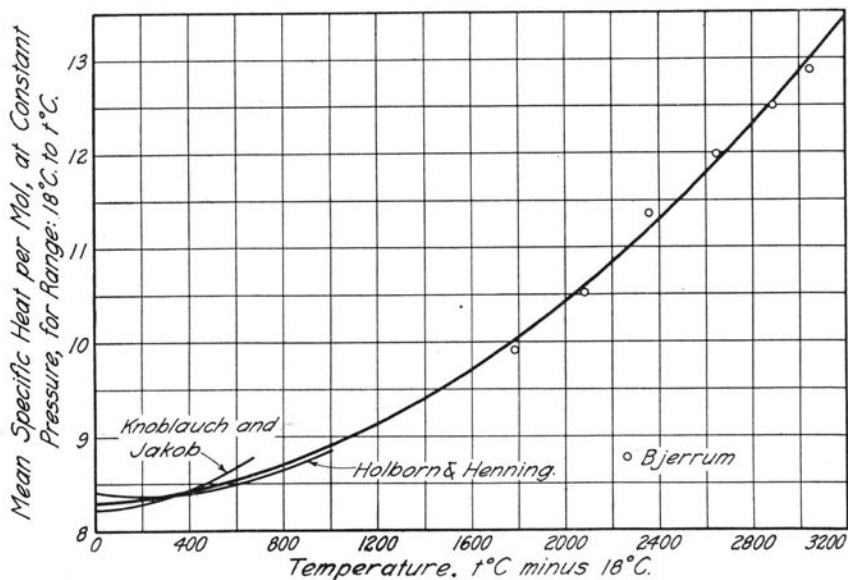
Fig. 20. Specific Heat of Water Vapor

ment consistent with a second degree equation with the Bjerrum points. The equation for the instantaneous specific heat per mol at constant pressure deduced in this way is

$$\gamma_p = 8.33 - 0.276 \cdot 10^{-3}T + 0.423 \cdot 10^{-6}T^2,$$

in which T denotes absolute temperature on the Fahrenheit scale.

6. *Comparison with Pye's Values of Specific Heat.*—In Pye's critical discussion of specific heats* is given a table of the specific heats at constant volume. The values were obtained by plotting energy-temperature curves, taking as a basis the figures given by Bjerrum and Swann. The table is here reproduced with the addition of the values calculated from the preceding equations, which are given in parentheses.

In the intermediate range, 1000 deg. to 2500 deg., the two sets of values agree closely, the difference being less than one per cent except in one or two cases. For the low range 100 deg. to 500 deg. the discrepancy is greater, and Pye's values are probably the more accurate. On the other hand, at 3000 deg. the values deduced from the equations are probably nearer the truth than these given by Pye.

TABLE 14

MEAN SPECIFIC HEAT PER MOL BETWEEN 100 DEG. C. AND t DEG. C.

Gas	100 deg. C. up to					
	500 deg.	1000 deg.	1500 deg.	2000 deg.	2500 deg.	3000 deg.
Nitrogen............	5.17 (5.08)	5.28 (5.24)	5.50 (5.46)	5.75 (5.74)	6.00 (6.09)	6.30 (6.51)
Water Vapor.........	6.25 (6.53)	6.94 (6.96)	7.64 (7.61)	8.42 (8.50)	9.71 (9.61)	11.20 (10.96)
Carbon Dioxide......	8.25 (8.52)	9.55 (9.50)	10.07 (10.14)	10.50 (10.56)	10.87 (10.89)	10.95 (11.17)

The probable accuracy of the values of γ_p deduced from the explosion experiments is estimated by Pye.

For nitrogen the error may be within ± 1 per cent up to 2000 deg. C. and ± 2 per cent up to 3000 deg. C.

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* Glazebrook's Dictionary of Applied Physics, V. 1, p. 418.

For water vapor there may be an error of ± 5 per cent up to 3000 deg. C. Up to 2000 deg. C. it seems likely that the possible error is not more than ± 2 per cent or ± 3 per cent.

For carbon dioxide, Bjerrum's values up to 2700 deg. C. may be taken as correct to ± 3 per cent or ± 4 per cent.

The preceding equations, based largely on the experimental results given by Bjerrum and Pier, may be regarded as having the degree of accuracy indicated by the statement just quoted.

7. *Specific Heats of Various Hydrocarbons.*—The experimental evidence on the specific heats of the hydrocarbon fuel constituents, such as CH_4, C_2H_4, C_2H_2, etc., is not sufficient for the deduction of equations having any claim to extreme accuracy. However, the amount of one of these constituents in a mixture of fuel and air is usually small, so that a considerable error in the specific heat of a single constituent may not introduce a perceptible error in the specific heat of the whole mixture.

From such experimental data as are available the following conclusions may be drawn:

(a) The specific heat may be taken as a first-degree function of the temperature.

(b) The rate of change of specific heat with temperature for these hydrocarbon fuel constituents is very large compared with the rate for nitrogen, CO_2, and H_2O.

Methane (CH_4)

Heuse's experiments at low temperatures give the following values:

t deg. C.	-80	-55	-30	5	15
γ_p	8.08	8.08	8.14	8.42	8.50

The linear equation

$$\gamma_p = 6.03 + 0.005\,T \quad (T = \text{abs. temp. F.})$$

represents these values fairly well, and gives for the mean specific heat between 18 deg. and 208 deg. C. the value 0.504, which agrees with that determined by Regnault and Lussana.

The latest investigation, that of Dixon, Campbell, and Parker, furnishes the equation

$$\gamma_p = 3.459 + 0.01056\,T.$$

The two equations give about the same result at temperatures around -30 deg. F.; but at higher temperatures the latter equation gives larger values of γ_p because the rate of increase is more than double the rate given by the first equation.

The choice between the two equations is based on the equilibrium of the reaction $C + 2H_2 = CH_4$. It is found that the equilibrium equation obtained from the use of Dixon, Campbell, and Parker's specific heat equation represents the experimental data much better than the equilibrium equation deduced from the first equation for specific heat. Hence for methane the expressions for specific heat are

$$\gamma_v = 1.473 + 0.01056\ T$$
$$\gamma_p = 3.459 + 0.01056\ T$$

Ethylene (C₂H₄)

Regnault and Lussana give the value 11.32 as the mean specific heat γ_{p_m} between 10 deg. and 202 deg. C. Heuse has also determined instantaneous values of γ_p at low temperatures. The equation

$$\gamma_p = 6.67 + 0.0068\ T\quad (T = \text{abs. temp. F.})$$

gives 11.31 compared with 11.32 obtained by Regnault; and it represents quite accurately the experiments of Heuse, as shown by the following comparison:

t deg. C.	18	—36	—68	—91
γ_p (Heuse)	10.22	9.17	8.79	8.66
γ (equation)	10.22	9.57	9.18	8.41

Ethane (C₂H₆)

The experiments of Heuse at low temperatures are supplemented by the experiments of Dixon, Campbell, and Parker at higher temperatures. The equation

$$\gamma_p = 7.10 + 0.0086\ T\quad (T = \text{abs. temp. F.})$$

gives a fair compromise between the two sets of experiments.

	Heuse			Dixon, Campbell, and Parker		
t deg. C.	—82	—35	+15	10	50	100
γ_p (exper.)	10.44	11.04	12.40	11.21	11.81	12.86
γ_p (equation)	10.06	10.78	11.56	11.49	12.11	12.88

Acetylene (C₂H₂)

Two values of the instantaneous specific heat are given by Heuse, namely,

t deg. C.	—71	18
γ_p	9.13	10.43

A straight line through the two points giving these values has the equation

$$\gamma_p = 6.19 + 0.0081\, T \quad (T = \text{abs. temp. F.})$$

Benzene Vapor (C_6H_6)

For benzene vapor the equation

$$\gamma_p = 4.00 + 0.0318\, T \quad (T = \text{abs. temp. F.})$$

represents accurately the available experiments, as shown by the following comparison:

Investigator	Temp. Range deg. C.	Specific Heat	
		Observed	Calculated
Wiedemann	34–115	23.337 (mean)	23.34
Wiedemann	35–180	25.913 "	25.91
Regnault	116–218	29.270 "	29.27
Thiabaut	350	38.947 (inst.)	38.95

Gasoline and Kerosene Vapor

Wilson and Barnard give the equation

$$c_p = 0.5 + 0.0006\, t$$

for the instantaneous specific heat of gasoline and kerosene (liquid or vapor) at constant pressure. Units are calories per gram and degrees centigrade.

Wilson and Barnard represent gasoline by the formula C_8H_{18} and kerosene by $C_{12}H_{26}$. Using these formulas and transferring to degrees Fahrenheit absolute, the molecular specific heats are given by the equations

Gasoline,

$$\gamma_p = 38.327 + 0.038\, T$$
$$\gamma_v = 36.342 + 0.038\, T$$

Kerosene,

$$\gamma_p = 57.154 + 0.05\,667\, T$$
$$\gamma_v = 55.169 + 0.05\,667\, T$$

8. *Specific Heat of Amorphous Carbon.*—The reliable experimental data are as follows:

(a) Weber gives the following values for the mean specific heat of one gram of wood charcoal:

$$0° - 24° \text{ C.} \quad 0.1653$$
$$0° - 99° \text{ C.} \quad 0.1933$$
$$0° - 224° \text{ C.} \quad 0.2385$$

(b)   Kunz gives the following values for the mean specific heat of beechwood charcoal from 0 deg. to t deg. C.:

t deg. C.	Specific Heat
435	0.243
561	0.290
728	0.328
925	0.358
1059	0.362
1197	0.378
1297	0.381

(c)   Nernst has shown that the specific heat of carbon at absolute zero is zero.

From the preceding data an equation has been deduced by the method of least squares for the instantaneous molecular specific heat of amorphous carbon. With T in degrees centigrade absolute it is

$$\gamma = 8.16 \cdot 10^{-3}T - 2.946 \cdot 10^{-6}\, T^2$$
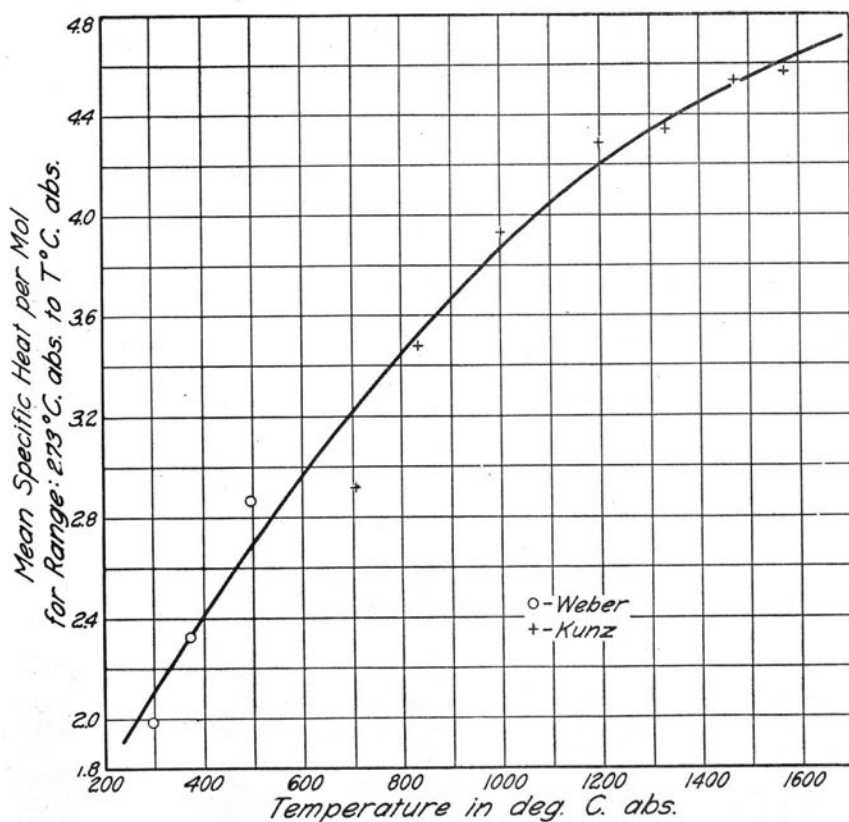
FIG. 21.   SPECIFIC HEAT OF AMORPHOUS CARBON

A comparison between the experimental values and the values calculated from the above equation is given in the following table. The data are shown graphically in Fig. 21.

SPECIFIC HEAT OF AMORPHOUS CARBON

No.	Temp. Range deg. C. (abs.)	Mean Molecular Specific Heat		Investigator
		Calculated	Observed	
1	273– 297	2.086	1.984	Weber
2	273– 372	2.322	2.322	Weber
3	273– 497	2.693	2.862	Weber
4	273– 708	3.247	2.916	Kunz
5	273– 834	3.520	3.480	Kunz
6	273–1001	3.872	3.936	Kunz
7	273–1198	4.198	4.296	Kunz
8	273–1332	4.376	4.344	Kunz
9	273–1470	4.522	4.536	Kunz
10	273–1570	4.605	4.572	Kunz

The equation satisfied Nernst's value at absolute zero. The agreement between the values given by the equation and the experimental values is satisfactory over the entire range of temperature.

The equation attains a maximum value at $T = 1384$ deg. C. (abs.) or 2492 deg. F. (abs.).

Changing to Fahrenheit absolute, the equation becomes for the instantaneous specific heat of amorphous carbon per mol,

$$\gamma = 4.533 \cdot 10^{-3} \, T - 0.9092 \cdot 10^{-6} \, T^2$$

Attention may be drawn to the fact that while the specific heat equations here developed are not entirely rational, they are serviceable and will give correct results as long as their use is limited to the range of temperatures defined by the experimental data. The uncertainty of extrapolated values is, of course, apparent.

The specific heat equations given in the foregoing discussion are collected in Table 15.

TABLE 15

SPECIFIC HEAT EQUATIONS

γ_p = Instantaneous Molecular Specific Heat at Constant Pressure
γ_v = Instantaneous Molecular Specific Heat at Constant Volume
T = degree F. (abs.) $\gamma_p = \gamma_v + 1.985$

No.	Gas	Specific Heat Equation
1	CO, O_2, N_2	$\gamma_p = 6.93 + 0.1200 \cdot 10^{-5}T^2$ $\gamma_v = 4.945 + 0.1200 \cdot 10^{-6}T^2$
2	H_2	$\gamma_p = 6.00 + 0.6667 \cdot 10^{-3}T$ $\gamma_v = 4.015 + 0.6667 \cdot 10^{-3}T$
3	CO_2 (T <2900)	$\gamma_p = 7.15 + 3.90 \cdot 10^{-3}T - 0.60 \cdot 10^{-6}T^2$ $\gamma_v = 5.165 + 3.90 \cdot 10^{-3}T - 0.60 \cdot 10^{-6}T^2$
4	CO_2 (T >2900)	$\gamma_p = 12.196 + 0.42 \cdot 10^{-3}T$ $\gamma_v = 10.211 + 0.42 \cdot 10^{-3}T$
5	CO_2 (Entire Range)	$\gamma_p = 6.4587 + 5.0668 \cdot 10^{-3}T - 1.2480 \cdot 10^{-6}T^2 + 0.1086 \cdot 10^{-9}T^3$ $\gamma_v = 4.5637 + 5.0668 \cdot 10^{-3}T - 1.2480 \cdot 10^{-6}T^2 + 0.1086 \cdot 10^{-9}T^3$
6	H_2O	$\gamma_p = 8.33 - 0.276 \cdot 10^{-3}T + 0.423 \cdot 10^{-6}T^2$ $\gamma_v = 6.345 - 0.276 \cdot 10^{-3}T + 0.423 \cdot 10^{-6}T^2$
7	CH_4	$\gamma_p = 3.459 + 10.56 \cdot 10^{-3}T$ $\gamma_v = 1.474 + 10.56 \cdot 10^{-3}T$
8	C_2H_2	$\gamma_p = 6.19 + 8.10 \cdot 10^{-3}T$ $\gamma_v = 4.205 + 8.10 \cdot 10^{-3}T$
9	C_2H_4	$\gamma_p = 6.67 + 6.80 \cdot 10^{-3}T$ $\gamma_v = 4.685 + 6.80 \cdot 10^{-3}T$
10	C_2H_6	$\gamma_p = 7.10 + 8.60 \cdot 10^{-3}T$ $\gamma_v = 5.115 + 8.60 \cdot 10^{-3}T$
11	C_6H_6	$\gamma_p = 4.00 + 31.80 \cdot 10^{-3}T$ $\gamma_v = 2.015 + 31.80 \cdot 10^{-3}T$
12	C_8H_{18} (Gasoline)	$\gamma_p = 38.327 + 38.00 \cdot 10^{-3}T$ $\gamma_v = 36.342 + 38.00 \cdot 10^{-3}T$
13	$C_{12}H_{26}$ (Kerosene)	$\gamma_p = 57.154 + 56.67 \cdot 10^{-3}T$ $\gamma_v = 55.169 + 56.67 \cdot 10^{-3}T$
14	Amorphous Carbon	$\gamma = +4.533 \cdot 10^{-3}T - 0.9092 \cdot 10^{-6}T^2$

NOTE—See "References on Specific Heat," page 155.

APPENDIX II

HEATS OF COMBUSTION

1. *Hydrogen* (H_2).—Leaving out of consideration investigations previous to 1849, the following is a brief outline of the methods used by the various investigators since that date for the determination of the heat of combustion of hydrogen:

Andrews, in 1848, first used the bomb calorimeter. Hydrogen and oxygen collected over water were introduced into the bomb in the theoretical proportions for combustion. The gas mixture, under a total pressure of one atmosphere, was ignited by an electric spark, the heat generated being absorbed by water surrounding the bomb. Andrews found as the average of four experiments the higher heat of combustion of one standard liter (0 deg. C., 760 mm.) of dry hydrogen at 20 deg. C. and constant volume to be 3036 calories (20-degree calorie).

Favre and Silbermann in 1852 burned hydrogen with oxygen in a closed vessel at a constant pressure of 16 centimeters of water above atmospheric. This burning was accomplished by leading two metal tubes, one for hydrogen and one for oxygen, into a small metal chamber. By regulating the flow of the gases a steady flame was maintained. The heat of combustion was absorbed by water which completely surrounded the combustion chamber. Since the flame was completely enclosed, the water formed by the combustion could not escape and so was condensed. At the beginning and end of each experiment the combustion chamber was weighed, the increase in weight being that due to the water formed. Correction was made for the non-condensed water vapor within the combustion chamber by weighing the chamber filled with wet and then with dry gases, the difference being the weight of non-condensed vapor. This weight of vapor was multiplied by the latent heat of steam at 18 deg. C. and the result was added to the experimental result. As the average of six experiments the higher heat of combustion of 1 mol of hydrogen at 18 deg. C. and constant pressure was found to be 68 924 calories (20-degree calorie).

J. Thomson in 1873, using the same method as Favre and Silbermann with minor changes in the apparatus, found the higher heat of combustion of one mol of hydrogen at 18 deg. C. and at constant pressure to be 68 357 calories (20-degree calorie). This is the average of three experiments.

In 1877 Schüller and Wartha used a Bunsen ice calorimeter wherein the heat of combustion was determined by measuring the amount of ice melted at 0 deg. C. The amount of ice melted was measured by the contraction in volume of a mixture of ice and water. The product of the volume of ice melted, the specific weight, and the latent heat of fusion of ice gave the heat absorbed by the ice. The closed end of a test tube was projected into the mixture of ice and water. Inside of the test tube was placed a previously weighed glass combustion pipette. This combustion pipette consisted simply of a small glass bulb into which were led two glass tubes, one for hydrogen and one for oxygen.

Burning occurred at constant pressure inside this bulb. Since there was no outlet the water formed condensed and remained in the bulb. At the end of an experiment the glass pipette was again weighed, the increase in weight being that due to the water formed. The experiments lasted 3 to 4 hours so that the small amount of vapor left uncondensed in the pipette introduced a negligible error. As an average of five experiments the higher heat of combustion of 1 mol of hydrogen at 0 deg. C. and at constant pressure was found to be 68 250 calories (mean calorie 0 deg. to 100 deg. C.).

In 1881 Than used the Bunsen ice calorimeter with a constant volume combustion pipette. In order to get an appreciable volume of gases in the pipette the calorimeter was quite large. Hydrogen and oxygen were introduced into the pipette under a total pressure of one atmosphere (barometer 760 mm.) and the mixture was exploded by an electric spark. The gases before combustion were saturated with water vapor so that all water vapor formed was condensed. The average result obtained from five experiments for the higher heat of combustion of 1 mol of hydrogen burned at 0 deg. C. and at constant volume was 67 644 calories (15-degree calorie).

Berthelot in 1883 revived Andrew's bomb calorimeter and much improved it. The bomb was first filled with dry hydrogen under a pressure of one atmosphere. Wet oxygen was next introduced into the bomb from a cylinder of compressed oxygen until the total gas pressure in the bomb was about 1.7 atmospheres. The excess of oxygen was used because the compressed oxygen contained a small percentage of nitrogen. The mixture was exploded by an electric spark. Since all the water vapor formed was condensed no correction was needed. Berthelot gives as the higher heat of combustion of 1 mol of hydrogen at constant volume and at 10 deg. C., 68 000 calories (10-degree calorie).

In 1903 Mixter, at Yale University, made further improvements on the bomb calorimeter. Dry hydrogen was first introduced into the bomb at atmospheric pressure (barometer 14.743 lb. per sq. in.). The

weight of hydrogen present was calculated from its known pressure, temperature, and volume. Dry oxygen was next introduced into the bomb until the total pressure was in excess of 1.5 atmospheres. The average of 14 experiments by Mixter gives for the higher heat of combustion of 1 mol of hydrogen at 18 deg. C. and at constant volume, omitting the correction for non-condensed water vapor, which will be considered later, 66 835 calories (20-degree calorie).

The latest work done on the heat of combustion of hydrogen is that of G. Rumelin in 1907. He used a bomb calorimeter of more elaborate design than those previously used. Dry hydrogen and oxygen in the theoretical proportions for combustion were introduced into the bomb under a total pressure of one atmosphere (barometer 14.32. lb. per sq. in.). As an average of six experiments, omitting the correction for non-condensed vapor left in the bomb, the observed result for the higher heat of combustion of 1 mol of hydrogen at 18 deg. C. and at constant volume was 66 940 calories (20-degree calorie).

Certain corrections must be applied to the experimental results before a proper comparison of the values can be made. In the first place, a common heat unit must be taken. For this, the mean B. t. u. is chosen. The experimental values are thus multiplied by 1.8 and by one of the following correction factors, which have been deduced from Callendar's equation for the specific heat of water. Secondly,

Temperature		Correction Factor	Logarithm of Correction Factor
Deg. C.	Deg. F.		
10	50	1.00 150	0̱.0 006 499
15	59	0.99 962	1̄.9 998 352
20	68	0.99 842	1̄.9 993 100

the experimental values must be corrected by the subtraction of the heat obtained by the condensation of the water. The so-called higher heats of combustion, which include the heat of condensation, are dependent on so many accidental circumstances that a comparison of them is not possible. For a fixed temperature, on the other hand, the lower heat of combustion is an invariant; hence comparison of such values are valid.

The following notation is used:

H'_p = higher heat of combustion at constant pressure.
H_p = lower heat of combustion at constant pressure.

H'_v = higher heat of combustion at constant volume.

H_v = lower heat of combustion at constant volume.

The difference $H'_p - H_p$ is the heat given up by the condensation of the water when the experiment is conducted at constant pressure.

The method of calculation employed in reducing from the high to the low heat of combustion may best be illustrated by two examples, one for combustion at constant volume, the other for combustion at constant pressure.

(a)   Rumelin's Experiment

Take dry hydrogen and oxygen under a pressure of 14.32 lb. per sq. in. and at a temperature of 64 deg. F.   Consider the reaction equation

$$H_2 + \tfrac{1}{2}O_2 = H_2O$$

The volume occupied by 1 mol or 18 lb. of H_2O vapor after combustion is the same as that occupied by $1\tfrac{1}{2}$ mols of mixture before combustion. At 62 deg. F. and a pressure of 14.7 lb. the volume of 1 mol is 380.6 cu. ft.   Hence the volume of $1\tfrac{1}{2}$ mols at 64 deg. and a pressure of 14.32 lb. is

$$380.6 \times 1.5 \times \frac{524}{522} \times \frac{14.7}{14.32} = 588.3 \text{ cu. ft.}$$

This is the volume of 18 lb. of water vapor; hence the volume per pound is $588.3 \div 18 = 32.68$ cu. ft.   Reference to the steam table shows that at a temperature of 202 deg. F. one pound of saturated steam has nearly this volume; hence in cooling the products of combustion the water vapor will start to condense at about 202 deg. and will continue condensing until the final temperature 64 deg. is reached. At 64 deg. the volume of 1 lb. of saturated steam is 1055 cu. ft.; hence the quality of the steam in the final state is $32.68 \div 1055 = 0.031$.   Since the water vapor remains at constant volume in condensing, the heat given up is equal to the decrease in energy.   The energy of 1 lb. of saturated steam at 202 deg. F. is 1075.9 B. t. u.; that of the mixture at 64 deg. F. having a quality 0.031 is $32.1 + 0.031 \times 998.4 = 63$ B. t. u.   The heat given up per pound is $1075.9 - 63 = 1012.9$ B. t. u. and per mol, $1012.9 \times 18 = 18\,232$ B. t. u.   If the water vapor had remained in the gaseous state during the cooling from 202 deg. F. to 64 deg. F. the decrease of energy would have been

$$\int_{524}^{662} \gamma_v dT$$

in which

$$\gamma_v = 6.345 - 0.276 \cdot 10^{-3}\,T + 0.423 \cdot 10^{-6}T^2$$

the specific heat per mol at constant volume.   The result is 874 B. t. u.   The difference $18\,232 - 874 = 17\,358$ B. t. u. is the amount

by which the higher heat of combustion exceeds the lower, and is therefore the amount to be subtracted from H'_v to get H_v. The observed H'_v reduced to mean B. t. u. per mol is

$H'_v = 66\ 940 \times 1.8 \times 0.99\ 842 = 120\ 300$ B. t. u. per mol.

Hence

$H_v = 120\ 300 - 17\ 358 = 102\ 942$ B. t. u.

and

$H_p = H_v + T = 102\ 942 + 524 = 103\ 466$ B. t. u. per mol.

(b) Thomsen's Experiments

The temperature of the combustion was 64 deg. F. and the pressure 14.7 lb. per sq. in. Since H_2O was the sole product of combustion, the water vapor at a pressure of 14.7 lb. began condensation at 212 deg. F., and at the final temperature, 64 deg. F., was entirely condensed, the volume of water vapor remaining in the small combustion pipette at the end of an experiment being negligible. The heat given up during condensation per pound of water was $i_1 - i_2$. For saturated steam at 212 deg. F. $i_1 = 1151.7$; for water at 64 deg. F. $i_2 = 32.1$: hence per mol the heat due to condensation was 18 (1151.7 $- 32.1) = 20\ 153$ B. t. u.

The heat that would have been given up in cooling at constant pressure from 212 deg. F. to 64 deg. F., if the water vapor had remained in the gaseous state, is

$$\int_{524}^{672} \gamma_p dT$$

which, when the proper value of γ_p is inserted, gives the result 1233 B. t. u. The difference $H'_p - H_p$ is therefore 20 153 $-$ 1233 $=$ 18 920 B. t. u. The observed value of H'_p properly reduced is

$H'_p = 68\ 357 \times 1.8 \times 0.99\ 842 = 122\ 849$ B. t. u. per mol.

Hence

$H_p = 122\ 849 - 18\ 920 = 103\ 929$ B. t. u. per mol.

The results obtained by the various investigators when reduced to the common basis of lower heat of combustion at constant pressure in mean B. t. u. per mol are as follows:

Year	Investigator	H_p
1848	Andrews	104 660
1852	Favre and Silbermann	104 950
1873	Thomsen	103 830
1877	Schüller and Wartha	103 690
1881	Than	103 980
1883	Berthelot	105 060
1903	Mixter	103 110
1907	Rumelin	103 470

It is obvious that in establishing the probable value of H_p different weights should be assigned to the various experiments. Any system of weighting is a matter of individual judgment and therefore subject to criticism. The earlier experiments of Andrews and of Favre and Silbermann gave values that are obviously too large in the light of the later and more accurate experiments. These values, and also the still higher value of Berthelot, are therefore rejected. Thomsen's value is given a weight of 2 because of the general high accuracy of his experiments, and because his result is the average of seven determinations in which a total of 18 grams of water was formed, a much larger quantity than in the experiments of any of the other investigators. Because of the comparatively recent date, the values of Mixter and Rumelin are given the weight 3. Mixter's value is the mean of fourteen experiments all of which are within 1.3 per cent of the average, and Rumelin's value is the mean of seven experiments all of which are within 0.7 per cent of the average. With this system of weighting, the probable value of H_p is found to be 103 530 B. t. u. per mol at 62 deg. F.

The heat of combustion H_v at constant volume is less than H_p by the product $\frac{1}{2}RT = 0.993 \times 522$. Hence

$$H_v \text{ at 62 deg. F.} = 103\ 010\ \text{B. t. u. per mol.}$$

The constant H_0, which is required in the equilibrium equations, is readily derived from the value of H_p or the value of H_v. Thus

$$H_0 = H_v + u_{H_2O} - u_{H_2} - \tfrac{1}{2} u_{O_2}$$

For the standard temperature 62 deg. F. ($T = 522$) the values of u per mol are as follows:

$$u_{H_2O} = 3295,\ u_{H_2} = 2187,\ u_{O_2} = 2587$$

Hence

$$H_0 = 103\ 010 + 3295 - 2187 - 1294 = 102\ 824,$$

or with sufficient accuracy

$$H_0 = 102\ 820\ \text{B. t. u. per mol}$$

2. *Carbon Monoxide* (CO).—The experimental results available for the heat of combustion of carbon monoxide are given in the following table:

Year	Investigator	Temp. deg. C.	Value
1848	Andrews	15	3057.0 cal/liter at const. vol.
1852	Favre and Silbermann	18	2402.7 cal/gram at const. press.
1873	Thomsen	18	67 960 cal/mol at const. press.
1881	Berthelot	10	68 200 cal/mol at const. press.

Andrews and Berthelot used the bomb calorimeter. Favre and Silbermann and Thomsen used the same apparatus as they did for hydrogen, except that the products of combustion were led out of the combustion chamber through a coil of small pipe of considerable length which was immersed in the water of the calorimeter, thus insuring that the products of combustion were brought back to the initial temperature.

Transferring the data given in the preceding table into mean B. t. u. per mol at constant pressure, using Callendar's specific heat ratios, and neglecting the correction to 62 deg. F. the following values for H_p at 62 deg. F. are obtained:

$$H_p$$

Andrews 123 800
Favre and Silbermann 120 900
Thomsen 122 130
Berthelot 122 920

Andrews' value cannot be considered because of the imperfection of his method. He took only one reading of the water temperature in his calorimeter after combustion, and that one just thirty seconds after combustion occurred. The apparatus had to be rotated in order to keep the water at a uniform temperature. To accomplish this rotation it was necessary to remove the thermometer and then, to get the temperature of the water, the rotation was stopped and the thermometer reinserted. Evidently such manipulation was subject to errors.

The carbon monoxide used by Favre and Silbermann in their experiments contained about 3 per cent hydrogen by weight. The correction for the heat of combustion of this hydrogen content amounted to about 30 per cent of the heat resulting from the combustion as observed in any one determination. The possibility of error in this correction is very great because of the methods of gas analysis in use at that time, and also because all the errors of their determination of the heat of combustion of hydrogen were automatically introduced.

Of the two remaining values, that of Thomsen's is chosen rather than Berthelot's for the following reasons: First, for any given determination the volume of gas used by Thomsen was about six times that used by Berthelot, this tending to reduce Thomsen's error; second, Berthelot's result is the average of five experiments where a total of about 1.3 liters of carbon monoxide were burned, while Thomsen's result is the average of ten closely accordant experiments wherein a total of about 16 liters of carbon monoxide were burned. The first six of the experiments were performed in one calorimeter while the last four were performed in another calorimeter. The average result of the first group of experiments is exactly equal to the average of the last group.

The heat of combustion of 1 mol of carbon monoxide at constant pressure at 62 deg. F. in terms of the mean B. t. u. is therefore taken as

$$H_p = 122\ 130$$

3. *Methane* (CH_4).—The experimental results available for the heat of combustion of methane are:

Year	Investigator	Temp. deg. C.	Higher Heat of Combustion cal. per mol
1848	Andrews	15	209 728 constant vol.
1852	Favre and Silbermann	18	209 000 constant press.
1880	Thomsen	20	213 630 constant press.
1881	Berthelot	18	212 400 constant vol.

The methane used by Andrews was obtained from a stagnant pool, and contained a large percentage of nitrogen. The Andrews value is therefore doubtful. It is also very probable that the Favre and Silbermann value is low because of impurities in the gas used by them.

Thomsen generated his methane from zinc methyl and hydrochloric acid, and purified it by bubbling through cuprous chloride solution. The tabular result is from Thomsen's latest work on methane, and is the average of nine experiments which show a maximum variation of 1.1 per cent. The calorimeter used was of the constant pressure type, the products of combustion being led out through a long tube winding around the combustion chamber, as described before. Correction was made for the non-condensed vapor in the products of combustion, this correction being very small.

Berthelot's value is the average of four determinations made with his bomb calorimeter. These four experiments show a variation of 1.6 per cent.

The results of Thomsen and Berthelot when reduced to the common basis of lower heat of combustion at constant pressure are as follows:

$$H_p$$

Thomsen 345 820
Berthelot 346 030

The mean, $H_p = 345\ 920$ B. t. u. per mol at 62 deg. F. is taken as the probable value. The value of H_v is the same.

4. *Acetylene* (C_2H_2).—The following are the available experimental values of the heat of combustion of acetylene:

Year	Investigator	Temp. deg. C.	Higher Heat of Combustion cal. per mol
1880	Thomsen	19	310 050 const. press.
1881	Berthelot	18	314 900 const. vol.
1906	Mixter	20	311 400 const. vol.

When reduced to the lower heat of combustion at constant pressure in mean B. t. u., these values become:

$$H_p$$

Thomsen 538 240
Berthelot 548 500
Mixter 542 680

If Thomsen's value is given the weight 2, Berthelot's 1, and Mixter's 3, the resulting value is

$$H_p = 542\ 170 \text{ B. t. u. per mol at 62 deg. F.}$$

For constant volume,

$$H_v = 541\ 650 \text{ B. t. u. per mol.}$$

5. *Ethylene* (C_2H_4).—Three sets of experiments give the following numbers for the higher heat of combustion:

Year	Investigator	Temp. deg. C.	Higher Heat of Combustion cal. per mol
1880	Thomsen	17.9	333 350 const. press.
1881	Berthelot-Matignon	16.8	340 000 const. vol.
1901	Mixter	18.8	345 080 const. vol.

The reduction to the lower H_p in mean B. t. u. gives the following values:

$$H_p$$

Thomsen 561 150
Berthelot 576 080
Mixter 584 590

Again assigning the weight of 1 to Berthelot, 2 to Thomsen, and 3 to Mixter, the resulting value of the heat of combustion of ethylene at constant pressure in mean B. t. u. per mol is

$$H_p = 575\ 370.$$

6. *Ethane* (C_2H_6).—The data are furnished by the experiments of Berthelot and Thomsen.

Year	Investigator	Temp. deg. C.	Higher Heat of Combustion cal. per mol
1893	Berthelot	13	370 900 const. vol.
1905	Thomsen	18	370 440 const. press.

The reduced values are:

$$H_p$$

Berthelot 614 305
Thomsen 608 360

and the mean, giving Thomsen's result double the weight of Berthelot's, is

$$H_p = 610\,340 \text{ B. t. u. per mol.}$$

7. *Benzene Vapor* (C_6H_6).—For the heat of combustion of benzene vapor the experimental value of Stohman, Rodatz, and Herzberger, which is 10 096 cal. per gram at 17 deg. C., is chosen as the best available. It is the average of twelve experiments. In the method used, a current of air was passed over a wad of cotton saturated with benzene liquid and the resulting mixture of vapor and air was burned in a constant pressure calorimeter. The products of combustion were led through a long spiral tube and then through absorbers to remove the moisture in the usual way.

If the oxygen and benzene in the benzene-air mixture were present in the theoretical proportions for combustion, the reaction equation would be $C_6H_6 + 7.5O_2 + 28.5N_2 = 6CO_2 + 3H_2O + 28.5N_2$. The partial pressure of the benzene vapor in the original mixture is $1/37 \times 14.7 = 0.40$ lb. per sq. in. According to Young, the saturation pressure of benzene vapor at 17 deg. C is 65 mm. of mercury or 1.25 lb. per sq. in. Since the assumed partial pressure of the benzene vapor in the initial mixture is only about one-third of the saturation pressure of benzene at 17 deg. C., the assumed partial pressure can be easily attained and is reasonable.

The partial pressure of the water vapor in the products of combustion, if not condensed, is

$$\frac{3}{37.5} \times 14.7 = 1.176 \text{ lb. per sq. in.}$$

The saturation temperature at this pressure is 107 deg. F.; and the condensation of water vapor between 107 deg. and 62 deg. gives a difference of 57 070 B. t. u. per mol between the observed higher heat of combustion and the lower heat of combustion. The observed higher value in mean B. t. u. per mol is

$$H'_p = 78.05 \times 10\,096 \times 1.8 \times 0.99\,842 = 1\,416\,460$$

Hence

$$H_p = 1\,359\,400 \text{ B. t. u. per mol.}$$

Since in the combustion the molecular volume increases by $\frac{1}{2}$ mol, the heat of combustion at constant volume exceeds H_p by $\frac{1}{2}RT = T$ approx.; hence

$$H_v = 1\,359\,920 \text{ B. t. u. per mol.}$$

8. *Gasoline.*—The values for the higher heat of combustion of liquid gasoline obtained from various handbooks range from 19 000

to 21 000 B. t. u. per pound. An average value of 20 000 B. t. u. per pound is taken. This when reduced to the lower value gives

$$H_p = 18\ 675 \text{ B. t. u. per lb. of liquid gasoline, taken as at}$$
$$520 \text{ deg. F. (abs.)}.$$

Wilson and Barnard give the heat of vaporization of gasoline as 70 gram calories per gram, and the molecular formula as C_8H_{18}. Adding in the heat of vaporization, the molecular heat of combustion is

$$H_p = 2\ 143\ 200 \text{ B. t. u. per mol of vapor taken as at 60 deg. F.}$$

from which

$$H_v = 2\ 146\ 840 \text{ B. t. u. per mol.}$$

9. *Kerosene.*—Here also an average value is obtained from those quoted by the handbooks and is 21 500 B. t. u. per pound for the higher heat of combustion. The lower heat of combustion is then

$$H_p = 20\ 220 \text{ B. t. u. per lb. of liquid kerosene.}$$

For kerosene, Wilson and Barnard give the value of 60 gram calories per gram for the heat of vaporization and the molecular formula $C_{12}H_{26}$. The molecular heat of combustion is

$$H_p = 3\ 456\ 100 \text{ B. t. u. per mol of vapor, taken as at 60 deg. F.};$$

also

$$H_v = 3\ 461\ 800 \text{ B. t. u. per mol.}$$

10. *Amorphous Carbon.*—The available experimental data on the heat of combustion of amorphous carbon are contained in the following:

Year	Investigator	Heat of Combustion cal. per gram
1848	Andrews	7678
1852	Favre and Silbermann	8080
1883	Gottlieb	8033
1889	Berthelot	8137

Andrews states in his discussion of the value given above, which is the average of eight determinations with highly purified wood charcoal in the bomb calorimeter, that in spite of the presence of excess oxygen, carbon monoxide was found in the products of combustion. This fact, of course, renders his value too low.

Favre and Silbermann also found carbon monoxide in the products of combustion. After determining the amount of carbon monoxide present in any one experiment, they added to the observed result the heat of combustion of this given amount of carbon monoxide so that their final results give the heat of combustion of carbon to carbon dioxide. This correction amounted to only about 3 per cent, so that errors introduced by using an incorrect value for the heat of combustion of carbon monoxide were insignificant. Eighteen experiments in three series were run, using highly purified wood charcoal. The values of the first series consisting of five experiments showed a maximum variation of 89 calories in the values given for the heat of combustion per gram. The average value from the first series is 8086 calories per gram. The next seven experiments, constituting the second series, showed a maximum variation of 31 calories. The average of the second series is 8081 calories per gram. In the last six experiments wood charcoal purified in different ways was used in different determinations to note if the method of purification had any effect on the results. In this last series the maximum variation between any two results was 19 calories, and the average of these six was 8080 calories per gram. This is the result quoted in the preceding table.

Gottlieb used a calorimeter very similar to the one used by Favre and Silbermann. The carbon used by Gottlieb was prepared by heating a five-gram ball of cotton in a loosely covered dish, slowly at first and then more intensely after all the combustible gases had been driven off. Later the cotton charcoal was transferred to a tightly covered platinum dish and heated to about 950 deg. C. for some hours and then cooled in a dessicator. This carbon absorbed moisture freely. Upon analysis the sample showed 1.5 per cent moisture. With a slight amount of moisture present in the sample as weighed, of course, the final result calculated on the basis of this weight will be slightly low. Therefore, Gottlieb's result, which is the average of six experiments, having a maximum variation of 7 calories per gram, points to the accuracy of the Favre and Silbermann values.

Berthelot's value was obtained by burning wood charcoal, very carefully purified and dried. Oxygen under 25 atmospheres pressure was used in the bomb calorimeter to insure complete combustion. The value given above is the average of six experiments, which show a maximum variation of 10 calories per gram.

Of the values quoted, the Favre and Silbermann value is chosen in preference to that of Berthelot.

Reducing the Favre and Silbermann value, which is in terms of the 20-degree calorie, to mean B. t. u. per mol, the heat of combustion of amorphous carbon at 62 deg. F. is

$$H = 174\ 250 \text{ B. t. u. per mol.}$$

<div align="center">TABLE 16</div>

<div align="center">HEATS OF COMBUSTION (LOW) IN MEAN B. T. U.</div>

Reaction	At Const. Pressure and 62 deg. F.			At Const. Volume and 62 deg. F.			At abs. zero H_0*
	per mol	per lb.	per. cu. ft.	per mol	per lb.	per cu. ft.	
$H_2 + \frac{1}{2}O_2 = H_2O$	103 530	51 354	272	103 010	51 096	271	102 820
$CO + \frac{1}{2}O_2 = CO_2$	122 130	4 362	321	121 610	4 343	320	120 930
$H_2 + CO_2 = H_2O + CO$	—18 600			—18 600			—18 110
C (amorph.) $+ CO_2 = 2CO$	—70 010			—68 970			—67 570
C (amorph.) $+ O_2 = CO_2$	174 250	14 521		174 250	14 521		174 290
C (amorph.) $+ 2H_2 = CH_4$	35 390			34 350			31 600
$CH_4 + 2O_2 = CO_2 + 2H_2O$	345 920	21 577	909	345 920	21 577	909	348 330
$C_2H_2 + 2\frac{1}{2}O_2 = 2CO_2 + H_2O$	542 170	20 840	1425	541 650	20 820	1423	541 580
$C_2H_4 + 3O_2 = 2CO_2 + 2H_2O$	575 370	20 525	1512	575 370	20 525	1512	577 220
$C_2H_6 + 3\frac{1}{2}O_2 = 2CO_2 + 3H_2O$	610 340	20 312	1604	610 850	20 329	1605	614 240
$C_6H_6 + 7\frac{1}{2}O_2 = 6CO_2 + 3H_2O$	1 359 400	17 418	3572	1 359 920	17 424	3573	1 364 200
C_8H_{18} (Gasoline Vapor) $+ 12\frac{1}{2}O_2 = 8CO_2 + 9H_2O$	2 143 200	18 800	5631	2 146 840	18 830	5641	2 145 610
$C_{12}H_{26}$ (Kerosene Vapor) $+ 18\frac{1}{2}O_2 = 12CO_2 + 13H_2O$	3 456 100	20 330	9081	3 461 800	20 360	9096	3 458 680

*In determining these values, the specific heat equation for CO_2 for the range 0–2900 deg. F. (abs.) has been used.

NOTE.—See "References on Heats of Combustion," page 156.

APPENDIX III

Chemical Equilibrium

1. *Statement of the Problem.*—As shown in Chapter III, Section 17, the general form of the expression that gives the equilibrium constant K_p as a function of the temperature T is

$$R\log_e K_p = \frac{H_0}{T} - \sigma'\log_e T - \tfrac{1}{2}\sigma''T - \tfrac{1}{6}\sigma'''T^2 + C$$

In this equation, the coefficients σ', σ'', σ''' are known from the specific heats of the constituents involved, and H_0, a heat of combustion, is also known. Hence, save for the constant C, the second member may be calculated for any temperature T. In the first member the constant K_p is a function of the partial pressures when the system is in equilibrium, which means that K_p is determined by the composition of the mixture in the equilibrium state. The first member is therefore determined by experiments on the chemical composition at various temperatures, the second member, except for the constant C, is determined from known thermal data, and by subtraction the constant C is thus found.

In this appendix the experimental evidence relating to the equilibrium of various reactions is reviewed, the constants are determined, and the agreement between the experiments and the theory is shown.

2. *Experimental Methods.*—A brief outline of the methods used in determining the equilibrium composition resulting from gaseous reactions at high temperature is desirable. For detailed descriptions and discussions of such experimental methods, see Haber's "Thermodynamics of Technical Gas Reactions" and Nernst's "Theoretical Chemistry."

I. Streaming Method

The gases involved in the reaction are passed through a tube, a section of which is heated to the desired temperature and the following section kept at a low temperature. The gases are assumed to attain equilibrium in the hot portion of the tube and to be cooled so rapidly in the cold portion of the tube that the reaction immediately stops. The equilibrium composition of the gas at the high temperature thus exists in the cooled gas, which can be easily analysed.

II. Semi-Permeable Membrane Method

A vessel which is permeable to one constituent only of the reaction is evacuated, and the reacting mixture of gases at the desired temperature is caused to circulate around the outside of the vessel. The partial pressure of the one constituent to which the vessel is permeable will soon exist inside the vessel and can be measured with a manometer. This method is applicable only to a study of the dissociation of H_2O since semi-permeable substances (palladium, platinum, and iridium) are known for hydrogen only.

III. Maximum Explosion Pressure Method

The original mixture of gases is exploded in a closed vessel and the maximum pressure of explosion measured. Since the maximum pressure is dependent on the heat of reaction, and the heat of reaction on the equilibrium composition, the equilibrium composition may be calculated from the maximum pressure. Also in those reactions which involve a change in the number of mols, the maximum pressure is directly influenced by the equilibrium composition.

IV. Method of the Heated Catalyst

(a) If a catalyst such as a platinum wire is heated electrically in an atmosphere of gas the equilibrium composition of the gas, at the temperature of the wire, will exist in the gas immediately surrounding the wire. Due to the circulation of the gas set up by the heated wire the gas in contact with the wire will be swept into the cooler regions and the reaction will thereby be "frozen." The process is allowed to continue until the composition of the whole gas volume becomes constant. This condition is determined by analysing samples of gas from time to time. Temperatures are determined by the change in the electrical resistance of the wire.

(b) A variation of this method is to heat a vessel containing the catalyst to the desired temperature and then to lead the gases through the vessel or enclose them in the vessel until equilibrium is established. Samples are drawn out from time to time and analysed.

V. Iridium Dust Method

Iridium dust is produced by heating strips of iridium electrically in various gases. The quantity of dust produced is dependent on the nature of the gas and the temperature to which the iridium is heated. This method is especially applicable to the measurement of the dissociation of carbon dioxide. Nitrogen and pure carbon monoxide produce no appreciable amount of dust while oxygen produces large quantities of dust. The amount of dust produced by carbon dioxide

at a given temperature of the iridium and at atmospheric pressure is assumed to be due to the oxygen liberated by the dissociation of the carbon dioxide. A mixture of nitrogen and oxygen is found which will produce the same amount of dust as the carbon dioxide under the same conditions. Assuming that the oxygen content of the two gases is the same, the equilibrium composition of the carbon dioxide reaction is then known.

VI. Measurement of Equilibrium in the Bunsen Flame

The inner and outer cones of the Bunsen flame are separated by fitting a glass tube as an extension on the end of the burner, the glass tube being of somewhat larger diameter than that of the burner. A stopper is made to fit tightly in the annular space between the burner and the glass tube. The inner cone then burns on the end of the regular Bunsen burner tube which is now inside the glass tube while the outer cone burns on the end of the glass tube. Samples of gas are withdrawn from the space between the two cones and are assumed to be in equilibrium. Temperatures are measured with thermocouples.

VII. Direct Determination of Equilibrium

(a)   When one of the constituents in the reaction is a solid, such as carbon, it can be placed in a porcelain tube and the whole heated in an electric furnace. The gas constituents are then passed through the porcelain tube at a rate sufficiently slow to give time for equilibrium to be established. The products are then analysed.

(b)   Carbon in the form of rods is heated by an electric current in an atmosphere of the gas. Reaction occurs at the surface of the rod and is "frozen" when the reacting gases diffuse into the colder regions.

In either (a) or (b) a catalytic agent, such as platinum, nickel, or cobalt, may or may not be used.

(c)   A study of the water-gas equilibrium is made by passing water vapor over glowing coals and analysing the resulting gases.

VIII. Equilibrium from Density Measurement

The dissociation of carbon dioxide can be measured by electrically heating a platinum bulb filled with carbon dioxide to a desired temperature and then dropping into the bulb a small piece of aluminum. Changes of volume are measured by the movement of a short thread of mercury in a horizontal capillary outlet tube fitted to the platinum bulb. The following reaction occurs:

$$2Al + 3CO_2 = Al_2O_3 + 3CO$$

According to this reaction no change in volume will occur if the carbon dioxide is undissociated, and if the assumption is made that equal weights of carbon monoxide and carbon dioxide have the same volumes under similar conditions of pressure and temperature. If the carbon dioxide is dissociated, a change in the number of mols will occur with the above reaction which is proportional to the amount of dissociation and can be measured by the change of volume.

3. *The Reaction* $CO + \frac{1}{2}O_2 = CO_2$.—For the combustion of CO with theoretical oxygen, or for the dissociation of CO_2 into CO and oxygen, the expression for K_p is

$$K_p = \frac{p_{CO_2}}{p_{CO} \cdot p_{O_2}^{\frac{1}{2}}} = \frac{x_0}{1-x_0} \sqrt{\frac{3-x_0}{1-x_0}} \frac{1}{\sqrt{P}}$$

When the total pressure is one atmosphere,

$$K_p = \frac{x_0}{1-x_0} \sqrt{\frac{3-x_0}{1-x_0}}$$

In the dissociation of CO_2, $100(1-x_0)$ is the percentage dissociated.

Table 17 gives the experimental data on the dissociation of CO_2 at atmospheric pressure.

In the case of CO_2 two expressions for γ_p are given; the first for temperature below 2900 deg. F. (abs.) and the second for temperatures above 2900 deg. F. (abs.). For the lower range the corresponding equilibrium equation is

$$4.571 \ \log_{10}K_p = \frac{120\,930}{T} - 7.4719 \ \log_{10}T + 1.95 \cdot 10^{-3}T$$
$$- 0.13 \cdot 10^{-6}T^2 + C$$

Making suitable adjustment, the equilibrium equation for temperatures above 2900 deg. is

$$4.571 \ \log_{10}K_p = \frac{125\,810}{T} + 4.147 \ \log_{10}T + 0.21 \cdot 10^{-3}T$$
$$- 0.13 \cdot 10^{-6}T^2 + C'$$

The value $C = 0.6$ brings the calculated values of K_p into good agreement with the experimental values within the range below 2900 deg. F. (abs.). The corresponding value of C' is $- 37.107$. This value is obtained by equating the two expressions for K_p at $T = 2900$ deg. F. Calculated values of $4.571 \ \log_{10}K_p$ are as follows:

T	=	2500	2900	3500	4000	4500	5000	5500
$4.571 \ \log_{10}K_p$	=	27.644	20.989	13.902	9.641	6.337	3.693	1.526

TABLE 17

DISSOCIATION OF CO_2 AT ONE ATMOSPHERE PRESSURE

No.	Temperature		$100 \ (1-x_0)$	$4.571 \log_{10} K_p$	Method	Investigator
	deg. C. (abs.)	deg. F. (abs.)				
1	1300	2340	0.00414	30.737	I	Nernst and von Wartenburg
2	1395	2511	0.0142	27.067	IV	Langmuir
3	1400	2520	0.01—0.02	26.904	I	Nernst and von Wartenburg
4	1443	2597	0.025	25.383	IV	Langmuir
5	1478	2660	0.029—0.035	24.648	I	Nernst and von Wartenburg
6	1481	2666	0.0281	25.036	IV	Langmuir
7	1498	2696	0.0471	23.503		
8	1565	2817	0.064	22.584		
9	1818	3272	0.45	16.725	VIII	Lowenstein
10	2243	4037	4.5	9.852	V	Emich
11	2423	4361	10.0—11.0	7.229		
12	2640	4752	21.00	4.966	III	Bjerrum
13	2879	5182	51.70	1.436		
14	2900	5220	49.20	1.674		
15	2945	5301	64.70	0.195		
16	3116	5609	76.10	—1.020		
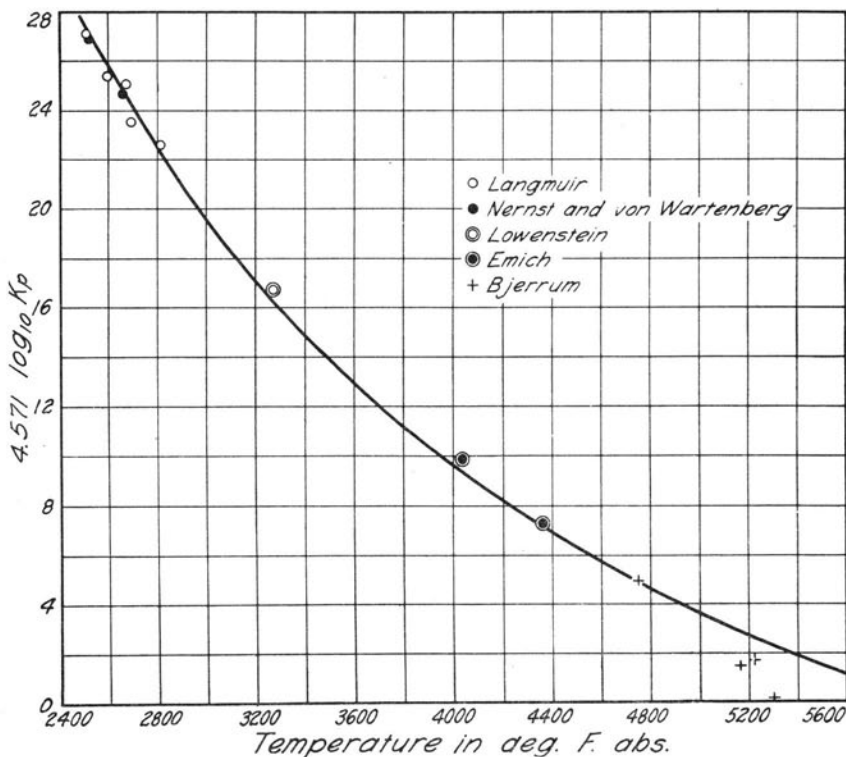
FIG. 22. AGREEMENT BETWEEN CALCULATED AND EXPERIMENTAL VALUES FOR THE EQUILIBRIUM CONSTANT FOR THE REACTION $CO + \frac{1}{2}O_2 = CO_2$

The curve, Fig. 22, represents the two equilibrium equations with the constants C and C' just quoted. The agreement with the experimental points is satisfactory.

4. *The Reaction* $H_2 + \frac{1}{2}O_2 = H_2O$.—The expression for K_p is

$$K_p = \frac{p_{H_2O}}{p_{H_2} \cdot p_{O_2}^{\frac{1}{2}}} = \frac{y_0}{1-y_0} \sqrt{\frac{3-y_0}{1-y_0}} \cdot \frac{1}{\sqrt{P}}$$

and when the total pressure P is one atmosphere

$$K_p = \frac{y_0}{1-y_0} \sqrt{\frac{3-y_0}{1-y_0}}$$

In the dissociation of H_2O into H_2 and O_2, $100(1-y_0)$ is the percentage of H_2O dissociated.

Table 18 gives the experimental data on the dissociation of H_2O at atmospheric pressure.

In certain cases several values for the dissociation were given for one temperature. In such cases the mean value has been taken.

The equilibrium equation deduced from the thermal data on specific heats and heat of combustion is

$$4.571 \log_{10}K_p = \frac{102\,820}{T} - 2.6135 \log_{10}T - 0.4713 \cdot 10^{-3}T$$
$$+ 0.0605 \cdot 10^{-6}T^2 + C$$

The value $C = -2.3$ brings the curve representing this equation into excellent agreement with the experimental points, as shown by Fig. 23. The following are the calculated values from which the curve is drawn:

T deg. F. (abs.)	2500	3000	3500	4000	4500	5000	5500
$R\log_e K_p$	29.144	22.016	16.906	13.074	10.105	7.753	5.857

FIG. 23. AGREEMENT BETWEEN CALCULATED AND EXPERIMENTAL VALUES FOR THE EQUILIBRIUM CONSTANT FOR THE REACTION $H_2 + \frac{1}{2}O_2 = H_2O$

TABLE 18

DISSOCIATION OF H_2O AT ONE ATMOSPHERE PRESSURE

No.	Temperature		$100\ (1-y_0)$	$4.571\ \log_{10} K_p$	Method	Investigator
	deg. C. (abs.)	deg. F. (abs.)				
1	1325	2385	0.0033	30.892	IV	Langmuir
2	1355	2439	0.0049	30.236		
3	1393	2507	0.0068	29.246		
4	1397	2515	0.0073	28.440	I	Nernst and von Wartenburg
5	1434	2581	0.0103	28.024	IV	Langmuir
6	1452	2614	0.0137	27.174		
7	1458	2624	0.0147	26.965		
8	1474	2653	0.0140	27.110		
9	1480	2664	0.0189	26.216	I	Nernst and von Wartenburg
10	1531	2756	0.0255	25.324	IV	Langmuir
11	1550	2790	0.0287	24.928		
12	1561	2810	0.034	24.467	I	Nernst and von Wartenburg
13	1705	3069	0.102	21.195	II	Lowenstein
14	1783	3209	0.182	19.470		
15	1863	3353	0.354	17.532		
16	1968	3542	0.518	16.350		
17	2155	3879	1.180	13.890	II	von Wartenburg
18	2257	4063	1.770	12.627		
19	2300	4140	2.60	11.561	III	Nernst
20	2642	4756	4.30	9.990	III	Bjerrum
21	2698	4856	7.50	8.282		
22	2761	4970	6.60	8.678		
23	2834	5101	9.80	7.447		
24	2929	5272	11.10	7.053		

5. *The Water-Gas Reaction,* $H_2 + CO_2 = H_2O + CO$.—By a combination of the two reactions

$$H_2 + \tfrac{1}{2}O_2 = H_2O$$
$$CO + \tfrac{1}{2}O_2 = CO_2$$
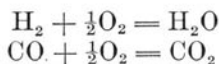
the water-gas reaction is obtained. Consequently the equilibrium equation of this reaction is obtained by subtracting the equilibrium equation of the CO reaction from that of the H_2 reaction. Two equations are thus obtained; for $T<2900$ deg. F. (abs.),

$$4.571 \log_{10}K_p = -\frac{18\,110}{T} + 4.8584 \log_{10}T - 2.4213 \cdot 10^{-3}T$$
$$+ 0.1905 \cdot 10^{-6}T^2 - 2.9$$

for $T>2900$ deg. F. (abs.),

$$4.571 \log_{10}K_p = -\frac{22\,990}{T} - 6.7605 \log_{10}T - 0.6813 \cdot 10^{-3}T$$
$$+ 0.0905 \cdot 10^{-6}T^2 + 34.807$$

The experimental data relative to the equilibrium of the water-gas reaction are given in Table 19. Fig. 24 shows the corresponding experimental points and the curve deduced from the preceding equations.

It will be noted that the constants — 2.9 and 34.807 are fixed by the corresponding constants in the H_2 and CO reactions; hence the
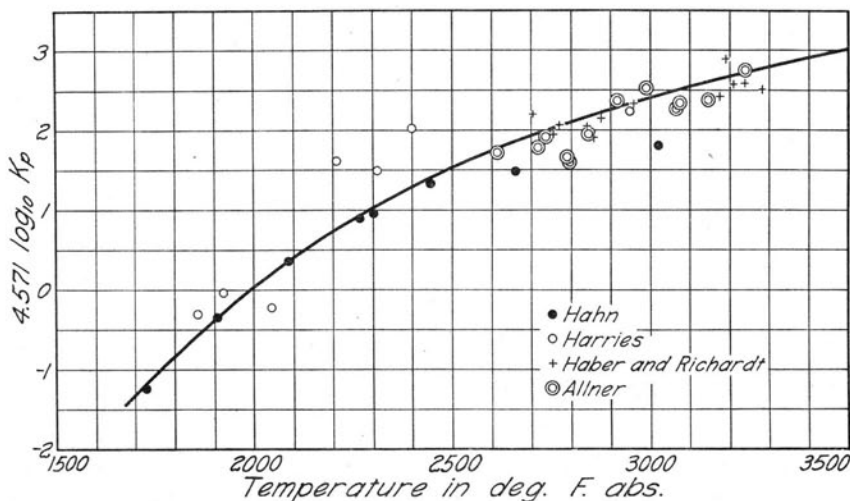
FIG. 24. AGREEMENT BETWEEN CALCULATED AND EXPERIMENTAL VALUES FOR THE EQUILIBRIUM CONSTANT FOR THE WATER-GAS REACTION

TABLE 19

EXPERIMENTAL DATA ON THE EQUILIBRIUM CONSTANT
FOR THE WATER-GAS REACTION

No.	Temperature		K_p	$4.571 \log_{10} K_p$	Method	Investigator
	deg. C. (abs.)	deg. F. (abs.)				
1	1453	2617	2.39	1.728	VI	Allner
2	1507	2715	2.46	1.787		
3	1519	2735	2.62	1.912		
4	1547	2787	2.31	1.662		
5	1553	2795	2.25	1.610		
6	1579	2842	2.69	1.965		
7	1619	2915	3.31	2.376		
8	1635	2944	3.10	2.246		
9	1659	2987	3.59	2.537		
10	1703	3065	3.13	2.265		
11	1706	3071	3.26	2.346		
12	1747	3145	3.31	2.376		
13	1798	3238	4.00	2.752		
14	1503	2705	3.04	2.207	VI	Haber and
15	1528	2752	2.66	1.942		Richardt
16	1538	2770	2.85	2.079		
17	1578	2840	2.80	2.044		
18	1586	2856	2.63	1.920		
19	1597	2875	2.93	2.134		
20	1643	2959	3.26	2.346		
21	1763	3174	3.39	2.424		
22	1773	3192	4.27	2.882		
23	1783	3210	3.65	2.573		
24	1795	3231	3.68	2.586		
25	1798	3237	4.04	2.772		
26	1824	3282	3.64	2.521		
27	959	1726	0.534	− 1.246	IV(b)	Hahn
28	1059	1906	0.840	− 0.346		
29	1159	2086	1.197	0.357		
30	1259	2266	1.570	0.895		
31	1278	2300	1.620	0.958		
32	1359	2446	1.956	1.332		
33	1478	2660	2.126	1.497		
34	1678	3020	2.490	1.811		
35	1031	1856	0.850	− 0.323	VII(c)	Harries
36	1111	1920	0.975	− 0.050		
37	1134	2041	0.890	− 0.231		
38	1227	2209	2.250	1.610		
39	1283	2309	2.120	1.492		
40	1333	2399	2.780	2.029		

position of the curve in Fig. 24 is fixed. The good agreement between the calculated and experimental values of K_p for the water-gas reaction confirms in a general way the accuracy of the specific heat equations and the constants H_0.

6. *The Reaction* $C + 2H_2 = CH_4$.—The equilibrium constant is given by

$$K_p = \frac{p_{CH_4}}{p^2_{H_2}}$$

The constants σ', σ'', σ''' are determined from the specific heat equations as follows:

For C $\gamma = 0$ $+ 4.533 \cdot 10^{-3}T - 0.9092 \cdot 10^{-6}T^2$
For $2H_2$ $2\gamma_p = 12$ $+ 1.3333 \cdot 10^{-3}T$
_____

               12 $+ 5.8667 \cdot 10^{-3}T - 0.9092 \cdot 10^{-6}T^2$
For CH_4 $\gamma_p = 3.459 + 10.56 \quad \cdot 10^{-3}T$
_____

               $8.541 - 4.6933 \cdot 10^{-3}T - 0.9092 \cdot 10^{-6}T^2$

$\sigma' = \quad 8.541$ $\sigma'' = -4.6933 \cdot 10^{-3}$ $\sigma''' = -0.9092 \cdot 10^{-6}$
$2.3026\,\sigma' = 19.6665$ $-\tfrac{1}{2}\sigma'' = 2.3467 \cdot 10^{-3}$ $-\tfrac{1}{6}\sigma''' = 0.1515 \cdot 10^{-6}$

The constant H_0 is determined from a combination of the three reactions

$C + O_2 = CO_2$ $H_0 = 174\,290$
$2H_2 + O_2 = 2H_2O$ $2H_0 = 2 \times 102\,820 = 205\,640$
$CH_4 + 2O_2 = 2H_2O$ $H_0 = 348\,330$
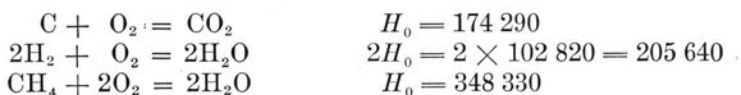
Adding the first two and subtracting the third from the sum, the constant H_0 for the reaction under consideration is

$$H_0 = 174\,290 + 205\,640 - 348\,330 = 31\,600$$

The equilibrium equation is therefore

$$4.571 \ \log_{10} K_p = \frac{31\,600}{T} - 19.6665 \ \log_{10} T + 2.3467 \cdot 10^{-3}T$$

$$+ 0.1515 \cdot 10^{-6}T^2 + C$$

Two sets of experiments furnish the data for the determination of the constant C. The figures are given in Table 20.

The points in Fig. 25 represent the experimental numbers. The curve represents the equilibrium equation with $C = 37.5$.

TABLE 20

EXPERIMENTAL DATA ON THE EQUILIBRIUM CONSTANT FOR THE
REACTION $C + 2H_2 = CH_4$

No.	Temperature		$4.571 \log_{10} K_p$	Method	Investigator
	deg. C.(abs.)	deg. F.(abs.)			
1	1373	2471	—11.031		
2	1493	2687	—11.085		
3	1548	2786	—11.117		
4	1623	2921	—12.114	VII (b) using	Pring and
5	1673	3011	—11.936	amorphous	Fairlie
6	1823	3281	—12.461	carbon rock	
7	1893	3407	—14.796		
8	1973	3551	—13.353		
9	748	1346	+ 3.298	VII (a)	
10	780	1404	+ 1.647	passing hy-	
11	809	1456	+ 1.326	drogen over	Mayer and
12	840	1512	+ 0.811	sugar carbon	Altmayer
13	850	1530	— 0.522	deposited on	
14	880	1584	— 1.119	nickel or cobalt	
15	898	1616	— 2.138	as catalyser	

NOTE.—In those cases where several values were given by the investigator for one temperature the mean value has been taken.

7. *The Reaction* $C + CO_2 = 2CO$.—The equilibrium constant K_p is the ratio $\dfrac{p^2_{CO}}{p_{CO_2}}$. The constant H_0 for this reaction is — 67 570. To determine the constants σ', σ'', σ''' the following specific heat equations are available:

For C $\quad \gamma = 0 \quad + 4.5333 \cdot 10^{-3}T — 0.9092 \cdot 10^{-6}T^2$
For CO_2 $\gamma_p = 7.15 \quad + 3.90 \quad \cdot 10^{-3}T — 0.60 \quad \cdot 10^{-6}T^2$

$\qquad\qquad 7.15 + 8.4333 \cdot 10^{-3}T — 1.5092 \cdot 10^{-6}T^2$
For 2CO $2\gamma_p = 13.86 \qquad\qquad\qquad\qquad + 0.24 \quad \cdot 10^6 \cdot T^2$

$\qquad — 6.71 \quad + 8.4333 \cdot 10^{-3}T — 1.7492 \cdot 10^{-6}T^2$

$\sigma' = — 6.71 \qquad \sigma'' = 8.4333 \cdot 10^{-3} \qquad \sigma''' = — 1.7492 \cdot 10^{-6}$
$2.3026\,\sigma' = — 15.4504 \qquad \tfrac{1}{2}\sigma'' = 4.2167 \cdot 10^{-3} \qquad \tfrac{1}{6}\sigma''' = — 0.2915 \cdot 10^{-6}$

Hence the equilibrium equation is

$$4.571 \log_{10} K_p = -\frac{67\,570}{T} + 15.4504 \log_{10} T - 4.2167 \cdot 10^{-3} T$$
$$+ 0.2915 \cdot 10^{-6} T^2 + C$$
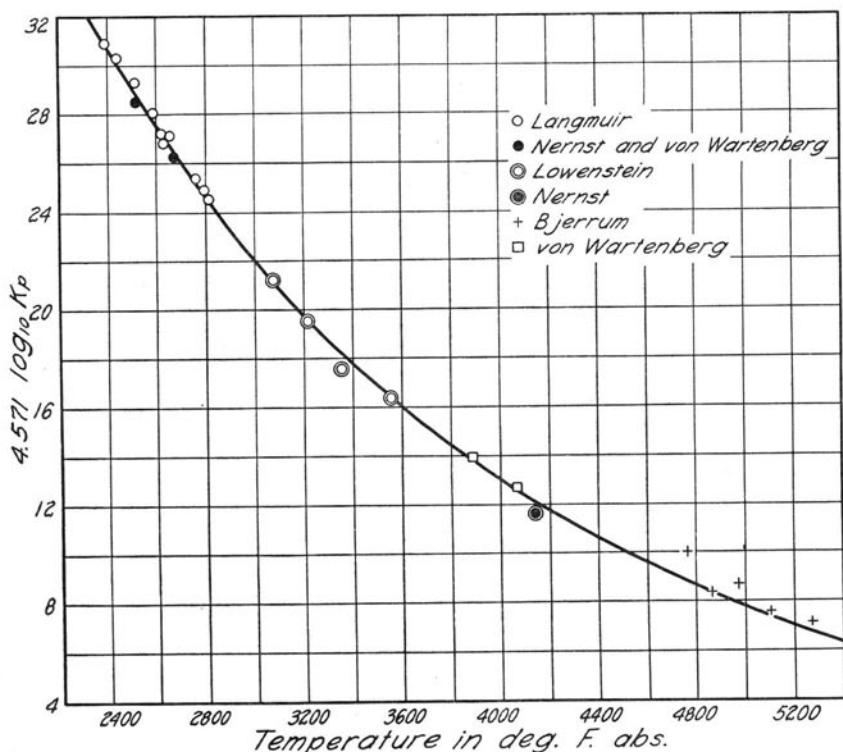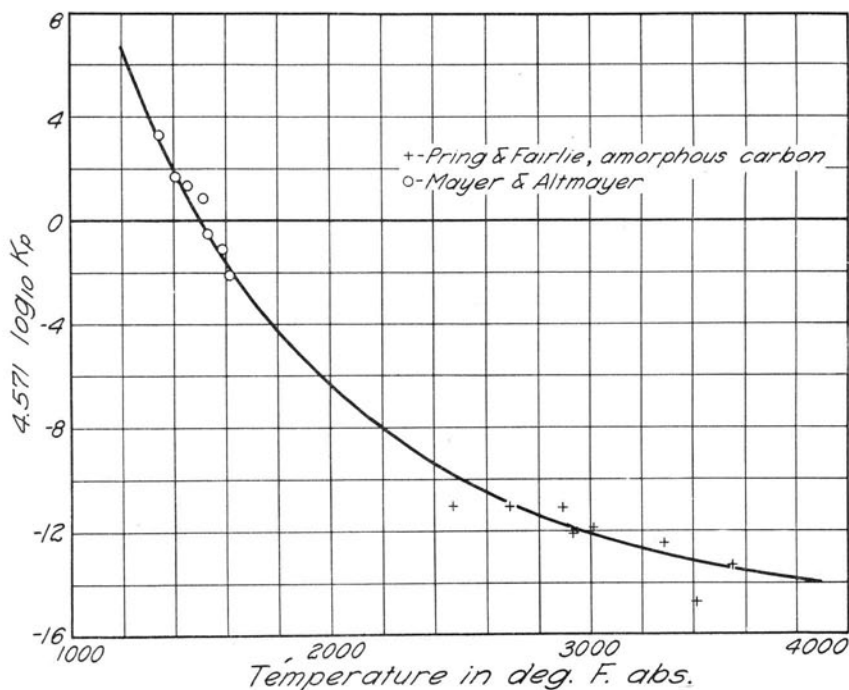

FIG. 25. AGREEMENT BETWEEN CALCULATED AND EXPERIMENTAL VALUES
FOR THE EQUILIBRIUM CONSTANT FOR THE REACTION
$C + 2H_2 = CH_4$

The experimental data on the equilibrium of this reaction is given in Table 21, and the points representing the experimental results are plotted in Fig. 26. The curve in this figure represents the preceding equilibrium equation with the value — 6.1 for the constant C. The equation agrees satisfactorily with the experiments of Boudouard and of Mayer and Jacoby and gives a fair compromise between the discordant results of Rhead and Wheeler and Clement and Adams.

8. *The Reaction* $CH_4 + 2O_2 = CO_2 + 2H_2O$.—The equilibrium equation is obtained indirectly by the addition of the equilibrium

TABLE 21

EXPERIMENTAL DATA ON THE EQUILIBRIUM CONSTANT FOR THE
REACTION $C + CO_2 = 2CO$

| No. | Temperature | | $4.571 \log_{10} K_p$ | Method | Investigator |
	deg. C. (abs.)	deg. F. (abs.)			
1	796	1433	—11.138		
2	861	1550	— 6.665		
3	896	1613	— 5.378	VII (a)	Mayer and
4	940	1692	— 3.266	using sugar carbon	Jacoby
5	1043	1877	2.577		
6	1091	1964	4.150		
7	1073	1931	— 1.067		
8	1123	2021	1.254		
9	1173	2111	3.519	VII (a)	Clement and
10	1198	2156	4.461	using charcoal	Adams
11	1273	2291	5.304		
12	1373	2471	7.913		
13	1173	2111	3.600		
14	1273	2291	3.832		
15	1373	2471	6.706	VII (a)	Clement and
16	1473	2651	8.571	using coke	Adams
17	1573	2831	10.947		
18	923	1661	— 2.755	VII (a)	
19	1073	1931	4.993	amorphous	Boudouard
20	1198	2156	6.230	carbon	
21	1073	1931	3.293		
22	1123	2021	5.257		
23	1173	2111	7.046		
24	1223	2201	8.297	VII (a)	Rhead and
25	1273	2291	9.729	amorphous	Wheeler
26	1323	2381	10.916	carbon	
27	1373	2471	12.376		
28	1473	2651	14.726		

equations for the following reactions:

$$2CO + O_2 = 2CO_2$$
$$2H_2 + O_2 = 2H_2O$$
$$C + CO_2 = 2CO$$
$$CH_4 = C + 2H_2$$
$$\overline{}$$
$$CH_4 + 2O_2 = CO_2 + 2H_2O$$
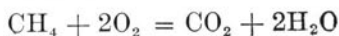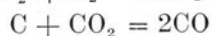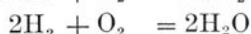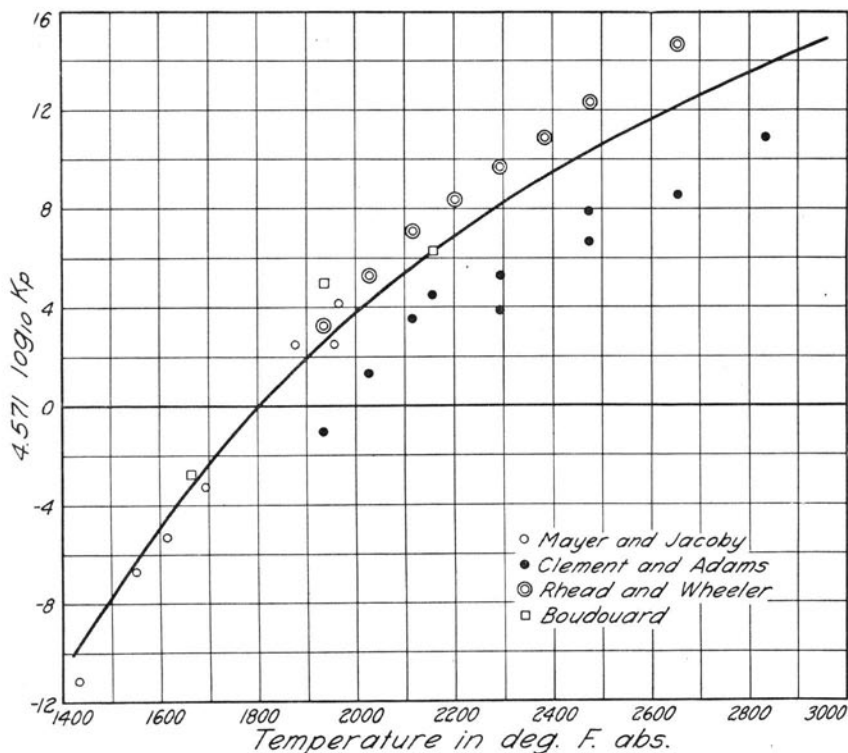
FIG. 26. AGREEMENT BETWEEN CALCULATED AND EXPERIMENTAL VALUES FOR THE
EQUILIBRIUM CONSTANT FOR THE REACTION $C + CO_2 = 2CO$

The resulting equilibrium equations are as follows:

For $T < 2900$ deg. F. (abs.)

$$4.571 \log_{10} K_p = \frac{348\,330}{T} + 14.9462 \log_{10} T - 3.606 \cdot 10^{-3} T$$

$$+ 0.001 \cdot 10^{-6} T^2 - 47.0$$

For $T > 2900$ deg. F. (abs.)

$$4.571 \log_{10} K_p = \frac{353\,210}{T} + 26.5651 \log_{10} T - 5.346 \cdot 10^{-3} T$$

$$+ 0.101 \cdot 10^{-6} T^2 - 84.7071.$$

$$K_p = \frac{p^2_{H_2O} \cdot p_{CO_2}}{p_{CH} \cdot p^2_O}$$

9. *The Reaction* $N_2 + O_2 = 2NO$.—The following equation is taken from Haber's "Thermodynamics of Technical Gas Reactions"[*]:

$$4.571 \log_{10} K_p = \frac{-77\,400}{T} + 4.9 \ (T = \text{abs. temp. F.})$$

$$K_p = \frac{p^2_{NO}}{p_{N_2} \cdot p_{O_2}}$$

10. *The Reaction* $H_2 = 2H$.—The equilibrium constant K_p is the ratio $\dfrac{p^2_H}{p_{H2}}$. Taking the specific heat of atomic hydrogen as $\frac{5}{2}R$ or 4.96 the expressions for K_p and H_0 are as follows:

For $H_2 \ \gamma_p = 6.00 + 0.6667 \cdot 10^{-3}T$
For $2H \ \gamma_p = 9.92$
$$\overline{ -3.92 + 0.6667 \cdot 10^{-3}T}$$

$$\sigma' = -3.92 \quad \sigma'' = 0.6667 \cdot 10^{-3} \quad \tfrac{1}{2}\sigma'' = 0.3333 \cdot 10^{-3}$$

$$H_0 = H_p - T(-3.92 + 0.3333 \cdot 10^{-3}T)$$

$$4.571 \log_{10} K_p = \frac{H_0}{T} + 9.0262 \log_{10}T - 0.3333 \cdot 10^{-3}T + C$$

TABLE 22

EXPERIMENTAL DATA ON THE EQUILIBRIUM CONSTANT FOR THE
REACTION $H_2 = 2H$ PRESSURE UNIT = ONE ATMOSPHERE

Temperatures		Values of $4.571 \log_{10}K_p$		
deg. C. (abs.)	deg. F. (abs.)	Total pressure = 0.207 mm. Hg.	Total pressure = 1.1 mm. Hg.	Total Pressure = 4.4 mm. Hg.
1800	3240	−28.2533	−29.4084	−27.9288
1900	3420	−25.4084	−26.1434	−25.2278
2000	3600	−22.8811	−22.8033	−23.2275
2100	3780	−20.4913	−20.4913	−20.9343
2200	3960	−18.6250	−18.5048	−18.7868
2300	4140	−16.8062	−16.4647	−16.7692
2400	4320	−15.0889	−14.6670	−15.0889
2500	4500	−12.8564	−12.8395	−13.3775
2600	4680	−11.2712	−11 4718	−11.6954
2700	4860	....	−10.0960	....
2800	5040	....	− 8.5578	....
2900	5220	....	− 6.2271	....

Langmuir has deduced values of K_p for this reaction from a study of heat losses by convection from heated tungsten wires sealed in hydrogen filled bulbs. His results transformed from millimeters of mercury as the pressure unit to atmospheres are given in Table 22.

[*] English edition, p. 104.

In this instance it is necessary to deduce values for both H_0 and C from the experimental values of K_p. Langmuir chooses the value H_p $= -90\,000$ calories per mol at 3 000 deg. C. (abs.). H_0 is then $-150\,550$ B. t. u. per mol. Giving C the value -11.7, the broken line curve in Fig. 27 is obtained. By taking the value $H_p = -100\,00$ calories per mol at 3000 deg. C. abs., the value $H_0 = -168\,550$ B. t. u. per
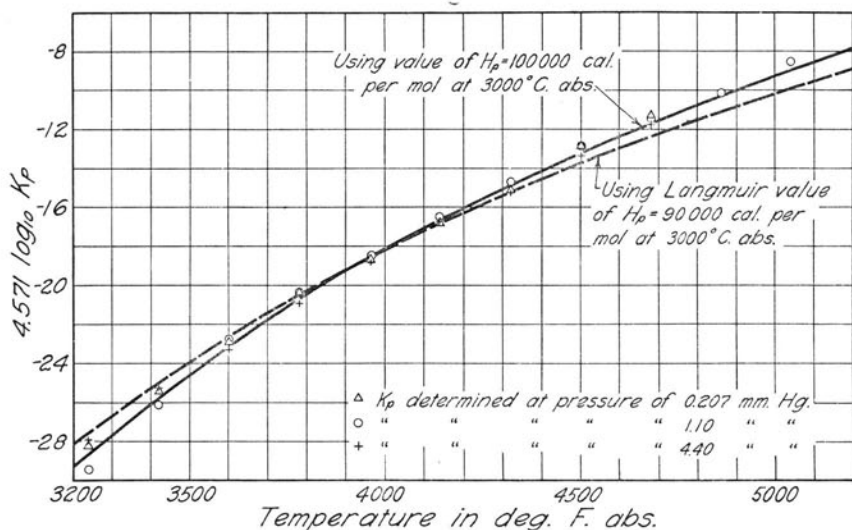
Fig. 27. Agreement between Calculated and Experimental Values for the Equilibrium Constant for the Reaction $H_2 = 2H$

mol is obtained. Taking $C = -7.2$, the solid curve Fig. 27 is obtained, and there is a better agreement between the curve and the experimental points. The equilibrium equation is then

$$4.571 \log_{10}K_p = \frac{-168\,550}{T} + 9.0262 \log_{10}T - 0.3333 \cdot 10^{-3}T - 7.2$$

The values used in plotting the solid curve in Fig. 27 are:

T deg. F. (abs.) =	3200	3600	4000	4400	4800	5200
$4.571 \log_{10}K_p$ =	−29.3009	−23.1194	−18.1575	−14.0874	−10.6874	−7.8053

The equilibrium equations given in this appendix are collected in Table 23.

TABLE 23

EQUILIBRIUM EQUATIONS

Pressure Unit = One Atmosphere
Reaction, $aA + bB = dD + eE$ $\qquad K_p = \dfrac{P_D^{\,d} \cdot P}{P_A^{\,a} \cdot P_B}$
T = Abs. temp. F.

| No.	Reaction	Equilibrium Equation
1	$H_2 + \frac{1}{2}O_2 = H_2O$ $4.571 \log_{10} K_p = \dfrac{102\,820}{T} - 2.6135 \log_{10} T - 0.4713 \cdot 10^{-3} T + 0.0605 \cdot 10^{-6} T^2 - 2.3$	
2	$CO + \frac{1}{2}O_2 = CO_2,\ T < 2900$ deg. F. (abs.) $4.571 \log_{10} K_p = \dfrac{120\,930}{T} - 7.4719 \log_{10} T + 1.95 \cdot 10^{-3} T - 0.1300 \cdot 10^{-6} T^2 + 0.6$	
3	$CO + \frac{1}{2}O_2 = CO_2,\ T > 2900$ deg. F. (abs.) $4.571 \log_{10} K_p = \dfrac{125\,810}{T} + 4.1470 \log_{10} T + 0.21 \cdot 10^{-3} T - 0.0300 \cdot 10^{-6} T^2 - 37.1070$	
4	$H_2 + CO_2 = H_2O + CO,\ T < 2900$ deg. F. (abs.) $4.571 \log_{10} K_p = \dfrac{-18\,110}{T} + 4.8584 \log_{10} T - 2.4213 \cdot 10^{-3} T + 0.1905 \cdot 10^{-6} T^2 - 2.9$	
5	$H_2 + CO_2 = H_2O + CO,\ T > 2900$ deg. F. (abs.) $4.571 \log_{10} K_p = \dfrac{-22\,990}{T} - 6.7605 \log_{10} T - 0.6813 \cdot 10^{-3} T + 0.0905 \cdot 10^{-6} T^2 + 34.8070$	
6	$C + 2H_2 = CH_4$ $4.571 \log_{10} K_p = \dfrac{31\,600}{T} - 19.6665 \log_{10} T + 2.3467 \cdot 10^{-3} T + 0.1515 \cdot 10^{-6} T^2 + 37.5$	
7	$C + CO_2 = 2CO,\ T < 2900$ deg. F. (abs.) $4.571 \log_{10} K_p = \dfrac{-67\,570}{T} + 15.4504 \log_{10} T - 4.2167 \cdot 10^{-3} T + 0.2915 \cdot 10^{-6} T^2 - 6.1$	
8	$CH_4 + 2O_2 = CO_2 + 2H_2O,\ T < 2900$ deg. F. (abs.) $4.571 \log_{10} K_p = \dfrac{348\,330}{T} + 14.9462 \log_{10} T - 3.6060 \cdot 10^{-3} T + 0.0010 \cdot 10^{-6} T^2 - 47.0$	
9	$CH_4 + 2O_2 = CO_2 + 2H_2O,\ T > 2900$ deg. F. (abs.) $4.571 \log_{10} K_p = \dfrac{353\,210}{T} + 26.5651 \log_{10} T - 5.346 \cdot 10^{-3} T + 0.1010 \cdot 10^{-6} T^2 - 84.7071$	
10	$N_2 + O_2 = 2NO$ $4.571 \log_{10} K_p = \dfrac{-77\,400}{T} + 4.9$	
11	$H_2 = 2H$ $4.571 \log_{10} K_p = \dfrac{-168\,550}{T} + 9.0262 \log_{10} T - 0.3333 \cdot 10^{-3} T - 7.2$	

NOTE—.See "References for Experimental Data on Equilibrium," page 157.

APPENDIX IV—Tables 24 to 36

TABLE 24

THERMAL ENERGY EQUATIONS

$_0U_T$ = B.t.u. required to Raise Temperature of 1 mol of Gas at constant volume from 0 deg. F. (abs). to T deg. F. (abs.)

No.	Gas	Thermal Energy
1	CO_2, $T < 2900$	$_0u_T = T(5.165 + 1.95 \cdot 10^{-3}T - 0.2 \cdot 10^{-6}T^2)$
2	CO_2, $T > 2900$	$_0u_T = T(10.211 + 0.21 \cdot 10^{-3}T) - 4878$
3	H_2O	$_0u_T = T(6.345 - 0.138 \cdot 10^{-3}T + 0.141 \cdot 10^{-6}T^2)$
4	CO, O_2, and N_2	$_0u_T = T(4.945 + 0.0400 \cdot 10^{-6}T^2)$
5	H_2	$_0u_T = T(4.015 + \frac{1}{3} \cdot 10^{-3}T)$
6	CH_4	$_0u_T = T(1.474 + 5.28 \cdot 10^{-3}T)$
7	C_2H_2	$_0u_T = T(4.205 + 4.05 \cdot 10^{-3}T)$
8	C_2H_4	$_0u_T = T(4.685 + 3.40 \cdot 10^{-3}T)$
9	C_2H_6	$_0u_T = T(5.115 + 4.30 \cdot 10^{-3}T)$
10	C_6H_6	$_0u_T = T(2.015 + 15.90 \cdot 10^{-3}T)$
11	C_8H_{18} (Gasoline Vapor)	$_0u_T = T(36.342 + 19.0 \cdot 10^{-3}T)$
12	$C_{12}H_{26}$ (Kerosene Vapor)	$_0u_T = T(55.169 + 28.333 \cdot 10^{-3}T)$
13	H (Atomic Hydrogen)	$_0u_T = 2.978T$

TABLE 25
THERMAL ENERGY OF CARBON DIOXIDE IN B. T. U. PER LB. MOL.

$T = $ abs. temp. F.

T	u	T	u	T	u
500	3 045	2700	24 224	4900	50 198
550	3 398	2750	24 791	4950	50 812
600	3 758	2800	25 359	5000	51 427
650	4 126	2850	25 929	5050	52 043
700	4 503	2900	26 500	5100	52 661
750	4 886	2950	27 072	5150	53 279
800	5 277	3000	27 645	5200	53 898
850	5 676	3050	28 219	5250	54 518
900	6 082	3100	28 794	5300	55 139
950	6 495	3150	29 370	5350	55 761
1000	6 915	3200	29 948	5400	56 384
1050	7 342	3250	30 526	5450	57 009
1100	7 775	3300	31 105	5500	57 635
1150	8 214	3350	31 685	5550	58 261
1200	8 661	3400	32 267	5600	58 889
1250	9 113	3450	32 849	5650	59 518
1300	9 571	3500	33 433	5700	60 148
1350	10 035	3550	34 018	5750	60 779
1400	10 504	3600	34 603	5800	61 411
1450	10 978	3650	35 190	5850	62 043
1500	11 460	3700	35 778	5900	62 677
1550	11 946	3750	36 366	5950	63 312
1600	12 437	3800	36 956	6000	63 948
1650	12 933	3850	37 546	6050	64 585
1700	13 434	3900	38 138	6100	65 223
1750	13 939	3950	38 731	6150	65 862
1800	14 448	4000	39 326	6200	66 502
1850	14 962	4050	39 921	6250	67 143
1900	15 481	4100	40 517	6300	67 786
1950	16 004	4150	41 114	6350	68 429
2000	16 530	4200	41 712	6400	69 074
2050	17 060	4250	42 312	6450	69 719
2100	17 594	4300	42 912	6500	70 366
2150	18 131	4350	43 513	6550	71 013
2200	18 672	4400	44 116	6600	71 662
2250	19 215	4450	44 719	6650	72 312
2300	19 761	4500	45 324	6700	72 963
2350	20 311	4550	45 929	6750	73 614
2400	20 863	4600	46 536	6800	74 267
2450	21 418	4650	47 143	6850	74 921
2500	21 975	4700	47 752	6900	75 576
2550	22 534	4750	48 362	6950	76 232
2600	23 096	4800	48 973	7000	76 888
2650	23 659	4850	49 585	....	......

TABLE 26

THERMAL ENERGY OF WATER VAPOR IN B. T. U. PER LB. MOL.

$T =$ abs. temp. F.

T	u	T	u	T	u
500	3 156	2700	18 901	4900	44 366
550	3 471	2750	19 338	4950	45 128
600	3 787	2800	19 779	5000	45 900
650	4 104	2850	20 226	5050	46 681
700	4 422	2900	20 679	5100	47 474
750	4 740	2950	21 137	5150	48 276
800	5 060	3000	21 600	5200	49 088
850	5 380	3050	22 069	5250	49 910
900	5 702	3100	22 544	5300	50 744
950	6 024	3150	23 024	5350	51 588
1000	6 348	3200	23 510	5400	52 442
1050	6 673	3250	24 004	5450	53 306
1100	7 001	3300	24 503	5500	54 181
1150	7 329	3350	25 008	5550	55 068
1200	7 659	3400	25 520	5600	55 966
1250	7 990	3450	26 038	5650	56 875
1300	8 325	3500	26 562	5700	57 795
1350	8 662	3550	27 094	5750	58 726
1400	9 000	3600	27 632	5800	59 670
1450	9 340	3650	28 176	5850	60 624
1500	9 682	3700	28 729	5900	61 590
1550	10 028	3750	29 288	5950	62 569
1600	10 376	3800	29 856	6000	63 558
1650	10 726	3850	30 429	6050	64 559
1700	11 080	3900	31 010	6100	65 574
1750	11 436	3950	31 600	6150	66 600
1800	11 796	4000	32 197	6200	67 639
1850	12 159	4050	32 800	6250	68 689
1900	12 525	4100	33 412	6300	69 753
1950	12 894	4150	34 032	6350	70 829
2000	13 266	4200	34 662	6400	71 918
2050	13 642	4250	35 298	6450	73 019
2100	14 022	4300	35 942	6500	74 134
2150	14 405	4350	36 595	6550	75 262
2200	14 792	4400	37 257	6600	76 403
2250	15 183	4450	37 927	6650	77 557
2300	15 579	4500	38 606	6700	78 724
2350	15 978	4550	39 294	6750	79 905
2400	16 382	4600	39 992	6800	81 099
2450	16 791	4650	40 697	6850	82 308
2500	17 203	4700	41 412	6900	83 530
2550	17 620	4750	42 137	6950	84 766
2600	18 042	4800	42 870	7000	86 017 .
2650	18 469	4850	43 613	....	......

TABLE 27

THERMAL ENERGY OF THE DIATOMIC GASES CO, O_2 AND N_2 IN B. T. U. PER LB. MOL.

$T =$ abs. temp. F.

T	u	T	u	T	u
500	2 478	2700	14 139	4900	28 936
550	2 726	2750	14 431	4950	29 329
600	2 976	2800	14 725	5000	29 725
650	3 226	2850	15 020	5050	30 124
700	3 475	2900	15 316	5100	30 525
750	3 725	2950	15 614	5150	30 929
800	3 976	3000	15 914	5200	31 337
850	4 227	3050	16 217	5250	31 749
900	4 480	3100	16 521	5300	32 164
950	4 732	3150	16 827	5350	32 582
1000	4 985	3200	17 134	5400	33 002
1050	5 239	3250	17 444	5450	33 425
1100	5 493	3300	17 756	5500	33 853
1150	5 747	3350	18 069	5550	34 283
1200	6 003	3400	18 385	5600	34 717
1250	6 259	3450	18 702	5650	35 152
1300	6 516	3500	19 022	5700	35 595
1350	6 774	3550	19 344	5750	36 038
1400	7 033	3600	19 668	5800	36 486
1450	7 293	3650	19 995	5850	36 936
1500	7 553	3700	20 323	5900	37 390
1550	7 814	3750	20 652	5950	37 849
1600	8 076	3800	20 985	6000	38 310
1650	8 339	3850	21 320	6050	38 774
1700	8 603	3900	21 657	6100	39 244
1750	8 869	3950	21 997	6150	39 716
1800	9 135	4000	22 339	6200	40 192
1850	9 401	4050	22 684	6250	40 672
1900	9 669	4100	23 032	6300	41 155
1950	9 939	4150	23 381	6350	41 643
2000	10 211	4200	23 732	6400	42 134
2050	10 483	4250	24 086	6450	42 629
2100	10 755	4300	24 444	6500	43 128
2150	11 029	4350	24 803	6550	43 631
2200	11 305	4400	25 165	6600	44 138
2250	11 582	4450	25 529	6650	44 647
2300	11 860	4500	25 897	6700	45 162
2350	12 140	4550	26 267	6750	45 681
2400	12 421	4600	26 641	6800	46 204
2450	12 704	4650	27 017	6850	46 730
2500	12 988	4700	27 394	6900	47 261
2550	13 274	4750	27 774	6950	47 796
2600	13 560	4800	28 159	7000	48 335
2650	13 849	4850	28 546	....	......

TABLE 28

THERMAL ENERGY OF HYDROGEN IN B. T. U. PER LB. MOL.

$T =$ abs. temp. F.

T	u	T	u	T	u
500	2 091	2700	13 271	4900	27 677
550	2 309	2750	13 562	4950	28 042
600	2 529	2800	13 855	5000	28 409
650	2 750	2850	14 150	5050	28 777
700	2 974	2900	14 447	5100	29 147
750	3 199	2950	14 745	5150	29 517
800	3 425	3000	15 045	5200	29 891
850	3 653	3050	15 346	5250	30 266
900	3 884	3100	15 650	5300	30 643
950	4 115	3150	15 955	5350	31 021
1000	4 348	3200	16 261	5400	31 401
1050	4 583	3250	16 570	5450	31 782
1100	4 819	3300	16 880	5500	32 166
1150	5 058	3350	17 191	5550	32 551
1200	5 298	3400	17 504	5600	32 938
1250	5 539	3450	17 819	5650	33 325
1300	5 783	3500	18 136	5700	33 715
1350	6 028	3550	18 454	5750	34 107
1400	6 279	3600	18 774	5800	34 500
1450	6 522	3650	19 095	5850	34 895
1500	6 772	3700	19 419	5900	35 292
1550	7 024	3750	19 744	5950	35 691
1600	7 277	3800	20 071	6000	36 090
1650	7 532	3850	20 399	6050	36 492
1700	7 789	3900	20 729	6100	36 895
1750	8 047	3950	21 060	6150	37 300
1800	8 307	4000	21 393	6200	37 707
1850	8 568	4050	21 728	6250	38 114
1900	8 832	4100	22 065	6300	38 524
1950	9 097	4150	22 403	6350	38 935
2000	9 363	4200	22 743	6400	39 349
2050	9 631	4250	23 084	6450	39 764
2100	9 902	4300	23 428	6500	40 181
2150	10 173	4350	23 773	6550	40 599
2200	10 446	4400	24 118	6600	41 019
2250	10 721	4450	24 468	6650	41 440
2300	10 998	4500	24 818	6700	41 864
2350	11 276	4550	25 169	6750	42 289
2400	11 556	4600	25 522	6800	42 716
2450	11 838	4650	25 877	6850	43 144
2500	12 121	4700	26 234	6900	43 574
2550	12 406	4750	26 592	6950	44 005
2600	12 693	4800	26 952	7000	44 439
2650	12 981	4850	27 314	....	.....

<p align="center">TABLE 29</p>

<p align="center">THERMAL ENERGY OF HYDROCARBON GASES IN B. T. U. PER LB. MOL.</p>

T deg. F. (abs.)	Methane CH₄	Acetylene C₂H₂	Ethylene C₂H₄	Ethane C₂H₆	Benzene Vapor C₆H₆	Gasoline Vapor C₈H₁₅	Kerosene Vapor C₁₂H₂₆
500	2 057	3 115	3 192	3 632	4 982	22 921	34 667
550	2 408	3 538	3 605	4 114	5 918	25 736	38 914
600	2 785	3 981	4 035	4 617	6 933	28 645	43 301
650	3 189	4 444	4 482	5 142	8 027	31 650	47 830
700	3 619	4 928	4 945	5 687	9 202	34 749	52 501
750	4 076	5 432	5 426	6 255	10 455	37 944	57 314
800	4 558	5 956	5 924	6 844	11 788	41 234	62 269
850	5 068	6 500	6 439	7 454	13 200	44 618	67 364
900	5 603	7 065	6 971	8 086	14 692	48 098	72 602
950	6 166	7 650	7 519	8 740	16 264	51 672	77 981
1000	6 754	8 255	8 085	9 415	17 915	55 342	83 502
1050	7 369	8 880	8 668	10 112	19 645	59 107	89 165
1100	8 010	9 526	9 268	10 830	21 456	62 967	94 969
1150	8 678	10 192	9 884	11 569	23 345	66 921	100 915
1200	9 372	10 878	10 518	12 330	25 314	70 971	107 002
1250	10 092	11 584	11 169	13 113	27 362	75 115	113 231
1300	10 839	12 311	11 836	13 917	29 490	79 355	119 603
1350	11 613	13 058	12 521	14 742	31 698	83 690	126 116
1400	12 412	13 825	13 223	15 589	33 985	88 119	132 770
1450	13 239	14 612	13 942	16 458	36 351	92 644	139 565
1500	14 091	15 420	14 678	17 348	38 798	97 264	146 502
1550	14 970	16 248	15 430	18 259	41 323	101 978	153 581
1600	15 875	17 096	16 200	19 192	43 928	106 788	160 803

TABLE 30

VALUES OF LOG_{10} K_p FOR THE REACTION $CO + \frac{1}{2}O_2 = CO_2$

T = abs. temp. F.   Pressure Unit = One Atmosphere

T	00	10	20	30	40	50	60	70	80	90
3000	4.28991	4.26081	4.23190	4.20318	4.17167	4.14635	4.11821	4.09025	4.06247	4.03488
3100	4.00747	3.98025	3.95320	3.92633	3.89963	3.87310	3.84675	3.82056	3.79454	3.76869
3200	3.74300	3.71748	3.69211	3.66691	3.64186	3.61697	3.59223	3.56765	3.54322	3.51894
3300	3.49482	3.47085	3.44701	3.42332	3.39977	3.37637	3.35311	3.32999	3.30701	3.28417
3400	3.26146	3.23889	3.21646	3.19417	3.17199	3.14995	3.12803	3.10625	3.08459	3.06306
3500	3.04166	3.02039	2.99923	2.97819	2.95727	2.93647	2.91579	2.89523	2.87479	2.85446
3600	2.83425	2.81415	2.79417	2.77430	2.75454	2.73489	2.71534	2.69590	2.67657	2.65735
3700	2.63823	2.61922	2.60031	2.58150	2.56279	2.54418	2.52568	2.50728	2.48897	2.47076
3800	2.45265	2.43463	2.41671	2.39888	2.38115	2.36351	2.34597	2.32852	2.31116	2.29389
3900	2.27671	2.25961	2.24261	2.22569	2.20885	2.19211	2.17545	2.15887	2.14238	2.12598
4000	2.10965	2.09341	2.07725	2.06117	2.04517	2.02925	2.01341	1.99765	1.98197	1.96636
4100	1.95083	1.93538	1.92000	1.90470	1.88947	1.87432	1.85924	1.84423	1.82930	1.81443
4200	1.79964	1.78492	1.77027	1.75569	1.74118	1.72674	1.71236	1.69805	1.68381	1.66964
4300	1.65553	1.64149	1.62751	1.61359	1.59974	1.58596	1.57223	1.55857	1.54498	1.53145
4400	1.51798	1.50457	1.49122	1.47793	1.46471	1.45154	1.43843	1.42538	1.41239	1.39946
4500	1.38659	1.37378	1.36102	1.34831	1.33566	1.32307	1.31053	1.29805	1.28562	1.27324
4600	1.26092	1.24865	1.23644	1.22428	1.21217	1.20011	1.18810	1.17614	1.16424	1.15238
4700	1.14058	1.12882	1.11712	1.10547	1.09386	1.08230	1.07079	1.05933	1.04792	1.03656
4800	1.02524	1.01396	1.00273	0.99155	0.98041	0.96932	0.95828	0.94728	0.93633	0.92542
4900	0.91456	0.90374	0.89296	0.88223	0.87154	0.86089	0.85029	0.83973	0.82920	0.81872

TABLE 30 (CONTINUED)

VALUES OF $\log_{10} K_p$ FOR THE REACTION $CO + \tfrac{1}{2}O_2 = CO_2$

T = abs. temp. F.   Pressure Unit = One Atmosphere

T	00	10	20	30	40	50	60	70	80	90
5000	0.80828	0.79788	0.78752	0.77720	0.76693	0.75670	0.74650	0.73634	0.72623	0.71615
5100	0.70611	0.69611	0.68614	0.67622	0.66633	0.65648	0.64667	0.63690	0.62716	0.61746
5200	0.60780	0.59817	0.58859	0.57902	0.56951	0.56003	0.55058	0.54117	0.53179	0.52244
5300	0.51315	0.50388	0.49464	0.48543	0.47626	0.46712	0.45802	0.44894	0.43990	0.43089
5400	0.42192	0.41297	0.40406	0.39518	0.38634	0.37752	0.36874	0.35999	0.35127	0.34258
5500	0.33392	0.32529	0.31669	0.30812	0.29958	0.29107	0.28259	0.27414	0.26572	0.25733
5600	0.24896	0.24062	0.23232	0.22404	0.21579	0.20757	0.19938	0.19121	0.18307	0.17496
5700	0.16688	0.15882	0.15080	0.14280	0.13482	0.12687	0.11895	0.11106	0.10319	0.09535
5800	0.08754	0.07975	0.07198	0.06424	0.05653	0.04884	0.04117	0.03353	0.02591	0.01832
5900	0.01076	0.00322	−0.00430	−0.01179	−0.01926	−0.02671	−0.03413	−0.04153	−0.04890	−0.05625
6000	−0.06358	−0.07089	−0.07817	−0.08543	−0.09267	−0.09988	−0.10707	−0.11424	−0.12138	−0.12850
6100	−0.13561	−0.14270	−0.14976	−0.15680	−0.16381	−0.17080	−0.17778	−0.18474	−0.19167	−0.19858
6200	−0.20547	−0.21234	−0.21919	−0.22602	−0.23282	−0.23961	−0.24638	−0.25313	−0.25985	−0.26655
6300	−0.27324	−0.27991	−0.28655	−0.29318	−0.29979	−0.30638	−0.31295	−0.31950	−0.32603	−0.33254
6400	−0.33904	−0.34552	−0.35197	−0.35841	−0.36483	−0.37123	−0.37761	−0.38398	−0.39033	−0.39666
6500	−0.40297	−0.40926	−0.41554	−0.42180	−0.42804	−0.43426	−0.44047	−0.44666	−0.45283	−0.45898
6600	−0.46512	−0.47124	−0.47734	−0.48342	−0.48949	−0.49554	−0.50158	−0.50760	−0.51360	−0.51959
6700	−0.52556	−0.53151	−0.53745	−0.54337	−0.54928	−0.55517	−0.56105	−0.56691	−0.57275	−0.57858
6800	−0.58439	−0.59019	−0.59598	−0.60175	−0.60751	−0.61325	−0.61897	−0.62468	−0.63037	−0.63605
6900	−0.64171	−0.64736	−0.65299	−0.65861	−0.66422	−0.66981	−0.67539	−0.68095	−0.68650	−0.69203

TABLE 31

VALUES OF LOG$_{10}$ K$_p$ FOR THE REACTION H$_2$ + $\frac{1}{2}$O$_2$ = H$_2$O

T = abs temp. F.   Pressure Unit = One Atmosphere

T	00	10	20	30	40	50	60	70	80	90
3000	4.81654	4.79056	4.76476	4.73913	4.71366	4.68836	4.66323	4.63826	4.61345	4.58880
3100	4.56430	4.53996	4.51577	4.49174	4.46786	4.44413	4.42055	4.39712	4.37383	4.35069
3200	4.32769	4.30484	4.28212	4.25955	4.23711	4.21481	4.19265	4.17062	4.14873	4.12697
3300	4.10533	4.08383	4.06245	4.04121	4.02009	3.99910	3.97823	3.95749	3.93687	3.91637
3400	3.89599	3.87573	3.85559	3.83557	3.81566	3.79587	3.77619	3.75663	3.73717	3.71783
3500	3.69860	3.67948	3.66046	3.64156	3.62276	3.60407	3.58548	3.56700	3.54862	3.53034
3600	3.51217	3.49410	3.47612	3.45824	3.44047	3.42279	3.40521	3.38772	3.37033	3.35304
3700	3.33584	3.31873	3.30172	3.28480	3.26796	3.25122	3.23457	3.21801	3.20153	3.18514
3800	3.16884	3.15263	3.13650	3.12046	3.10450	3.08863	3.07284	3.05714	3.04151	3.02597
3900	3.01050	2.99512	2.97981	2.96458	2.94943	2.93436	2.91937	2.90445	2.88961	2.87484
4000	2.86015	2.84554	2.83100	2.81653	2.80213	2.78781	2.77356	2.75938	2.74527	2.73123
4100	2.71727	2.70337	2.68954	2.67578	2.66209	2.64847	2.63491	2.62142	2.60799	2.59463
4200	2.58134	2.56811	2.55494	2.54184	2.52880	2.51583	2.50292	2.49007	2.47728	2.46455
4300	2.45189	2.43929	2.42675	2.41426	2.40183	2.38946	2.37715	2.36490	2.35271	2.34058
4400	2.32850	2.31648	2.30451	2.29260	2.28075	2.26895	2.25721	2.24552	2.23389	2.22231
4500	2.21078	2.19930	2.18788	2.17651	2.16520	2.15393	2.14272	2.13156	2.12046	2.10941
4600	2.09840	2.08744	2.07653	2.06567	2.05486	2.04410	2.03338	2.02272	2.01210	2.00153
4700	1.99101	1.98054	1.97011	1.95973	1.94939	1.93910	1.92885	1.91865	1.90850	1.89839
4800	1.88833	1.87831	1.86834	1.85841	1.84852	1.83868	1.82888	1.81912	1.80941	1.79974
4900	1.79010	1.78051	1.77097	1.76147	1.75200	1.74257	1.73319	1.72385	1.71455	1.70529

TABLE 31 (CONTINUED)

VALUES OF LOG_{10} K_p FOR THE REACTION $H_2 + \frac{1}{2}O_2 = H_2O$

T = abs. temp. F.   Pressure Unit = One Atmosphere

T	00	10	20	30	40	50	60	70	80	90
5000	1.69607	1.68688	1.67774	1.66863	1.65957	1.65054	1.64156	1.63261	1.62370	1.61482
5100	1.60599	1.59719	1.58844	1.57972	1.57103	1.56238	1.55377	1.54519	1.53665	1.52815
5200	1.51968	1.51125	1.50285	1.49449	1.48616	1.47787	1.46961	1.46139	1.45320	1.44504
5300	1.43692	1.42883	1.42078	1.41276	1.40477	1.39682	1.38890	1.38101	1.37315	1.36533
5400	1.35754	1.34978	1.34205	1.33435	1.32669	1.31905	1.31145	1.30388	1.29634	1.28883
5500	1.28135	1.27390	1.26649	1.25910	1.25175	1.24442	1.23712	1.22985	1.22262	1.21541
5600	1.20823	1.20108	1.19396	1.18687	1.17980	1.17276	1.16576	1.15878	1.15183	1.14490
5700	1.13801	1.13115	1.12431	1.11750	1.11071	1.10395	1.09722	1.09052	1.08384	1.07719
5800	1.07057	1.06397	1.05740	1.05085	1.04433	1.03784	1.03137	1.02493	1.01851	1.01212
5900	1.00575	0.99942	0.99311	0.98682	0.98055	0.97430	0.96809	0.96190	0.95574	0.94960
6000	0.94348	0.93739	0.93132	0.92527	0.91925	0.91325	0.90728	0.90133	0.89540	0.88950
6100	0.88362	0.87776	0.87193	0.86612	0.86033	0.85457	0.84883	0.84311	0.83741	0.83173
6200	0.82608	0.82045	0.81484	0.80925	0.80369	0.79815	0.79263	0.78713	0.78165	0.77619
6300	0.77076	0.76535	0.75995	0.75457	0.74922	0.74389	0.73858	0.73329	0.72802	0.72277
6400	0.71754	0.71233	0.70715	0.70199	0.69684	0.69171	0.68661	0.68153	0.67646	0.67141
6500	0.66639	0.66139	0.65640	0.65143	0.64649	0.64156	0.63665	0.63176	0.62689	0.62204
6600	0.61721	0.61240	0.60760	0.60282	0.59806	0.59332	0.58860	0.58390	0.57921	0.57454
6700	0.56990	0.56527	0.56065	0.55605	0.55148	0.54692	0.54238	0.53786	0.53335	0.52886
6800	0.52440	0.51995	0.51551	0.51109	0.50669	0.50231	0.49794	0.49359	0.48926	0.48495
6900	0.48065	0.47637	0.47211	0.46786	0.46363	0.45942	0.45522	0.45104	0.44688	0.44273

TABLE 32

VALUES OF K_p FOR THE REACTION $H_2 + CO_2 = H_2O + CO$.

T = abs. temp. F.

T	00	10	20	30	40	50	60	70	80	90
3000	3.3623	3.3866	3.4109	3.4352	3.4594	3.4836	3.5078	3.5320	3.5561	3.5802
3100	3.6043	3.6283	3.6523	3.6763	3.7002	3.7241	3.7480	3.7718	3.7956	3.8194
3200	3.8431	3.8668	3.8905	3.9141	3.9377	3.9613	3.9848	4.0083	4.0318	4.0552
3300	4.0786	4.1020	4.1253	4.1486	4.1718	4.1950	4.2182	4.2413	4.2644	4.2875
3400	4.3105	4.3335	4.3564	4.3793	4.4022	4.4251	4.4479	4.4707	4.4934	4.5161
3500	4.5388	4.5614	4.5840	4.6065	4.6290	4.6515	4.6739	4.6963	4.7187	4.7410
3600	4.7633	4.7856	4.8078	4.8300	4.8522	4.8743	4.8964	4.9185	4.9405	4.9625
3700	4.9844	5.0063	5.0282	5.0501	5.0720	5.0938	5.1156	5.1373	5.1590	5.1807
3800	5.2024	5.2240	5.2456	5.2672	5.2887	5.3103	5.3318	5.3533	5.3747	5.3961
3900	5.4175	5.4389	5.4602	5.4815	5.5028	5.5241	5.5453	5.5665	5.5877	5.6089
4000	5.6300	5.6511	5.6722	5.6933	5.7143	5.7354	5.7564	5.7774	5.7984	5.8194
4100	5.8403	5.8613	5.8822	5.9031	5.9240	5.9449	5.9657	5.9866	6.0074	6.0283
4200	6.0491	6.0699	6.0907	6.1115	6.1323	6.1531	6.1739	6.1947	6.2155	6.2363
4300	6.2570	6.2778	6.2985	6.3193	6.3400	6.3608	6.3815	6.4022	6.4229	6.4436
4400	6.4643	6.4850	6.5056	6.5263	6.5470	6.5677	6.5883	6.6090	6.6297	6.6504
4500	6.6710	6.6916	6.7123	6.7330	6.7537	6.7744	6.7951	6.8158	6.8366	6.8573
4600	6.8781	6.8989	6.9196	6.9404	6.9612	6.9820	7.0029	7.0238	7.0446	7.0655
4700	7.0864	7.1073	7.1282	7.1491	7.1701	7.1911	7.2121	7.2331	7.2541	7.2752
4800	7.2963	7.3174	7.3385	7.3596	7.3808	7.4020	7.4232	7.4444	7.4657	7.4870
4900	7.5083	7.5296	7.5510	7.5724	7.5938	7.6152	7.6367	7.6582	7.6798	7.7014

Table 32 (Continued)

Values of K_p for the Reaction $H_2 + CO_2 = H_2O + CO$

T = abs. temp. F.

T	00	10	20	30	40	50	60	70	80	90
5000	7.7230	7.7447	7.7664	7.7881	7.8099	7.8317	7.8536	7.8755	7.8974	7.9193
5100	7.9413	7.9633	7.9854	8.0075	8.0297	8.0519	8.0741	8.0964	8.1187	8.1411
5200	8.1635	8.1859	8.2084	8.2309	8.2535	8.2762	8.2989	8.3217	8.3445	8.3673
5300	8.3902	8.4131	8.4361	8.4592	8.4823	8.5055	8.5287	8.5520	8.5753	8.5987
5400	8.6222	8.6457	8.6693	8.6929	8.7166	8.7404	8.7642	8.7881	8.8121	8.8361
5500	8.8602	8.8844	8.9086	8.9329	8.9572	8.9816	9.0061	9.0307	9.0554	9.0801
5600	9.1049	9.1298	9.1547	9.1797	9.2048	9.2300	9.2552	9.2805	9.3059	9.3314
5700	9.3569	9.3825	9.4082	9.4340	9.4599	9.4859	9.5119	9.5380	9.5642	9.5905
5800	9.6169	9.6434	9.6699	9.6965	9.7232	9.7500	9.7769	9.8039	9.8310	9.8582
5900	9.8855	9.9129	9.9404	9.9680	9.9956	10.0234	10.0513	10.0793	10.1074	10.1356
6000	10.1639	10.1923	10.2208	10.2495	10.2782	10.3071	10.3360	10.3651	10.3943	10.4236
6100	10.4530	10.4825	10.5122	10.5420	10.5719	10.6020	10.6321	10.6623	10.6926	10.7231
6200	10.7537	10.7844	10.8153	10.8463	10.8773	10.9085	10.9398	10.9712	11.0028	11.0346
6300	11.0664	11.0984	11.1304	11.1626	11.1949	11.2274	11.2600	11.2928	11.3257	11.3587
6400	11.3919	11.4252	11.4586	11.4922	11.5259	11.5598	11.5939	11.6281	11.6625	11.6970
6500	11.7317	11.7665	11.8015	11.8366	11.8719	11.9073	11.9429	11.9787	12.0146	12.0507
6600	12.0869	12.1233	12.1599	12.1966	12.2335	12.2706	12.3078	12.3452	12.3827	12.4204
6700	12.4583	12.4964	12.5346	12.5730	12.6115	12.6502	12.6892	12.7283	12.7676	12.8071
6800	12.8468	12.8867	12.9268	12.9671	13.0075	13.0481	13.0890	13.1300	13.1713	13.2128
6900	13.2544	13.2963	13.3383	13.3806	13.4231	13.4658	13.5086	13.5516	13.5950	13.6386

TABLE 33

EQUATIONS FOR HEAT OF COMBUSTION

H_p =lower heat of comb., B. t. u. per mol, at const. press. at temp. T.
H_v =lower heat of comb., B. t. u. per mol, at const. vol. at temp. T.
T =abs. temp. F.

No.	Gas	Heat of Combustion
1	H_2	$H_p = 102\ 820 + T(1.135 + 0.4713 \cdot 10^{-3}T - 0.1210 \cdot 10^{-6}T^2)$ $H_v = 102\ 820 + T(0.143 + 0.4713 \cdot 10^{-3}T - 0.1210 \cdot 10^{-6}T^2)$
2	CO, $T < 2900$	$H_p = 120\ 930 + T(3.245 - 1.95 \cdot 10^{-3}T + 0.2600 \cdot 10^{-6}T^2)$ $H_v = 120\ 930 + T(2.253 - 1.95 \cdot 10^{-3}T + 0.2600 \cdot 10^{-6}T^2)$
3	CO, $T > 2900$	$H_p = 125\ 810 + T(-1.801 - 0.21 \cdot 10^{-3}T + 0.0600 \cdot 10^{-6}T^2)$ $H_v = 125\ 810 + T(-2.793 - 0.21 \cdot 10^{-3}T + 0.0600 \cdot 10^{-6}T^2)$
4	CH_4, $T < 2900$	$H_p = 348\ 330 + T(-6.491 + 3.606 \cdot 10^{-3}T - 0.0020 \cdot 10^{-6}T^2)$ $H_v = 348\ 330 + T(-6.491 + 3.606 \cdot 10^{-3}T - 0.0020 \cdot 10^{-6}T^2)$
5	C_2H_2, $T < 2900$	$H_p = 541\ 580 + T(-0.885 + 0.288 \cdot 10^{-3}T + 0.3590 \cdot 10^{-6}T^2)$ $H_v = 541\ 580 + T(-0.107 + 0.288 \cdot 10^{-3}T + 0.3590 \cdot 10^{-6}T^2)$
6	C_2H_4, $T < 2900$	$H_p = 577\ 220 + T(-3.50 - 0.2240 \cdot 10^{-3}T + 0.2380 \cdot 10^{-6}T^2)$ $H_v = 577\ 220 + T(-3.50 - 0.2240 \cdot 10^{-3}T + 0.2380 \cdot 10^{-6}T^2)$
7	C_2H_6, $T < 2900$	$H_p = 614\ 240 + T(-7.935 + 0.8140 \cdot 10^{-3}T + 0.1170 \cdot 10^{-6}T^2)$ $H_v = 614\ 240 + T(-6.943 + 0.8140 \cdot 10^{-3}T + 0.1170 \cdot 10^{-6}T^2)$
8	C_6H_6, $T < 2900$	$H_p = 1\ 364\ 200 + T(-11.915 + 4.6140 \cdot 10^{-3}T + 1.0770 \cdot 10^{-6}T^2)$ $H_v = 1\ 364\ 200 + T(-10.923 + 4.6140 \cdot 10^{-3}T + 1.0770 \cdot 10^{-6}T^2)$
9	C_8H_{18}, $T < 2900$ (Gasoline Vapor)	$H_p = 2\ 145\ 610 + T(-7.218 + 4.642 \cdot 10^{-3}T + 0.831 \cdot 10^{-6}T^2)$ $H_v = 2\ 145\ 610 + T(-0.271 + 4.642 \cdot 10^{-3}T + 0.831 \cdot 10^{-6}T^2)$
10	$C_{12}H_{26}$, $T < 2900$ (Kerosene Vapor)	$H_p = 3\ 458\ 680 + T(-8.732 + 6.729 \cdot 10^{-3}T + 1.310 \cdot 10^{-6}T^2)$ $H_v = 3\ 458\ 680 + T(-2.186 + 6.729 \cdot 10^{-3}T + 1.310 \cdot 10^{-6}T^2)$
11	(Reaction) ($H_2 = 2H$)	$H_p = -168\ 550 + T(-3.920 + 0.3333 \cdot 10^{-3}T)$ $H_v = -168\ 550 + T(-1.935 + 0.3333 \cdot 10^{-3}T)$

TABLE 34

HEAT OF COMBUSTION OF CARBON MONOXIDE AT CONSTANT VOLUME
IN B. T. U. PER LB. MOL.

$T = $ abs. temp. F.

T	H_v	T	H_v	T	H_v
500	121 602	2400	118 700	4300	114 688
600	121 636	2500	118 438	4400	114 566
700	121 641	2600	118 176	4500	114 456
800	121 618	2700	117 915	4600	114 358
900	121 568	2800	117 658	4700	114 274
1000	121 493	2900	117 408	4800	114 201
1100	121 395	3000	117 161	4900	114 141
1200	121 274	3100	116 921	5000	114 095
1300	121 135	3200	116 688	5100	114 063
1400	120 976	3300	116 462	5200	114 045
1500	120 800	3400	116 245	5300	114 041
1600	120 608	3500	116 035	5400	114 052
1700	120 402	3600	115 833	5500	114 078
1800	120 183	3700	115 640	5600	114 121
1900	119 955	3800	115 456	5700	114 179
2000	119 716	3900	115 282	5800	114 253
2100	119 470	4000	115 118	5900	114 344
2200	119 217	4100	114 964	....	......
2300	118 960	4200	114 820	....	......

TABLE 35

LOWER HEAT OF COMBUSTION OF HYDROGEN AT CONSTANT VOLUME
IN B. T. U. PER LB. MOL.

$T = $ abs. temp. F.

T	H_v	T	H_v	T	H_v
500	102 994	2400	104 205	4300	102 528
600	103 049	2500	104 232	4400	102 266
700	103 110	2600	104 251	4500	101 981
800	103 174	2700	104 261	4600	101 673
900	103 242	2800	104 260	4700	101 341
1000	103 313	2900	104 247	4800	100 983
1100	103 386	3000	104 223	4900	100 601
1200	103 461	3100	104 188	5000	100 193
1300	103 537	3200	104 139	5100	99 957
1400	103 612	3300	104 076	5200	99 294
1500	103 687	3400	103 988	5300	98 803
1600	103 760	3500	103 906	5400	98 283
1700	103 830	3600	103 798	5500	97 732
1800	103 899	3700	103 672	5600	97 150
1900	103 963	3800	103 529	5700	96 539
2000	104 024	3900	103 369	5800	95 895
2100	104 078	4000	103 188	5900	95 218
2200	104 127	4100	102 989	....	.....
2300	104 170	4200	102 769	....	.....

TABLE 36

LOWER HEATS OF COMBUSTION OF HYDROCARBON GASES AT CONSTANT VOLUME
IN B. T. U. PER LB. MOL.

$T = $ abs. temp. F.

T	Methane CH_4	Acetylene C_2H_2	Ethylene C_2H_4	Ethane C_2H_6	Benzene Vapor C_6H_6	Gasoline Vapor C_8H_{18}	Kerosene Vapor $C_{12}H_{26}$
500	345 986	541 643	574 443	610 987	1 360 027	2 146 739	3 461 619
600	345 733	541 697	575 091	610 393	1 359 540	2 147 299	3 462 697
700	345 552	541 769	574 742	609 819	1 359 184	2 147 980	3 463 956
800	345 444	541 862	574 399	609 267	1 358 966	2 148 789	3 465 405
900	345 408	541 979	574 062	608 736	1 358 891	2 149 732	3 467 053
1000	345 443	542 120	573 734	608 228	1 358 968	2 150 812	3 468 905
1100	345 551	542 289	573 416	607 743	1 359 201	2 152 025	3 470 970
1200	345 729	542 487	573 109	607 283	1 359 598	2 153 405	3 473 257
1300	345 981	542 716	572 814	606 847	1 360 164	2 154 929	3 475 772
1400	346 304	542 979	572 534	606 436	1 360 906	2 156 609	3 478 523
1500	346 701	542 279	572 271	606 052	1 361 832	2 158 453	3 481 521
1600	347 168	542 616	572 022	605 694	1 362 947	2 160 464	3 484 770

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