RP546

STANDARD STATES FOR BOMB CALORIMETRY

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ABSTRACT

An examination of the thermodynamics of the conditions existing in bomb calorimetry shows that the heat of combustion per unit mass of substance burned is a function of the mass of sample used, of the initial oxygen pressure, of the amount of water placed in the bomb, and of the volume of the bomb. In order to eliminate the effects of these at present unstandardized variables and to obtain a more generally useful thermal quantity which characterizes the pure chemical reaction for stated conditions, it is suggested that every bomb-calorimetric determination be first corrected (where such correction is significant) so as to give the value of ΔU_R, the change of "intrinsic" energy for the pure isothermal reaction under the pressure condition of 1 normal atmosphere for both reactants and products.

From this value the more generally useful quantity, Q_p, the heat of the pure reaction at a constant pressure of 1 atmosphere is readily calculable. An equation for calculating the correction is given and illustrated by examples. The magnitude of the correction varies from a few hundredths of 1 per cent up to several tenths of 1 per cent according to the nature of the substance burned and the conditions prevailing in the bomb during the combustion.

It is further recommended that, in approving, for the purpose of standardizing a calorimeter, a particular value for the heat of combustion (in the bomb) of a standardizing substance, such as benzoic acid, the value approved be accompanied by specification of the oxygen concentration and of the ratios to the bomb volume of (1) the mass of the sample and (2) the mass of water, together with appropriate tolerances.

An equation is given for correcting to any desired standard temperature the heat measured in the bomb calorimeter.

CONTENTS

I. NOMENCLATURE

(Additional subscripts and superscripts are used in the text as further distinguishing marks)

A	Maximum work.
a, b, c	Coefficients in the chemical formula, $C_aH_bO_c$.
C	Concentration; molal heat capacity.
c	Specific heat.
g	Gram.
(g)	Gaseous state.
h	$=1.70x\ (1+x)$.
g. f. w.	Gram-formula-weight.
(l)	Liquid state.
M	Molecular weight; g. f. w.
m	Mass of sample burned.
m_w	Number of grams of water placed in the bomb.
n	Number of moles or of g. f. w. of substance burned.
n_D	Number of moles of CO_2 in solution in the water in the bomb.
n_M	Number of moles of gas in the bomb after the combustion.
n_{O_2}	Number of moles of O_2 in the bomb before the combustion.
P	Pressure; per cent by weight.
p	Pressure or partial pressure.
p_1	Pressure in the bomb before the combustion.
p_2	Pressure in the bomb after the combustion.
p_w	Vapor pressure of water.
Q	Heat absorbed.
R	Gas constant.
S	Solubility.
s	Heat capacity.
(s)	Solid state.
T	Absolute centigrade temperature.
t	Centigrade temperature.
t_H	Standard temperature °C.
U	Total or intrinsic energy content.

$-\Delta U_B$	Heat evolved during the combustion, per g. f. w. of substance burned.
$-\Delta U_R$	Decrease in intrinsic energy for the pure chemical reaction under standard conditions.
V	Volume of the bomb.
v	Volume.
W	External work.
x	Mole fraction of CO_2 in the gases of the bomb after the combustion.
α	See p. 555.
Δ	Symbol indicating an increase in.
ϕ	Number of moles of O_2 consumed to produce nongaseous products.
π	See p. 539.
μ	See p. 534.

II. INTRODUCTION

The technic of modern calorimetry has been developed to such a degree of precision that it is to-day possible, in some cases, to determine heat of combustion in a calorimetric bomb with a precision approaching 0.01 per cent. If full advantage is to be taken of this degree of precision it is obvious that the process or reaction involved must be defined with the necessary accuracy as regards all factors which can separately or in combination influence the result to this degree of precision. At the present time it is not so defined. In fact, the heat of the bomb process per unit mass of substance burned varies with the actual mass burned and does not belong to any completely defined and clean-cut chemical reaction, and the initial and final states of the system are either incompletely defined or are thermodynamically uninteresting or trivial.

Consider, for example, what takes place in a bomb-calorimetric determination. A certain mass, m, of the substance to be burned is placed in a bomb of volume V (in some cases not stated), together with a small quantity (usually 1 g) of water. The bomb is then filled with oxygen at some pressure, p, and at some temperature, t, neither of which is standardized and one or both of which are, in some cases, not stated. The amount of this initial oxygen is from 3 to 10 times that which is consumed during the combustion. After the completion of the combustion, the system consists of a gaseous phase made up of a mixture of oxygen and carbon dioxide (in some cases in unknown proportions) saturated with water vapor, and a liquid phase which is substantially an aqueous solution of carbon dioxide. These are the conditions for the combustion of substances which contain no elements other than carbon, hydrogen, and oxygen.

The heat obtained in the above process per unit mass of substance burned is a function of the mass of the sample employed, of the volume of the bomb used, of the initial concentration of the oxygen, and of the amount of water initially placed in the bomb. If each of these factors, together with the chemical composition of the material burned, were quantitatively known, the initial and final states of the system would be definite but thermodynamically uninteresting.

If, as is not infrequently the case, the value of some one or more of these factors is not stated by the investigator, the initial or the final state of the system, or both, will be indefinite and the process to which the heat effect belongs will be inadequately defined. It is obvious from the above picture that the process which takes place within the bomb does not start from a definite and standardized initial condition nor end with a definite final condition, either chemically or physically.

Now the initial condition should obviously be (1) pure substance or definite material in a definite phase state or states (solid and/or liquid); and (2) pure gaseous oxygen at some standard concentration; and the final condition should be pure gaseous carbon dioxide and pure liquid water each under some standard pressure. Furthermore, if the excess oxygen undergoes, as it does, a change in condition which is accompanied by a heat effect, due correction must be made therefor, so that only the oxygen consumed will be involved in the process to which the final heat quantity belongs.

At present the bomb calorimeter appears to have no serious competitor for the precise determination of heat of combustion of organic solids and liquids of low volatility, and the exact standardization of conditions as here proposed is necessary, if one is to take full advantage of the highest precision attainable.

The purpose of this discussion is to propose suitable standard states and to describe methods by which the heat of the bomb process may be corrected so as to yield the total or intrinsic energy change for the reaction defined by these standard states. Without such standardization it is impossible to obtain from the existent precise data of bomb calorimetry the frequently wanted quantity ordinarily called the "heat of the reaction at constant pressure." This is to-day almost universally calculated by the simple addition of a ΔnRT quantity to the result obtained with the calorimetric bomb, a procedure which is thermodynamically inexact when applied to calorimetric data of high precision.

III. CALORIMETRY AND THE FIRST LAW OF THERMODYNAMICS

According to the first law of thermodynamics

$$U_2 - U_1 = \Delta U = Q - W \tag{1}$$

U_2 (or U_1, respectively) is the "total," "internal," or "intrinsic" energy of any system in the state 2 (or 1, respectively). ΔU is the increase in this intrinsic energy which takes place when the system changes from state 1 to state 2 by any path. Q is the quantity of heat absorbed by the system during the process and W is the work done by the system on the surroundings. The quantity ΔU is independent of the path and is completely defined by the initial and final states. For isothermal processes three cases are, for practical or conventional reasons of special interest, as follows:

Case 1. $W=0$. For this case $Q_{W=0} = \Delta U$; that is, the increase in intrinsic energy is equal to the heat absorbed. The heat of a process (any process whatsoever) under these conditions is usually designated by Q_v and is commonly called the "heat at constant volume." This designation is somewhat unfortunate for three reasons: (1) Because in general a constant-volume process is not necessarily a zero-work process (for example, when accompanied by external electrical work); (2) because a zero-work process is not necessarily a constant-volume process (for example, when a gas expands into a vacuum); and (3) because constancy of volume alone is not a sufficient characterization of an isothermal zero-work process (since the heat of such a process may also be a function of the pressure, for example).

Case 2. $W = \int p dv = p\Delta v$, where Δv is the volume increase under a constant external pressure p. The heat of the process under these conditions is usually designated by Q_p and is commonly called "the heat at constant pressure." This designation is likewise correct and complete only when the value of the pressure is stated or implied and when all of the work done in the surroundings is accounted for by the volume change in the system.

Case 3. $W = W_{\text{max.}} = A$, where A is the maximum work or "free energy" of the process. This case is rarely encountered in calorimetry except when it is identical with case 2. The corresponding heat quantity has received no special designation although its ratio to the absolute temperature is the "entropy of the process."

Any one of the above heat quantities is, in principle, calculable from any other, but for conventional reasons the quantity Q_p for $p = 1$ atmosphere appears to be the most wanted one.

It will be advantageous therefore to standardize the initial and final states of bomb calorimetry in such a manner as to facilitate the computation of Q_p for $p = 1$ atmosphere. This can be conveniently accomplished by first correcting the quantity Q_v of the bomb process in such a way as to obtain the quantity ΔU for the reaction standardized for a pressure of 1 atmosphere, from which quantity the value of Q_p can be readily computed.

IV. THE NATURE OF THE BOMB PROCESS

Given a substance (or a material) whose composition is expressed by the empirical formula $C_aH_bO_c$. m grams ($= n$ gram-formula-weights) of this material in a thermodynamically defined physical state or states (solid and/or liquid) are placed in the bomb.[1] m_w grams of water are also placed in the bomb, this amount being at least sufficient to saturate the gas phase (volume $= V$ liters) with water vapor. The bomb is then closed and filled with n_{O_2} moles of oxygen, this amount being at least sufficient to ensure complete combustion.

The above quantities will completely define the initial system and this definition will subsist, if the quantities are all increased in the same ratio; that is, the initial state of the system is completely defined by the specification of the quantitative composition and physical state of the substance, by the temperature, and by three ratios; for example, m/V, m_w/V, and n_{O_2}/V.

When the calorimeter fore period has been established, the charge is ignited with the aid of a known amount of electrical energy. When the after period has been established, the heat liberated is computed, corrected to some definite temperature, t_H, and divided by n so as to obtain the quantity $-\Delta U_B$ which we shall designate as the evolved heat of the bomb process per g. f. w. (gram-formula-weight) of material burned at the temperature t_H. $\Delta U_B = Q_v$.

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[1] If the material is volatile, it must be inclosed in a suitable capsule in order to prevent evaporation, and in some cases a combustible wick or admixture with some more easily combustible material must be employed in order to ensure complete combustion. In the latter case we are dealing with a mixture of combustible materials, and the formula $C_aH_bO_c$ should express the empirical composition of this mixture. The heat of combustion of the added material must be separately determined and the two heats are, in principle, not additive in the bomb process.

V. PROPOSED STANDARD STATES FOR CONSTANT-VOLUME COMBUSTION REACTIONS

For the purpose of recording such thermodynamic quantities as heat of formation, free energy of formation, entropy of formation, heat content, etc., for chemical substances, it is necessary to adopt some standard reference state, at least for each of the chemical elements.

From some points of view a logical standard state for each element might be the state of a monatomic gas at zero degrees absolute.[2] For obvious practical reasons, however, it has not hitherto been feasible to advantageously utilize a standard state defined in this way. Most of the compilations of thermodynamic properties of chemical substances define the standard state of a chemical element as the thermodynamically stable form of the element under a pressure of 1 normal atmosphere at the standard temperature (usually 18° or 25° C.).

The immediate requirements of bomb calorimetry will be met, if, in conformity with this general practice, we adopt the following standard states:

1. *For O_2 and CO_2.*—The pure gaseous substance under a pressure of 1 normal atmosphere [3] at the temperature t_H.
2. *For H_2O.*—The pure liquid under a pressure of 1 normal atmosphere [4] at the temperature t_H.
3. *For the substance or material burned.*—In a thermodynamically defined state or states (solid and/or liquid [5]) under a pressure of 1 normal atmosphere [6] at the temperature t_H.

The temperature t_H is the temperature at which the heat of the reaction is desired. For purposes of record this is usually made either 18°, 20°, or 25° C. The utility of thermodynamic data for chemical substances and reactions would be increased, if this temperature could be standardized by international agreement. At all events the temperature coefficient should be stated for each new determination of the heat of a reaction which is recorded in the literature.

The above definitions will make it possible to obtain from the data of bomb calorimetry a clearly defined and generally useful thermodynamic quantity.[7]

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[2] A still more fundamental (but likewise inaccessible) reference state might be pure proton gas and pure electron gas at zero degrees absolute.

[3] For the purposes of bomb calorimetry this pressure is at present indistinguishable from 1 bar (megabarye).

[4] For a condensed phase not in the neighborhood of its critical temperature this pressure is at present calorimetrically indistinguishable from its own vapor pressure or in fact from zero pressure.

[5] For pure substances only one state, solid or liquid, is involved, but for mixtures more than one state or phase may be present. The gaseous state is excluded from the present discussion for two reasons: First, because the heat content of the gas and of its mixtures with oxygen must be evaluated as a function of the pressure; and second, because the bomb calorimeter is not the best instrument for the determination of heats of combustion of gases (or of volatile liquids). The flame calorimeter is more accurate and convenient for such cases. (See Rossini, B. S. Jour. Research, vol. 6, pp. 1, 37, 1931; vol. 7, p. 329, 1931; and vol. 8, p. 119, 1932.)

[6] See footnote 4.

[7] For purposes of computing heats of formation from heats of combustion it is further necessary to adopt standard states for hydrogen and for carbon, and it would be desirable to agree upon values for the heats of formation of water and of carbon dioxide, such international values being subject to revision when desirable, in the same manner as the atomic weight table. Discussion of these questions is, however, outside the scope of this paper. For the combustion of substances which contain elements other than carbon, hydrogen, and oxygen it is likewise necessary to adopt standard states for these elements and for their products of combustion. These cases will not, however, be discussed in the present paper, which will be confined to materials the composition of which can be expressed by the formula $C_aH_bO_c$.

VI. COMPARISON OF THE ACTUAL BOMB PROCESS WITH THAT DEFINED BY THE PROPOSED STANDARD STATES

As contrasted with the actual bomb process, the nature of which has already been discussed in detail, the analogous process defined by the proposed standard states consists solely in the reaction of unit quantity of the substance with an equivalent amount of pure oxygen gas, both under a pressure of 1 atmosphere and at the temperature t_H, to produce pure carbon dioxide gas and pure liquid water, both under a pressure of 1 atmosphere and at the same temperature t_H, the reaction taking place without the production of any external work.

This process is not experimentally realizable. The intrinsic energy change associated with this process is, however, a definite and useful thermodynamic quantity and is equal to $-\Delta U_R$, the decrease in intrinsic energy for the following reaction at t_H° C:

$$C_aH_bO_{c(s)\text{ or }(l),\ 1\text{ atm.}}+\left(a+\frac{b-2c}{4}\right)O_{2(g),\ 1\text{ atm.}}$$

$$=aCO_{2(g),\ 1\text{ atm.}}+\frac{b}{2}H_2O_{(l),\ 1\text{ atm.}} \qquad (2)$$

From this quantity, the heat, Q_p, of the isobaric reaction at 1 atmosphere can be readily calculated by adding the appropriate work quantity.

The quantity, $-\Delta U_R$, of course, differs but slightly from $-\Delta U_B$, the heat of the actual bomb process, and for many purposes the difference is of no importance. Indeed, only a few years ago the two were calorimetrically indistinguishable. To-day, however, this is not always the case. The difference, while small, may be many times the uncertainty in determining the heat of the bomb process and may amount to from a few hundredths of 1 per cent up to several tenths of a per cent of this value, depending upon the particular substance and the experimental conditions of the measurement.

To obtain from the heat, $-\Delta U_B$, of the bomb process, the energy quantity, $-\Delta U_R$, for the process defined by the standard states requires the computation of certain "corrections" the nature of which we will now proceed to discuss.

VII. THE TOTAL ENERGY OF COMBUSTION DEFINED BY THE PROPOSED STANDARD STATES

Since the quantity ΔU for any process is completely defined by the initial and final states of the system, the proposed standard states do not define any particular path. In order to arrive at the value of ΔU_R we are therefore at liberty to make use of any desired imaginary process as long as it does nor violate the first law of thermodynamics. The process employed for this purpose should obviously contain the actual bomb process as one of its steps. Its other steps should be selected on the basis of the availability of the necessary data for computing the ΔU terms for these steps.

A review of the available data for various alternative processes indicates that the following process will yield trustworthy values of the ΔU terms. The process is isothermal at the temperature t_H.

Step 1.—n_{O_2} moles of oxygen at $t_H°$ and 1 atm. are compressed into the bomb which contains n g. f. w. of the substance to be burned and m_w g of liquid H_2O. The initial pressure of the oxygen in the bomb is p_1 atm. at $t_H°$.

$$\Delta U_1 = \Delta U_{O_2}\Big]_1^{p_1} + \Delta U_w + \Delta U_{DO_2} + \Delta U_s \tag{3}$$

ΔU_1 represents the value of ΔU for step 1 and the terms on the right obviously have the following significance:

$\Delta U_{O_2}\Big]_1^{p_1}$ is the increase in the total energy of the oxygen which takes place when it is compressed from 1 to p_1 atm. at $t_H°$;

ΔU_w is the increase in the total energy of the water which accompanies its compression and the evaporation of the amount necessary to saturate the bomb volume, V, which is filled with oxygen at p_1 atm.

ΔU_{DO_2} is the corresponding quantity for the solution of the amounts of oxygen which dissolve in the water and in the substance; and

ΔU_s is the increase in total energy which accompanies the compression of the substance and the evaporation of whatever amount evaporates before the ignition.

Step 2.—The combustion is carried out in the usual way and the quantity $-\Delta U_B$ is calculated for $t_H°$. The final pressure in the bomb is $p_2 + p_w$ atm. at $t_H°$, p_w being the partial pressure of the water vapor in the final system.

$$\Delta U_2 = n\Delta U_B \tag{4}$$

Step 3.—The aqueous solution of $CO_2 + O_2$ is separated from the gas phase and is confined under the pressure $p_2 + p_w$ atm.

$$\Delta U_3 = 0 \tag{5}$$

Step 4.—With the aid of a membrane permeable only to CO_2 the dissolved CO_2 is allowed to escape from its aqueous solution into a space at zero pressure after which it is compressed to 1 atmosphere. The value of ΔU for this process will be called ΔU_D.

$$\Delta U_4 = \Delta U_D \tag{6}$$

Step 5.—The pressure on the water is now reduced to 1 atmosphere and the dissolved oxygen is removed as a gas at 1 atmosphere. At the same time the water vapor present in the bomb at the completion of the combustion is removed in the form of pure liquid water under a pressure of 1 atmosphere.

$$\Delta U_5 = \Delta U'_{DO_2} + \Delta U'_w \tag{7}$$

Step 6.—The gas phase $(O_2 + CO_2)$ in the bomb is now expanded to zero pressure

$$\Delta U_6 = \Delta U_M\Big]_{p_2}^0 \tag{8}$$

in which the subscript M is used to indicate the mixture of O_2 and CO_2.

Step 7.—The O_2 and CO_2 are now demixed at zero pressure

$$\Delta U_7 = 0 \tag{9}$$

Step 8.—The O_2 and CO_2 are each compressed to 1 atmosphere.

$$\Delta U_8 = \Delta U_{O_2}]^1_0 + \Delta U_{CO_2}]^1_0 \tag{10}$$

We started with pure substance, pure water, and pure oxygen at 1 atmosphere and $t°_H$ and we have ended with pure oxygen, pure carbon dioxide and pure water under the same conditions. Consequently ΔU_R for the reaction expressed by equation (2) is given by

$$n\Delta U_R = \Delta U_{O_2}]_1^{p_1} + \Delta U_w + \Delta U_{DO_2} + \Delta U_s + n\Delta U_B + 0 + \Delta U_D + \Delta U'_{DO_2}$$
$$+ \Delta U'_w + \Delta U_M]^0_{p_2} + 0 + \Delta U_{O_2}]^1_0 + \Delta U_{CO_2}]^1_0 = n\Delta U_B + \Delta U_{corr.} \tag{11}$$

and

$$\Delta U_R = \Delta U_B\left(1 + \frac{\Delta U_{corr.}}{n\Delta U_B}\right) \tag{12}$$

The percentage correction which must be applied to ΔU_B in order to obtain ΔU_R is therefore given by

$$(\text{Per cent corr.})_{\text{Total}} = \frac{100\Delta U_{corr.}}{n\Delta U_B} \tag{13}$$

The quantity $\Delta U_{corr.}$ is given by

$$\Delta U_{corr.} = \Delta U'_{corr.} + \Delta U''_{corr.} \tag{14}$$

where

$$\Delta U'_{corr.} = \Delta U_{O_2}]_1^{p_1} + \Delta U_M]^0_{p_2} + \Delta U_{O_2}]_0^1 + \Delta U_{CO_2}]_0^1 + \Delta U_D \tag{15}$$

and

$$\Delta U''_{corr.} = \Delta U_w + \Delta U'_w + \Delta U_{DO_2} + \Delta U'_{DO_2} + \Delta U_s \tag{16}$$

The quantity $\Delta U''_{corr.}$, will be found to be negligibly small in most actual combustions. We shall therefore neglect it in the first instance and return to it later.

The quantity $\Delta U'_{corr.}$ can be written

$$\Delta U'_{corr.} = \Delta U_{gas} + \Delta U_D \tag{17}$$

where

$$\Delta U_{gas} = \Delta U_{O_2}]_1^{p_1} + \Delta U_M]^0_{p_2} + \Delta U_{O_2}]_0^1 + \Delta U_{CO_2}]_0^1 \tag{18}$$

We shall therefore continue our discussion under the following topics:

1. Definitions of some auxiliary quantities.
2. The energy content of the dissolved CO_2. This will give us the quantity ΔU_D.
3. The energy content of the gases. This will give us the quantity ΔU_{gas}.
4. The negligible energy quantities. This will deal with the quantity $\Delta U''_{corr}$.

VIII. DEFINITIONS OF SOME AUXILIARY QUANTITIES

1. THE INITIAL SYSTEM

Given a bomb of volume V liters in which are placed n_{O_2} moles of oxygen and n g. f. w. of the substance or mixture having the composition expressed by the formula $C_aH_bO_c$ and whose heat of combustion in the bomb is $-\Delta U_B$ energy units per g. f. w. There are also placed in the bomb m_w grams of water, a quantity sufficient to saturate the oxygen.

The gram-formula-weight (g. f. w.) of the substance is evidently

$$12a + 1.0078b + 16c \tag{19}$$

The number of moles of oxygen required for the combustion is

$$n_r = \left(a + \frac{b-2c}{4}\right)n + \phi \tag{20}$$

where ϕ is the oxygen consumed in producing nongaseous products other than CO_2 and H_2O; for example, HNO_3, Fe_2O_3, etc. The initial oxygen pressure in the bomb will be

$$p_1 = \frac{n_{O_2}RT(1-\mu_{O_2}p_1)}{V} \tag{21}$$

in which $\mu_{O_2}p_1$ is a small correction term calculable from the equation of state. At 20° C.

$$\mu_{O_2} = 0.0_3732 - 0.0_5225_6p \tag{22}$$

For O_2 pressures between 20 and 40 atmospheres (the range ordinarily met with in bomb calorimetry) this relation may be replaced by the following approximate but sufficiently exact equation:

$$\mu_{O_2} = 0.0_3664 \tag{23}$$

2. THE FINAL SYSTEM

After the combustion, the bomb will contain $(n_{O_2} - n_r)$ moles of O_2, n_{CO_2} $(=an)$ moles of CO_2, and $(\frac{1}{2}bn + \frac{1}{18}m_w)$ moles of water. Part of the water will be in the gaseous state and part of the O_2 and CO_2 in the dissolved state in the liquid water. As explained in steps 3 and 5 of the preceding section, all of the water and the dissolved CO_2 are removed from the bomb leaving a gas phase which contains

$$n_M = n_{O_2} - n_r + n_{CO_2} - n_D \tag{24}$$

moles of gas, where n_D is the number of moles of dissolved CO_2 removed with the liquid water. The dissolved O_2 may be neglected in equation (24).

$$n_M = n_{O_2} - \left(\frac{b-2c}{4}\right)n - n_D - \phi \tag{25}$$

The mole fraction of the CO_2 in the gas phase will be

$$x = \frac{an - n_D}{n_{O_2} - \left(\frac{b-2c}{4}\right)n - n_D - \phi} \tag{26}$$

The pressure of the mixture will be

$$p_2 = \frac{n_M RT(1-\mu_M p_2)}{V} \tag{27}$$

At 20° C., μ_M is given by the equation [8]

$$\mu_M/\mu_{O_2} = 1 + 3.21x(1+1.33x) \tag{28}$$

IX. CORRECTION FOR DISSOLVED CARBON DIOXIDE

After the combustion, the bomb contains $m_w + 9\mathrm{b}n$ g of water. Of this, the amount (see Appendix I, equation (119), p. 556).

$$VC_w = 0.0173V + (0.0_455 + 0.0_328x)p_2V, \text{ g} \tag{29}$$

is in the vapor state at 20° C. Since this will in general be only about 1 per cent of the total, we may substitute the average values $p_2 = 30$ atm., and $x = 0.15$, and the above equation may, with sufficient accuracy for our present purposes, be written

$$VC_w = V[0.0173 + (0.0_455 + 0.0_328 \times 0.15)30] = 0.02V, \text{ g} \tag{30}$$

and the amount of liquid water will be

$$m_w + 9\mathrm{b}n - 0.02V, \text{ g} \tag{31}$$

This amount of liquid water will be saturated with CO_2 at the partial pressure p_2x.

For the range of p_2x values encountered in bomb calorimetry (1 to 8 atmospheres) it will be sufficiently accurate, for the purpose of correcting for dissolved CO_2, to assume that the solubility is proportional to the partial pressure, using a proportionality constant computed from the solubility of CO_2 at about 7 atmospheres. (See fig. 1.) With this assumption the number, S_{CO_2}, of moles of dissolved CO_2 per cm³ of liquid water will be

$$S_{CO_2} = 0.0_3038_2 p_2x, \ M/\text{cm}^3 \text{ at } 20° \text{ C.} \tag{32}$$

The total number, n_D, of moles of dissolved CO_2 will therefore be

$$n_D = 0.0_3038_2 p_2x(m_w + 9\mathrm{b}n - 0.02V) \tag{33}$$

Now the total energy of vaporization of CO_2 from its aqueous solution at 20° C. to produce pure CO_2 gas at 1 atmosphere is 181 liter-atm. per mole.[9] For the n_D moles of dissolved CO_2 we have, therefore,

$$\Delta U_D = 181 \times n_D, \text{ liter-atm.} \tag{34}$$

Since, as will appear later, this term is a small part of the total correction, we may write with sufficient accuracy

$$p_2x = \mathrm{a}nRT(1-\mu_M p_2)/V \tag{35}$$

From equations (23) and (28) we have for $x = 0.15$, $\mu_M = 10^{-3}$. Hence for 20° C. and $p_2 = 30$ atm.

$$p_2x = \mathrm{a}n \times 24.05(1 - 10^{-3} \times 30)/V \tag{36}$$

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[8] From unpublished measurements in this laboratory by the method described by Washburn, B. S. Jour. Research, vol. 9, p. 271, 1932.

[9] Computed from the temperature coefficient of the solubility of CO_2 in water.

and equation (33) becomes

$$n_D=0.0_39\ an(m_w+9bn-0.02V)/V \tag{37}$$

or putting $m_w=1$ g, $9bn=0.55$ g, and $V=1/3$ liter

$$n_D=\text{(approx.)},\ 0.0_39an(1+0.55-0)/0.33 \tag{38}$$
$$=0.004an\ \text{(approx.)} \tag{39}$$

for average calorimetric conditions.

The discussion of this correction is continued on page 541.

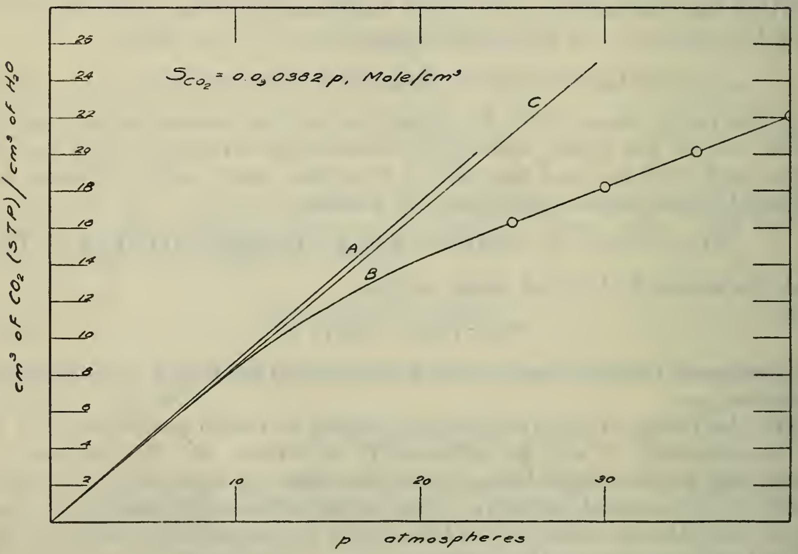

FIGURE 1.—*Solubility of CO_2 in H_2O as a function of the pressure at 20° C.*

The points indicated are taken from International Critical Tables, vol. 3, p. 260. The line *A* is determined by the values at 0 and 1 atmosphere. The locus of the curve *B* is estimated. The line *C* is drawn so as to pass through 0 and the point for 7 atmospheres on the curve *B*. The equation of this line is that shown.

X. THE ENERGY CONTENT OF THE GASES AS A FUNCTION OF THE PRESSURE

Direct calorimetric measurements of $\Delta U]^{p}{}_{1}$ for oxygen and for mixtures of oxygen with carbon dioxide have been made by Rossini and Frandsen.[10] Their results reduced to 20° C. give

$$-\Delta U_{O_2}]^{p}{}_{0}=0.0663p,\ \text{liter-atm./mole at 20° C.} \tag{40}$$

and

$$-\Delta U_{M}]^{p}{}_{0}=0.0663(1+h)p=0.0663[1+1.70x(1+x)]p,\ \text{liter-atm./mole at 20° C.} \tag{41}$$

Both relations are valid for pressures up to 45 atmospheres and for values of x up to 0.4.

For CO_2 between 0 and 1 atmosphere, we shall employ the relation

$$-\Delta U_{CO_2}]^{p}{}_{0}=0.287p,\ \text{liter-atm./mole at 20° C.} \tag{42}$$

which is derived from the Beattie-Bridgeman equation of state.[11]

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[10] Rossini, F. D., and Frandsen, M., B. S. Jour. Research, vol. 9, p. 745, 1932.

[11] See Washburn, B. S. Jour. Research, vol. 9, p. 522, 1932. It is of interest tonote that equation (41) above, when extrapolated to $x=1$ gives $-\Delta U_{CO_2}]^{p}{}_{0}=0.291p$.

XI. CORRECTION FOR THE CHANGE IN ENERGY CONTENT OF THE GASES

We are now in a position to evaluate the quantity ΔU_{gas} as given by equation (18) above, using the number of moles of gas involved.

Performing the summation indicated by that equation between 1 and p atmosphere gives us

$$\begin{aligned}-\Delta U_{\text{gas}} = {} & n_{O_2}\times 0.0663(p_1-1) + n_{\text{M}}\times 0.0663(1+h)(0-p_2) \\ & + n_{CO_2}\times 0.287(1-0) + (n_{O_2}-n_r)0.0663(1-0), \text{ liter-atm.}\end{aligned} \tag{43}$$

This may also be written

$$\begin{aligned}-\Delta U_{\text{gas}} = 0.0663 n_{CO_2}\Bigg[& \frac{n_{O_2}}{n_{CO_2}}p_1 - \frac{n_{O_2}}{n_{CO_2}} - (n_{\text{M}}/n_{CO_2})(1+h)p_2 + \frac{0.287}{0.0663} \\ & + (n_{O_2}-n_r)/n_{CO_2}\Bigg]\end{aligned} \tag{44}$$

or putting $x = n_{CO_2}/n_{\text{M}} = n_{CO_2}/(n_{O_2}-n_r+n_{CO_2})$,

$$-\Delta U_{\text{gas}} = 0.0663 n_{CO_2}\left[p_1\frac{(1-x)}{x} - \frac{(1+h)p_2}{x} + 4.33 + \frac{n_r}{n_{CO_2}}(p_1-1)\right] \tag{45}$$

If we now introduce the relations

$$n_r = \left(\text{a} + \frac{\text{b}-2\text{c}}{4}\right)n + \phi$$

and

$$n_{CO_2} = \text{a}n - n_D = 0.996\text{a}n, \text{ approx.} \quad \text{(See equation (39).)}$$

we have

$$n_r/n_{CO_2} = 1.004\left[1 + \frac{\text{b}-2\text{c}}{4\text{a}} + \phi/\text{a}n\right] \text{approx.} \tag{46}$$

and

$$\begin{aligned}-\Delta U_{\text{gas}} = 0.0660\text{a}n\Bigg[& p_1\frac{(1-x)}{x} - \frac{(1+h)p_2}{x} \\ & + 4.33 + 1.004p_1\left(1+\frac{\text{b}-2\text{c}}{4\text{a}}+\phi/\text{a}n\right) - 1.004\left(1+\frac{\text{b}-2\text{c}}{4\text{a}}+\phi/\text{a}n\right)\Bigg]\end{aligned} \tag{47}$$

$$\begin{aligned}-\Delta U_{\text{gas}} = 0.0660\text{a}n\Bigg[& \frac{p_1-p_2}{x} - p_1 - \frac{hp_2}{x} + 3.33 + 1.004p_1 \\ & + 1.004p_1\left(\left(\frac{\text{b}-2\text{c}}{4\text{a}}\right)+\phi/\text{a}n\right) - 1.004\left(\frac{\text{b}-2\text{c}}{4\text{a}}+\phi/\text{a}n\right)\Bigg]\end{aligned} \tag{48}$$

$$\begin{aligned}-\Delta U_{\text{gas}} = 0.0660\text{a}n\Bigg[& \frac{p_1-p_2}{x} - \frac{hp_2}{x} + 0.004p_1 \\ & + \frac{1.004(p_1-1)(\text{b}-2\text{c}+4\phi/n)}{4\text{a}} + 3.33\Bigg]\end{aligned} \tag{49}$$

and

$$\begin{aligned}(\text{Per cent corr.})_{\text{gas}} = \frac{100\Delta U_{\text{gas}}}{n\Delta U_B} = \frac{6.60\text{a}}{-\Delta U_B}[& (p_1-p_2)/x + 0.004p_1 \\ & - p_2h/x + 1.004(p_1-1)((\text{b}-2\text{c})/4\text{a}+\phi/\text{a}n) + 3.33]\end{aligned} \tag{50}$$

Since one unit in the first decimal place of the terms within the brackets corresponds to less than 0.001 per cent of ΔU_B and since $p_1 \ngtr 45$ atmospheres, it will be sufficiently accurate for all purposes to write

$$(\text{Per cent corr.})_{\text{gas}} = \frac{6.60\text{a}}{-\Delta U_B}\left[-\Delta p\left(\frac{1}{x}+\frac{h}{x}\right)-p_1 h/x + (p_1-1)\left((\text{b}-2\text{c})/4\text{a}+\phi/\text{a}n\right)+3.47\right] \tag{51}$$

which is valid for p_1 and Δp, $(=p_2-p_1)$, in atmospheres and ΔU_B in liter-atmosphere/mole.

XII. CALCULATION OF THE CHANGE IN PRESSURE RESULTING FROM THE COMBUSTION

For computing small pressure changes in the neighborhood of any pressure between 25 and 45 atmospheres, at room temperatures, the pressure of a gas can be taken as given by the relation

$$p = nRT(1-\mu p)/V \tag{52}$$

in which μ is a constant characteristic of the gas, and the temperature. The drop in pressure following the combustion will therefore be

$$-\Delta p = p_1 - p_2 = p_1 - \frac{n_{\text{M}}RT}{V}(1-\mu_{\text{M}}p_2) \tag{53}$$

If we put (see equation (25))

$$n_{\text{M}} = n_{\text{O}_2} - \frac{(\text{b}-2\text{c})n}{4} - n_D - \phi = (\text{a}n - n_D - \phi)/x = \text{a}n/x \text{ (Approx.)} \tag{54}$$

and

$$n_{\text{O}_2} = p_1 V/RT(1-\mu_{\text{O}_2}p_1) \tag{55}$$

this becomes

$$-\Delta p = p_1^2\left[\frac{\mu_{\text{M}}-\mu_{\text{O}_2}+\mu_{\text{M}}\Delta p/p_1}{1-\mu_{\text{O}_2}p_1}+\frac{(1+\Delta p/p_1)x}{p_1}\left(\frac{\text{b}-2\text{c}}{4\text{a}}+\frac{n_D+\phi}{\text{a}n}\right)\right] \tag{56}$$

and

$$-\Delta p = \frac{p_1\left[p_1(\mu_{\text{M}}/\mu_{\text{O}_2}-1)\mu_{\text{O}_2}+(1-\mu_{\text{O}_2}p_1)x\left(\frac{\text{b}-2\text{c}}{4\text{a}}+\frac{n_D+\phi}{\text{a}n}\right)\right]}{1+p_1(\mu_{\text{M}}/\mu_{\text{O}_2}-1)\mu_{\text{O}_2}+(1-\mu_{\text{O}_2}p_1)x\left(\frac{\text{b}-2\text{c}}{4\text{a}}+\frac{n_D+\phi}{\text{a}n}\right)} \tag{57}$$

At 20° C.,

$$\mu_{\text{M}}/\mu_{\text{O}_2}-1 = 3.21x(1+1.33x) \quad \text{(see equation (28).)}$$

$$\mu_{\text{O}_2} = 6.64\times10^{-4} \quad \text{(see equation (23).)}$$

and the above equation becomes

$$-\frac{\Delta p}{p_1}=\frac{x}{1+x}\,\frac{\left[10^{-3}p_1 3.21\,(1+1.33x)\times 0.664+(1-6.64\times 10^{-4}p_1)\left(\frac{\mathrm{b}-2\mathrm{c}}{4\mathrm{a}}+\frac{n_D+\phi}{\mathrm{a}n}\right)\right]}{\left[10^{-3}p_1 3.21\,(1+1.33x)\times 0.664+(1-6.64\times 10^{-4}p_1)\left(\frac{\mathrm{b}-2\mathrm{c}}{4\mathrm{a}}+\frac{n_D+\phi}{\mathrm{a}n}\right)\right]}. \tag{58}$$

or

$$\frac{-\Delta p}{p_1}=\frac{\pi}{1+\pi} \tag{59}$$

For $\frac{n_D}{\mathrm{a}n}$ we have (see equation (37)), for 20° C.

$$\frac{n_D}{\mathrm{a}n}=0.0_39\;\frac{(m_w+9\mathrm{b}n-0.02V)}{V} \tag{60}$$

This gives

$$\pi=x\left[10^{-3}p_1 2.07(1+1.33x)+(1-6.64\times 10^{-4}p_1)\left\{\frac{\mathrm{b}-2\mathrm{c}}{4\mathrm{a}}+\phi/\mathrm{a}n+0.0_39(m_w+9\mathrm{b}n-0.02V)/V\right\}\right] \tag{61}$$

If $\phi=0$, the second term in the expression for π is positive except when $2\mathrm{c}>\mathrm{b}$. π and hence also Δp may therefore be either positive or negative according to circumstances.

The term containing $(m_w+9\mathrm{b}n-0.02V)/V$ is usually very small, almost negligible in fact. For $V=1/3$ liter, and $m_w=1\mathrm{g}$, it ordinarily lies within the range $(42\pm 7)\times 10^{-4}$, and in many cases it will suffice to assume this value for it. In certain particular cases, however, this term is the principal one in the expression for π.

Thus for the case[12] $x=0.149$, $p_1=22$ atm., $\phi=0$, and $\frac{\mathrm{b}-2\mathrm{c}}{4\mathrm{a}}=-1/18$, we have

$$\pi=x[0+0.0_39(m_w+9\mathrm{b}n-0.02V)/V]$$

$$=0.149\times(42\pm 7)\times 10^{-4}=0.0_363\pm 0.0_31 \tag{62}$$

and

$$-\Delta p/p_1=\pi/(1+\pi)=0.0_363\pm 0.0_31 \tag{63}$$

This is negligibly small. In fact any value of $\frac{\Delta p}{p_1}$ within the limits ± 0.001, may be taken as zero.

For most cases an approximate form of equiation (61) will be sufficiently exact. This can be obtained by substituting the average values 0.15 for x and 42×10^{-4} for the last term, giving

$$\pi=x\left[2.07\times 10^{-3}p_1(1+1.33\times 0.15)+\frac{\mathrm{b}-2\mathrm{c}}{4\mathrm{a}}+\phi/\mathrm{a}n+42\times 10^{-4}\right]$$

$$\pi=x\left[2.5\times 10^{-3}p_1+\frac{\mathrm{b}-2\mathrm{c}}{4\mathrm{a}}+\phi/\mathrm{a}n+42\times 10^{-4}\right] \tag{64}$$

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[12] For example, myristicinic acid, $C_9H_8O_5$, or dimethoxydihydroxybenzoic acid, $C_9H_{10}O_6$.

XIII. THE NEGLIGIBLE ENERGY QUANTITIES

1. THE ENERGY CONTENT OF THE WATER

(a) THE CHANGE IN THE ENERGY CONTENT OF THE WATER VAPOR

As a result of the bomb reaction the amount of water present as vapor in the final system at $t_H°$ is greater than that present in the initial system at this temperature. The increase, ΔC_w, in the concentration of water vapor for $t_H = 20°$ C., is given by the equation (see equation (122), Appendix I)

$$\Delta C_w = p_2x\left[0.0_334 - 0.0_305_5\left(1 - \frac{\Delta p}{p_2x}\right)\right], \text{ g/liter} \qquad (65)$$

This increase is accompanied by the absorption of $V\Delta C_w \times 22.82$ liter-atm. of heat energy, 22.82 liter-atm. being the total energy of vaporization of 1 g of H_2O. We have, therefore,

$$\Delta U_w^{\text{vap.}} = 22.82\,Vp_2x\left[0.0_334 - 0.0_305_5\left(1 - \frac{\Delta p}{p_2x}\right)\right], \text{ liter-atm.} \qquad (66)$$

An extreme case would be the following: $V = \frac{1}{2}$ liter, $p_2 = 45$ atm., $x = 0.3$ and $-\Delta p = 2$ atm., and this would give

$$\Delta U_w^{\text{vap.}} = 0.043 \text{ liter-atm.} = 1.0_4 \text{ cal.} \qquad (67)$$

This will rarely amount to more than 0.01 per cent of the heat of the bomb process and will usually be negligible. Since it is opposite in sign to that arising from the quantity ΔU_D, for the dissolved CO_2, a partial compensation will occur and the expressions for the two corrections may advantageously be combined into a single expression representing the algebraic sum of the two effects. This will be done in section 2, below.

(b) THE CHANGE IN THE ENERGY CONTENT OF THE LIQUID WATER

The increase, ΔU_w^{liq}, in the total energy content of liquid water as a function of the pressure upon it is displayed in graphic form by Bridgeman.[13] At 20° C.and for the pressure range encountered in bomb calorimetry this increase is expressed with sufficient accuracy by the equation:

$$\Delta U_w^{\text{liq.}} = -54 \times 10^{-6}P, \text{ liter-atm./g} \qquad (68)$$

In the process defined by the proposed standard states, m_w grams of liquid water are compressed from 1 atmosphere to $(p_1 + p_w)$ atmosphere and $(m_w + 9\text{b}n)$ grams are decompressed from $(p_2 + p_w)$ to 1 atmosphere.

Since we are dealing with a very small energy quantity, we will write $p_1 + p_w = p_2 + p_w = \frac{1}{2}(p_1 + p_2 + 2p_w) = P$ and the net change in the energy content of the liquid water becomes

$$-\Delta U_w^{\text{liq.}} = 9\text{b}n \times 54 \times 10^{-6}P, \text{ liter-atm.} \qquad (69)$$

An extreme case would berep resented by $9\text{b}n = 2\text{g}$ and $P = 45$ atmospheres for which case

$$-\Delta U_w^{\text{liq.}} = 0.005 \text{ liter-atm.} = 0.1 \text{ cal.} \qquad (70)$$

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[13] Bridgeman, P. W., Proc. Am. Acad., vol. 48, p. 348, 1912.

a wholly negligible quantity. Hence for all practical purposes the quantity $\Delta U_w + \Delta U'_w$ is equal to $\Delta U_w^{\text{vap.}}$ as given by equation (66) above.

2. COMBINED ENERGY CORRECTIONS FOR WATER VAPOR AND FOR DISSOLVED CARBON DIOXIDE

The correction for dissolved CO_2 is (see equations (33) and (34))

$$-\Delta U_D = -181 \times 0.0_3038_2 p_2x(m_w + 9\text{b}n - 0.02V), \text{ liter-atm.} \tag{71}$$

and that for the excess water vapor in the final system is (equation (66))

$$-\Delta U_w^{\text{vap.}} = 22.82\ Vp_2x\left[0.0_334 - 0.0_305_5\left(1 - \frac{\Delta p}{p_2x}\right)\right], \text{ liter-atm.} \tag{72}$$

For p_2x we have at 20° C. (see equation (36))

$$p_2x = 23._3\text{a}n/V, \text{ approx.} \tag{73}$$

The sum of equations (71) and (72) combined with (73) and divided by $-0.01n\ \Delta U_B$ will give us the net correction in per cent arising from the two effects in question. We thus obtain the following relation:

$$\text{Per cent corr. } (\Delta U_D + \Delta U_w + \Delta U'_w) = \frac{23._3\text{a}}{0.01\Delta U_B}\left[-0.0066 + 0.0069\frac{(m_w + 9\text{b}n)}{V} - 0.0012_5\frac{V\Delta p}{23._3\text{a}n}\right] =$$
$$\frac{-16.1}{-\Delta U_B/\text{a}}\left[-0.96 + \frac{m_w + 9\text{b}n}{V} - \frac{0.007_8V\Delta p}{\text{a}n}\right] \tag{74}$$

The quantity $-\Delta U_B/\text{a}$, the heat of combustion per gram-atom of carbon, will have its minimum value in the case of oxalic acid, say 1,200 liter-atm., and its maximum value for hydrocarbons, say 7,500 liter-atm. The net correction given by equation (74) will therefore vary in practice (for $V = 1/3$ liter and $m_w = 1$ g) only between about -0.06 and -0.008 per cent. In the majority of cases it will be found to lie between -0.01 and -0.03 per cent.

3. THE ENERGY CONTENT OF THE DISSOLVED OXYGEN

At 20° C. the solubility of O_2 in water is approximately [14]

$$S_{O_2} = 1.2 \times 10^{-6} p_{O_2}, \text{ mole/cm}^3 \tag{75}$$

The amount of O_2 dissolved in the initial water will therefore be

$$n_{DO_2} = 1.2 \times 10^{-6} m_w p_1, \text{ moles} \tag{76}$$

and that in solution in the final water will be

$$n'_{DO_2} = 1.2 \times 10^{-6}(m_w + 9\text{b}n)p_2(1 - x) \tag{77}$$

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[14] Int. Crit. Tables, vol. 3, p. 257 and Frolich, Tauch, Hogan and Peer, Ind. Eng. Chem., vol. 23, p. 549, 1931.

The total energy of vaporization of O_2 from its aqueous solutions at 20° C. to produce O_2 gas at 1 atmosphere is 115 liter-atm./mole. Consequently, if we neglect the oxygen dissolved or adsorbed by the substance,

$$\Delta U_{DO_2} + \Delta U'_{DO_2} = 115\ (n'_{DO_2} - n_{DO_2}),\ \text{liter-atm.} \tag{78}$$

An extreme case would be represented by the following:

$$m_w = 1,\ 9\text{b}n = 2,\ p_1 = 45\ \text{atm.},\ p_2\,(1-x) = 30\ \text{atm.}$$

For this case

$$n_{DO_2}\ \text{is}\ 55 \times 10^{-6},\ n'_{DO_2}\ \text{is}\ 110 \times 10^{-6}$$

and

$$\Delta U_{DO_2} + \Delta U'_{DO_2}\ \text{is}\ 0.0061\ \text{liter-atm.} = 0.15\ \text{cal.}$$

a negligible quantity. Moreover, this correction is opposite in sign to that arising from the quantity $\Delta U_w^{\text{liq.}}$ (equation (69)) and roughly of the same order of magnitude. The two corrections, in addition to being each negligibly small, will therefore substantially cancel each other.

4. THE ENERGY CONTENT OF THE SUBSTANCE

The energy quantity ΔU_s consists of the energy of compression of the substance from 1 to p_1 atmosphere plus the energy of vaporization of whatever amount evaporates before ignition. We shall discuss the two effects separately.

(a) THE ENERGY OF COMPRESSION OF THE SUBSTANCE

By integrating the thermodynamic relation

$$-\left(\frac{\partial U}{\partial p}\right)_T = p\left(\frac{\partial v}{\partial p}\right)_T + T\left(\frac{\partial v}{\partial T}\right)_p \tag{79}$$

between 0 and p atmosphere at any temperature T and reducing the quadratic to the linear equation passing through the value for $p = 30$ atmospheres the following sufficiently exact relation is obtained

$$-\Delta U]_0^p = \alpha p,\ \text{liter-atm./g} \tag{80}$$

in which α is a constant characteristic of the substance and the temperature. In deriving the numerical value for α, the term in the integral which arises from the compressibility $\left(\frac{\partial v}{\partial p}\right)_T$, may be neglected without introducing a significant error for the pressures used in bomb calorimetry.

Table 1 displays the values of α and of $-\Delta U$ for compression to 45 atmospheres, for a number of substances. The last column of the table shows the energy of compression expressed as per cent of the heat of combustion. In all the cases shown the energy of compression is negligible in comparison with the present accuracy with which $-\Delta U_B$ is known.

TABLE 1.—*Energy of isothermal compression*

$$-\Delta U\Big]_0^P=\alpha P, \text{ liter-atm./g}$$

[Data taken from International Critical Tables. M=molecular weight]

Substance	t	$10^6\,\alpha$	$-\Delta U]_0^{45}=45\alpha$	$-\Delta U_B/M$	Per cent corr. $=\frac{M\Delta U}{-0.01\Delta U_B}$
	° C.	*liter/g*	*liter-atm./g*	*liter-atm./g*	
H_2O	20	59	2.6×10^{-3}		
n-Heptane	20	540	24×10^{-3}	475	0.005
n-Heptadecane	25	325	15×10^{-3}	467	.003
Naphthalene	25	82	3.7×10^{-3}	403	.001
Methanol	20	420	19×10^{-3}	220	.009
Acetone	25	417	19×10^{-3}	304	.006
Formic acid	25	248	11×10^{-3}	56.4	.02
Acetic acid	20	305	14×10^{-3}	142	.01
n-Capric acid	25	270	12×10^{-3}	348	.003
Oxalic acid	20	127	5.7×10^{-3}	27.6	.02
Benzoic acid[1]	20	121	5.4×10^{-3}	260	.002

[1] Thermal expansion determined by E. R. Smith (B. S. Jour. Research, vol. 7, p. 903, 1931).

(b) THE ENERGY OF VAPORIZATION OF THE SUBSTANCE

The energy of vaporization of the substance must either be made negligibly small, by suitable inclosure of the sample when necessary, or must be computed and corrected for. A safe rule to follow is to inclose every substance whose vapor pressure is more than 1 mm Hg. If it is not so inclosed, the investigator must show that the energy of vaporization is negligible or he must make the necessary correction.[15]

XIV. THE TOTAL CORRECTION FOR REDUCTION TO THE STANDARD STATES

1. GENERAL CORRECTION EQUATION

By adding together equations (74) and (51) and converting to cal. units, we obtain equation (13) in the form

$$(\text{Per cent corr.})_{\text{Tot.}}=\frac{0.160\,p_1}{-\Delta U_B/\text{a}}\left[\frac{-\Delta p}{p_1}\left(\frac{1}{x}+\frac{h}{x}\right)-h/x+(1-1/p_1)\left(\frac{\text{b}-2\text{c}}{4\text{a}}\right.\right.$$
$$\left.\left.+\phi/\text{a}n\right)-2.4_4(m_w+9\text{b}n)/p_1V+5.8/p_1+\frac{0.019V\Delta p/p_1}{\text{a}n}\right] \qquad (81)$$

in which V is the volume of the bomb in liters; p_1 is the initial O_2 pressure at 20° C., p_2 is the final pressure in the bomb at 20° C., both in atmospheres; $\Delta p=p_2-p_1$; x is the mole fraction of CO_2 in the final system; $h=1.70x(1+x)$; n is the number of gram-formula-weights of the material, $C_aH_bO_c$, burned; m_w is the mass of H_2O initially placed in the bomb; ϕ is the number of moles of O_2 consumed by auxiliary reactions; and $-\Delta U_B$ is the evolved heat of the bomb process in kg-cal.$_{15}$ per gram-formula-weight.

By evaluating this relation for a given combustion we obtain the total correction in per cent which must be applied to the value of $-\Delta U_B$, in order to obtain $-\Delta U_R$, the decrease in intrinsic energy for the chemical reaction, for the standard conditions at 20° C., (equation (2)).

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[15] See footnote 5, p. 530.

Because of the small magnitude of this correction and the small temperature coefficient of ΔU_B, the value of ΔU_B used in equation (81) may be the value for any room temperature and the correction given by the equation may for the same reasons be directly applied to the value of ΔU_B at any room temperature, except possibly in certain extreme cases.

In deriving this relation we have neglected ΔU_s, the energy of compression of the substance plus the energy content of its vapor. This energy quantity is at present negligible and is in any case specific for each substance and is not therefore included in equation (81). It may, however, become significant for some substances, if the accuracy of the determination of $-\Delta U_B$ is increased. (See Table 1.)

If the sample is inclosed in a sealed glass capsule which it does not fill, the quantity ΔU_s becomes zero but in its place we would have the probably negligible energy of compression of the capsule.

We have also neglected the heat of adsorption of water by the sample. When the perfectly dry weighed sample is placed in the bomb and the latter closed, the sample is in contact with saturated water vapor. It immediately proceeds to adsorb water and to evolve or absorb heat. The amount of water adsorbed depends upon the nature of the sample, the surface exposed and the time of contact with the water vapor. Presumably the amount thus adsorbed has become substantially constant by the time the calorimeter fore period has been determined. The charge is now ignited and the adsorbed water appears as liquid water in the final system. The observed heat of combustion will therefore be less than the true value by the amount of heat required to convert this adsorbed water into liquid water. Since the correction here involved is specific for the substance burned and varies with the surface exposed and the conditions of the experiment, it can not be provided for in equation (81). For hygroscopic substances it might be very appreciable and difficult to determine and correct for. Such substances should therefore be inclosed in a suitable capsule.

2. AN APPROXIMATE CORRECTION EQUATION

The calculation of the total correction by means of equation (81) is somewhat time consuming and it is desirable for many purposes to have available a simpler equation for rapid calculation. Such an equation can be obtained, with some loss of accuracy and generality, by introducing certain approximations into equation (81) and taking advantage of certain fortuitous compensations for typical calorimetric conditions. In this way the following approximate equation may be obtained, for p_1 in atmosphere, for $-\Delta U_B$ in kg-cal$_{.15}$ per g. f. w., for a bomb volume of ⅓ liter, for $\phi = 0$, and for $m_w = 1$ g.

$$(\text{Per cent corr.})_{\text{Total}} = \frac{0.30 p_1}{-\Delta U_B/\text{a}}\left[-1 + 1.1\frac{\text{b}-2\text{c}}{4\text{a}} - \frac{2}{p_1}\right] \text{ approx.} \qquad (82)$$

This approximate equation will in general give a value for the (per cent corr.)$_{\text{Total}}$ which is accurate within 15 per cent of itself, a degree of accuracy which is sufficient for correcting most of the now-existing data of bomb calorimetry.

XV. THE MAGNITUDE OF THE CORRECTION IN RELATION TO THE TYPE OF SUBSTANCE BURNED

It will be noted that of the terms in the parenthesis of equation (82), only the second depends upon the nature of the substance burned. The extreme values possible for this term are: (1), 1.1×0.5 for all hydrocarbons and mixtures of hydrocarbons whose net composition is approximately expressed by the empirical formula C_aH_{2a}; and (2), $1.1\ (-0.75)$ for oxalic acid; with the value zero for all carbohydrates, carbon itself, and certain aldehydes.

The magnitude of the correction for these three types of substances is illustrated in Table 2 for three different values of the initial O_2-pressure.

TABLE 2.—*Illustrating the magnitude of the correction for reducing the data of bomb calorimetry to the proposed standard states*

$$\text{Per cent corr.}_{\text{Approx.}} = \frac{0.30p_1}{(-\Delta U_B)/a}\left[-1+1.1\frac{b-2c}{4a}-\frac{2}{p_1}\right]$$

Type of substance	$\frac{b-2c}{4a}$	$\frac{(-\Delta U_B)}{a}$	Per cent correction for		
			$p_1=20$	$p_1=30$	$p_1=40$ atm.
		kg-cal.$_{15}$			
Hydrocarbons of the types $CaH_{2a\pm\not>2}$	0.5	150	-0.02_2	-0.03_1	-0.04_0
Carbohydrates, certain aldehydes, etc	.0	110	$-.06_0$	$-.08_7$	$-.11_4$
Oxalic acid	−.75	30	$-.3_8$	$-.5_6$	$-.7_5$

XVI. COMPUTATION OF THE CORRECTION

1. GENERAL REMARKS

In computing the correction for reduction to the standard states, it is necessary to reduce each experimental value separately; that is, before averaging, unless the experimental conditions (values of p_1, m, and m_w) are substantially the same for all experiments. By making these conditions the same (see Table 5), the values of $-\Delta U_B$ may be averaged first and the correction applied to the average, thus greatly reducing the amount of computation required.

Before averaging, each observed value of $-\Delta U_B$ must first be corrected to the same temperature, t_H. The method of making this correction is discussed below. (See Sec. XVIII.)

A convenient computation form is illustrated by the chart of Table 3. The first horizontal section of the chart provides for the entry of the necessary numerical values of the initial conditions. The second section provides similarly for the final conditions. The third section contains the steps in the calculation and the final result to which they lead.

In case the sample is a pure substance, the coefficients a, b, and c in the empirical formula, $C_aH_bO_c$, will be known. If the sample is a mixture, the exact composition of which is unknown, this composition must first be determined. This may be accomplished in all cases by making a combustion analysis, from the results of which an empirical formula for the mixture can be computed. If, as is frequently the case, the mixture is made up of known amounts of two constituents, of known compositions, then the composition of the mixture and its empirical formula are calculable. (See Appendix II.)

TABLE 3.—*Illustrating the computation of the correction for reduction to the standard states*

$$(\text{Per cent corr.})=\frac{0.160p_1}{-\Delta U_B/a}\left[\frac{-\Delta p}{p_1}\left(\frac{1}{x}+\frac{h}{x}\right)-\frac{h}{x}+(1-1/p_1)\left(\frac{b-2c}{4a}+\frac{\phi}{an}\right)-2.44\ (m_w+9bn)/p_1V+5.8/p_1+0.019V(\Delta p/p_1)/an\right]$$

				R. D. and B.	J. and S.	D.	F. and W.	Oxalic acid+kerosene		Kerosene
1	2	3	4	5	6	7	8	9	10	11
Initial conditions	1	Substance or material $=C_aH_bO_c$		$C_7H_6O_2$	$C_7H_6O_2$	$C_7H_6O_2$	$C_7H_6O_2$	$CH_{1.624}O_{0.0564}$	$CH_{1.370}O_{1.326}$	$CH_{2.12}$
	2	M=g. f. w.=12a+1.0078b+16c	gram	122.05	122.05	122.05	122.05	27.47	34.59	14.14
	3	m=mass of sample	do	.81±.08	.88	1.51	.9	1.3632	2.287	.45
	4	$n=m/M$		.0066	.0072	.0124	.0074	.0496	.0661	.0318
	5	V=volume of bomb	liter	.3	.280	.275	.275	⅓	⅓	⅓
	6	$-\Delta U_B$=heat of combustion per g. f. w	kg-cal$_{15}$/g. f. w	772	772	772	772	101.8	75.0	156.5
	7	m_w=mass of initial H_2O	g	1	1	1	.5	1	1	1
	8	p_T=initial pressure of O_2 at (T°K.=t°C)	Atmosphere	35 (20° C.)	45.5 (20° C.)	30 (20° C.)	45 (20° C.)	35 (20° C.)	35 (20° C.)	35 (20° C.)
	9	$n_{o_2}=p_TV/RT[1+(890-11.3t)10^{-6}p_T]$		.4463	.545	.350	.530	.496	.496	.496
	10	$p_1=n_{o_2}\times 24.05[1-664\times 10^{-6}p_1/V$	Atmosphere	35	45.5	30	45	35	35	35
Final conditions	11	an		0.0462	0.0504	0.0868	0.518	0.0496	0.0661	0.0318
	12	$(b-2c)n/4$		.0033	.0036	.0062	.0037	−.00129	−.0212	+.0169
	13	$n_D=0.0_390an(m_w+9bn-0.02V)/V$=approx. 0.004a$n$.	Equation (37)	.00405an	.00444an	.00545an	.00293an	.00464an	.00488an	.00432an
	14	$x=(an-n_D)/[no_2-(b-2c)n/4-n_D-\phi/an]$	Equation (26)	.1039	.0926	.2513	.0981	.0992	.1274	.0660
	15	$\pi=x[2.5\times 10^{-3}p_1+(b-2c)/4a+\phi/an+0.004_2]$	Equation (64)	.01697	.01755	.03782	.01846	.00652	−.02917	.0410
	16	$-\Delta p/p_1=\pi/(1+\pi)$	Equation (59)	.01668	.01724	.03648	.01812	.00648	−.03005	.0394
	17	$-h/x=-1.70(1+x)$	Equation (41)	−1.876.	−1.857	−2.129	−1.866	−1.868	−1.917	−1.811
	17a	ϕ/an	Equation (88+89)	Assumed to be negligible						
Computation	18	$(-\Delta p/p_1)(1/x+h/x)$		0.1915	0.2182	0.223	0.2184	0.0774	−0.2930	0.6690
	19	$(1-1/p_1)[(b-2c)/4a+\phi/an]$		.0694	.0698	.0690	.0698	−.0253	−.3113	+.515
	20	$-2.44(m_w+9bn)/p_1V$		−.315	−.266	−.494	−.1824	−.361	−.379	−.336
	21	$5.8/p_1$		.166	.127	.193	.129	.166	.166	.166
	22	$0.019V(\Delta p/p_1)/an$		−.0021	−.0018	−.0022	−.0018	−.0008	+.0029	−.0079
	23	Σ Items (17+18+19+20+21+22)		−1.765	−1.710	−2.140	−1.627	−2.012	−2.731	−.805
	24	$0.160p_1/(-\Delta U_B/a)$		.0508	.0660	.0435	.0653	.0550	.0747	.0357
	25	Per cent corr.=item 23×item 24	Per cent	−.0898	−.113	−.093	−.106	−.111	−.204	−.0286
	26	Per cent corr. by approx. equation (equation (82))	do	$-.09_3$	$-.11_9$	$-.080_7$	$-.11_8$	$-.11_2$	$-.19_8$	$-.03_2$

R. D. and B.=Roth, Doepke, and Banse; J. and S.=Jaeger and von Steinwehr; D.=Dickinson; F. and W.=Fischer and Wrede.
NOTE.—Without introducing a significant error, item 13 may in all cases be taken as equal to 0.004an (being in most cases negligible) and item 22 may be taken as zero.

2. COMPUTATION FOR BENZOIC ACID

Columns 5 to 8, inclusive, of Table 3 show the details of the computation for benzoic acid in accordance with experimental data obtained in four different laboratories. In this computation the values shown for p_1 and m are the average values used by the experimenter. The actual values varied somewhat in the different experiments of the same set.

In the computation, the quantity ϕ has been taken as zero, although in each instance some oxygen was consumed in the formation of nitric acid. The inclusion of this quantity would, however, change the final value of $-\Delta U_R$ by less than 0.01 per cent of itself.

For comparison there are entered, as item 26, the values of the (per cent corr.) as computed from the simplified approximate formula (equation (82)).

3. COMPUTATION FOR A MIXTURE

The method of computing the correction for the combustion of mixtures may be illustrated by the case of oxalic acid.

Owing to the low heat of combustion of oxalic acid, the correction for this substance is the maximum which will ever be encountered. The heat of combustion of oxalic acid is however always determined by mixing it with some other material having a higher heat of combustion. The most precise data available for this substance appear to be those of Verkade, Hartman, and Coops,[16] who burned a mixture of oxalic acid with a "paraffin oil" (apparently a kerosene) using varying proportions of the two in different experiments. In order to obtain, from data of this character, the heat of combustion of oxalic acid under standard conditions, it is necessary to reduce to standard conditions the heat of combustion of the mixture and the heat of combustion of the paraffin oil and to take the difference of the reduced values. In Table 4 are given the experimental data and final results of two of the Verkade experiments. The two selected are those representing the extremes of the ratio of oxalic acid to paraffin oil.

TABLE 4.—*Heat of combustion of oxalic acid*

g of oxalic acid m	g of paraffin oil m'	Formula of mixture [1]	Temperature rise Δt_B	Calculated heat of combustion of oxalic acid H	100γ= per cent corr.	True heat of combustion for standard conditions $=-\Delta U_R/M$
1	2	3	4	5	6	7
			° *C.*	*g-cal.*$_{15}$/*g*		*g-cal.*$_{15}$/*g*
0.96620	0.39700	$CH_{1.624}O_{0.864}$	1.6690	678.8	0.661	674.$_3$
1.97320	.31395	$CH_{1.370}O_{1.326}$	1.5900	676.9	.659	672.$_4$

[1] Calculated on the assumption that the paraffin oil contained 15 per cent of hydrogen. For detail of calculation see Appendix II, p. 557.

The values, H, in column 5 are those computed by Verkade by the customary procedure, namely, by subtracting from the total heat the amount $m'H'$ and dividing the difference by m; H' being the heat of

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[16] Verkade, P. E., Hartman, H., and Coops, J., Rec. trav. chim., vol. 45, p. 376, 1926.

combustion, per gram, of the paraffin oil as determined in a separate experiment in which m is made zero and m' such as to give about the same temperature rise, 1.6° C.

Now if 100 γ is the correction in per cent which must be subtracted from the values of H in column 5 in order to obtain the true value for the heat of combustion of oxalic acid under standard conditions, then it can be readily shown that

$$\gamma = \gamma_M + \frac{m'H'}{mH}\left(\gamma_M - \gamma'\right) \tag{83}$$

where 100 γ' is the corresponding per cent correction for the combustion of the paraffin oil alone and 100 γ_M the correction for the mixture of the oxalic acid and the paraffin oil.

In order to compute the corrections γ' and γ_M it is necessary to know the empirical composition of the paraffin oil used. This is not stated by Verkade, and consequently the actual corrections can not be computed. If, however, we proceed on the assumption that the oil is composed of 15 per cent hydrogen and 85 per cent carbon, we will obtain a value for 100 γ which at all events will be of the right order of magnitude and which will serve to illustrate the great importance of the correction in this instance.

In computing the corrections the volume of the bomb used by Verkade will be assumed to be 1/3 liter. The actual volume is unfortunately not stated by Verkade.

The computation of the correction γ_M for the two mixtures shown in Table 4, as well as the computation of γ' for the combustion of 0.450 g of the paraffin oil in the same bomb, is shown in Table 3, columns 9, 10, and 11.

Substituting these values in equation (83) we obtain the values of 100 γ shown in column 6 of Table 4 and the correspondingly corrected values of H shown in column 7.

XVII. CORRECTIONS FOR IRON WIRE AND FOR NITROGEN

Most of the existing heats of combustion have been corrected by the observers for the heats of formation of small amounts of Fe_2O_3 and of $HNO_3aq.$, the latter of which is formed when nitrogen is present in the oxygen used. If we call the corrections (in per cent) thus applied by the observer (per cent corr. $_{Fe}$) and (per cent corr.$_N$), respectively, then the amount of HNO_3 produced must have been

$$n_{HNO_3} = (\text{per cent corr.}_N) \times (-\Delta U_R)n/1{,}455, \text{ mole} \tag{84}$$

where 14.55 kg-cal.$_{15}$ is the total energy of formation, from N_2, O_2 and H_2O(l) of 1 mole of $HNO_3aq.$ at the average normality $\frac{N}{4}$ and $(-\Delta U_R)$ is expressed in kg-cal.$_{15}$/mole.

The formation of this HNO_3 affects the situation principally in three ways. It changes the value of x, it reduces the amount of water vapor in the final system, and it affects the solubility of carbon dioxide in the water.

We shall consider the three effects separately.

The effect on x.—Since the amount of N_2 in the bomb before ignition is almost never recorded by the investigator and is usually not known to him, we shall make use of the approximate equivalence of the molecular weights and energy contents of N_2 and O_2 and shall assume that the N_2, except so far as it combines with the O_2, can be treated as so much excess O_2. Its only effect upon the quantity ΔU_{gas} will therefore reside in its effect upon x. A corresponding effect will also be produced by the combustion of any iron wire. These two effects will combine and equation (26) will read as follows:

$$x \quad \frac{\mathrm{a}n - n_D}{n_{\mathrm{O2}} - \left(\frac{\mathrm{b}-2\mathrm{c}}{4}\right) n - n_D - \phi_{\mathrm{N}} - \phi_{\mathrm{Fe}}} \tag{85}$$

in which ϕ_{N} is given by

$$\phi_{\mathrm{N}} = \frac{7}{4}\,(\text{per cent corr.}_{\mathrm{N}})(-\Delta U_{\mathrm{R}})n/1{,}455 \tag{86}$$

and ϕ_{Fe}

$$\phi_{\mathrm{Fe}} = \frac{3}{2}\,(\text{per cent corr.}_{\mathrm{Fe}})\ (-\Delta U_{\mathrm{R}})\ n/19{,}000 \tag{87}$$

Example

$$\phi_{\mathrm{N}} = \frac{7}{4}\,(\text{per cent corr.}_{\mathrm{N}})\left(-\frac{\Delta U_{\mathrm{R}}}{\mathrm{a}}\right)\mathrm{a}n/1{,}455 \tag{88}$$

Put $\quad -\frac{\Delta U_{\mathrm{R}}}{\mathrm{a}} = 100$ and (per cent corr.$_{\mathrm{N}}$) $= 0.2$

Hence

$$\phi_{\mathrm{N}} = 0.024\mathrm{a}n$$

$$\phi_{\mathrm{Fe}} = \frac{3}{2}\,(\text{per cent corr.}_{\mathrm{Fe}}) \times 100\mathrm{a}n/19{,}000$$

$$= 0.0079\ (\text{per cent corr.}_{\mathrm{Fe}})\ \mathrm{a}n \tag{89}$$

Put (per cent corr.$_{\mathrm{Fe}}$) $= 0.05$.
Hence $\phi_{\mathrm{Fe}} = 0.0_34\mathrm{a}n$.
Total

$$\phi_{\mathrm{N}} + \phi_{\mathrm{Fe}} = 0.0244\mathrm{a}n \tag{90}$$

which may be compared with $n_D = 0.004\mathrm{a}n$ and $n_{\mathrm{O_2}} \nless 3\mathrm{a}n$, in equation (85).

It is obvious that the combustion of the iron wire in the amount ordinarily employed is wholly negligible as regards its effect upon x. The effect of the nitrogen on x is appreciable, but also probably negligible for all practical purposes. Since, however, its effect can be readily computed all doubt can be eliminated by computing the quantity x by means of equation (85).

Effect on $\Delta U_w^{\mathrm{vap.}}$.—In the final system in the bomb the concentration of water vapor is (see equation (119), Appendix I).

$$C'_w = 0.0173 + (0.0_455 + 0.0_328x)p_2$$

$$= 0.0173 + 0.0_455 \times 30 + 0.0_328p_2x$$

$$= 0.019 + 0.0_328 \times 24\mathrm{a}n/V$$

$$= (0.019 + 0.0069\mathrm{a}n/V),\ \text{g/liter} \tag{91}$$

If now the water contains HNO_3 at such concentration ($N_{\mathrm{HNO_3}}$ mole/liter) that its partial vapor pressure is reduced by the fractional amount $-\frac{\Delta p_w}{p_w}$, its concentration in the vapor will be reduced by the amount

$$\frac{-\Delta C'_w}{C'_w}=\frac{-\Delta p_w}{p_w}=0.03N_{\mathrm{HNO_3}} \tag{92}$$

and

$$\begin{aligned}-\Delta C'_w&=0.03N_{\mathrm{HNO_3}}(0.019+0.0069\mathrm{a}n/V)\\&=\frac{[0.03(\text{per cent corr.}_{\mathrm{N}})(-\Delta U_{\mathrm{R}})n/1{,}455](0.019+0.0069\mathrm{a}n/V)}{(m_w+9\mathrm{b}n)\times 10^{-3}}\\&=\frac{0.0206(\text{per cent corr.}_{\mathrm{N}})(-\Delta U_{\mathrm{R}})n(0.019+0.0069\mathrm{a}n/V)}{(m_w+9\mathrm{b}n)},\ \text{g/liter}\end{aligned} \tag{93}$$

The energy required to evaporate this water is therefore $22.82V\Delta C'_w$, liter-atm.

or

$$\Delta(\Delta U_w^{\mathrm{vap.}})=\frac{0.0114V(\text{per cent corr.}_{\mathrm{N}})(-\Delta U_{\mathrm{R}})n(0.019+0.0069\mathrm{a}n/V)}{m_w+9\mathrm{b}n} \tag{94}$$

or

$$\frac{100\Delta(\Delta U_w^{\mathrm{vap.}})}{(-\Delta U_{\mathrm{R}})n}=\frac{1.14\ V\ (\text{per cent corr.}_{\mathrm{N}})\ (0.019+0.0069\mathrm{a}n/V)}{m_w+9\mathrm{b}n} \tag{95}$$

In practice $\mathrm{a}n/V$ usually varies between 0.1 and 0.3, whence

$$\begin{aligned}\frac{100\Delta(\Delta U_w^{\mathrm{vap.}})}{(-\Delta U_{\mathrm{R}})n}&=\frac{1.14\ V\,(\text{per cent corr.}_{\mathrm{N}})\ (0.0203\pm0.0_38)}{m_w+9\mathrm{b}n}\\&=\frac{(0.023\pm0.0_39)\ V\ (\text{per cent corr.}_{\mathrm{N}})}{m_w+9\mathrm{b}n}\end{aligned}$$

For $V=1/3$ liter, $(\text{per cent corr.}_{\mathrm{N}})=0.2$ and $m_w+9\mathrm{b}n=1.5$ this gives 0.001 per cent, a wholly negligible quantity.

Effect on the amount of dissolved carbon dioxide.—There are no data on the solubility of carbon dioxide in aqueous solutions of nitric acid for CO_2-pressures of the magnitudes encountered in bomb calorimetry. For pressures in the neighborhood of 1 atmosphere the data in International Critical Tables (vol. 3, p. 279) indicate that the solubility of CO_2 in 1/4 N HNO_3 at 25°C. is about 0.9 per cent greater than in pure water. Such a difference would of course be negligible, since the total CO_2 correction will never exceed 0.06 per cent.

In view, however, of the various corrections and uncertainties introduced by the presence of nitrogen in the bomb it is obvious that in bomb calorimetry of the highest accuracy nitrogen-free oxygen should be employed and the air should be swept out of the bomb.

XVIII. REDUCTION OF BOMB CALORIMETRIC DATA TO A COMMON TEMPERATURE

In the actual calorimetric determination, the calorimeter and its contents undergo a rise in temperature

$$\Delta t_B=t_2-t_1 \tag{96}$$

as a result of the bomb reaction. In order to obtain, from this observed temperature rise, the heat of the bomb process at some constant known temperature, t_H, it is necessary to know the effective heat capacity, s_I, of the initial system and/or the effective heat capacity, s_F, of the final system. The effective heat capacity of any system, substance or material is the quantity of heat which must be added thereto in order to raise its temperature from t to t', divided by $(t'-t)$.

If s_B is the effective heat capacity of the calorimetric system itself, then the heat evolved by the bomb process at the constant temperature, $t_H°$, will be

$$-\Delta U_B n = s_B(t_2-t_1)+s_I(t_H-t_1)+s_F(t_2-t_H) \qquad (97)$$

The temperature, t_H, may be any desired value whatsoever. If, as is usually the case (although not at all necessary), it is made equal to t_1 or to t_2, one of the terms in the above expression reduces to zero.

For use in equation (97) above, the following values (average for 25° C.) for s_I and s_F are sufficiently accurate for any value of Δt_B within the region of room temperatures.

$$s_I = 5.01 n_{O_2} + 0.995 m_w + 0.7V + \Sigma m c_p + 0.108 m_{Fe}, \text{ cal.}_{15} \text{ deg.}^{-1}\text{C} \qquad (98)$$

$$s_F = 5.01 n_{O_2} + 0.995 m_w + 0.7V + 0.158 m_{Fe} + n[(1.77_1 + 0.0112 p_2)\text{a} + 7.74\text{b} + 2.5\text{c}] - 34 n_{HNO_3}, \text{ cal.}_{15} \text{ deg.}^{-1}\text{C} \qquad (99)$$

in which

n_{O_2} = g-moles of O_2 in the bomb initially.
m_w = g of H_2O in the bomb initially.
V = volume of bomb in liter.
$\Sigma m c_p$ = the total heat capacity, at constant pressure, of the carbonaceous material or materials burned, cal.$_{15}$ deg.$^{-1}$ C.
n = the number of gram-formula-weights of carbonaceous material burned, the total composition of which is expressed by the empirical formula $C_aH_bO_c$.
$p_2 = p_1 + \Delta p$ = final pressure in the bomb.
m_{Fe} = g of iron wire burned to Fe_2O_3.
n_{HNO_3} = gram-formula-weights of HNO_3 formed.
= (per cent corr.) $_{HNO_3}$ $(-\Delta U_B)n/1{,}455$.
(Per cent corr.)$_{HNO_3}$ = per cent correction applied to $-\Delta U_B$ for the heat of formation of a small amount of HNO_3.

In deriving equations (98) and (99) account has been taken of the variation of the heat capacity of the gases and of the liquid water with pressure. The term $0.7V$ takes care of the latent heat of vaporization of the water and the term $34 n_{HNO_3}$ of the heat capacity of the dissolved HNO_3.

XIX. THE TEMPERATURE COEFFICIENT OF THE HEAT OF COMBUSTION

Using the specific heat data given in International Critical Tables, the following equation, valid strictly over the interval between 20° and 30° C., but sufficiently accurate for all practical purposes over any temperature interval in the region of room temperatures, can be readily derived

$$\frac{100(\Delta U'_{\mathrm{R}}-\Delta U_{\mathrm{R}})}{\Delta U_{\mathrm{R}}(t'-t)}=\frac{-100}{-\Delta U_{\mathrm{R}}}(1.78\mathrm{a}+7.74\mathrm{b}+2.492\mathrm{c}-C^{s}_{p}),\text{ per cent per deg.} \qquad (100)$$

in which $-\Delta U_{\mathrm{R}}$ is the evolved heat of the reaction (decrease in intrinsic energy) for standard conditions and C^{s}_{p} the heat capacity (under constant pressure) of the substance, both for 1 gram-formula-weight and in cal.$_{15}$ units. A survey of the existing data for CH and CHO compounds shows that in all cases this coefficient is less than 0.01 per cent per degree, and if we assume that it will never be applied over a range of more than 10°, then it is obvious that the allowable error in the coefficient is >0.0005; that is, >5 per cent of the coefficient itself.

The temperature coefficient of $-\Delta U_B$, the heat of the bomb process, differs from equation (100) only to a negligible extent for any temperature range in which it should ever be required. It can be obtained from the difference between equations (98) and (99).

XX. STANDARDIZING SUBSTANCES

The effective heat capacity of a bomb calorimeter is customarily determined by making a series of combustions with a substance for which the value of $-\Delta U_B$ is accurately known. The substance benzoic acid is the working standard chosen for this purpose and the value selected for its heat of combustion at 20° C. is based upon determinations made by several laboratories. The value selected in this way has been approved by the International Union of Chemistry as the official value of $-\Delta U_B$ for benzoic acid.

In specifying this particular value, however, the conditions under which it is valid are, unfortunately, inadequately defined. The conditions under which the various determinations of the value have been made were quite different in several respects, and the rather close agreement obtained by the different laboratories has apparently been interpreted as indicating that specification of these conditions is unnecessary. This, however, can not be the case, as will be shown below, and the close agreement obtained by the various observers must have resulted to a considerable degree from the fortuitous compensation of several influences and to some extent perhaps from an accidental compensation of errors.

XXI. STANDARD CONDITIONS FOR CALORIMETRIC STANDARDIZATIONS

For determining the thermal quantities associated with a chemical reaction or physical process it is essential to so define the initial and final states that the resultant thermal quantities will be utilizable for combining with other available thermodynamic data.

For the combustion of a standard substance used to determine the effective heat capacity of a calorimeter, however, this is not essential. All that is required is a sufficient definition of the initial conditions and a knowledge of the value of $-\Delta U_B$ for the substance under these conditions. For a given standardizing substance, for example benzoic acid, it is sufficient to specify the values of the following ratios: m/V, m_w/V, n_{O_2}/V, and the temperature, t_H.

m/V.—The mass of benzoic acid per liter of bomb space has in practice usually varied between about 1.9 and 3.9 g. Apparently

any convenient value between these limits might be selected as the standard value for this quantity.

m_w/V.—The mass of initial water per liter of bomb space has usually been about 3 g, and this is a satisfactory value.

n_{O_2}/V.—This factor will be completely determined, if the initial oxygen pressure at some temperature is specified. In practice this pressure, at room temperatures, has varied between about 22 and 45 atmospheres. Apparently any value within these limits is sufficient to ensure complete combustion, although more accurate data on this question are needed. Perhaps 30 atmospheres at 20° C. would be a good value to adopt.

Should it ever be necessary or desirable to depart from one or more of these standard conditions in using benzoic acid for standardizing a calorimeter, the corresponding change which should be made in the standard value of $-\Delta U_B$ is calculable.

Once having agreed upon the standard conditions, the tolerance for each value should also be stated. An example is shown in Table 5.

TABLE 5.—*Illustrating standard conditions and tolerances for benzoic acid as a standardizing substance for bomb calorimetry*

Assumed standard conditions	Assumed tolerance ±	Error produced by just exceeding the tolerance. ± per cent of $-\Delta U_B$
p_1=30 atmospheres at 20° C	1.0 atmosphere	0.003_4
$\frac{m}{V}$=3 g/liter	0.5 g/liter	$.002_5$
$\frac{m_w}{V}$=3 g/liter	0.3 g/liter	$.001_1$
Maximum error, per cent		.007

XXII. THE HEAT OF COMBUSTION OF STANDARD BENZOIC ACID

The various determinations of the heat of combustion of benzoic acid have recently been reviewed by Roth.[17] After reducing them to the same energy and mass units he finds the following values for 20° C.

	Int. kj. per g
Fischer and Wrede	26. 449
Dickinson	26. 436
Jaeger-v. Steinwehr	26. 437
Roth, Doepke, Banse	26. 433

Roth selects the average of the last three values, namely, 26.435, as the "best value."

Now the four determinations in question were obtained under different experimental conditions; that is, with different values of p_1, m/V, m_w/V, and the apparent good agreement is partly fortuitous. In order to compare these values we must first correct them to a common set of conditions. We shall adopt for this purpose the

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[17] Roth, Z. physik. Chem., vol. 136, p. 317, 1928.

conditions $p_1 = 30$ atm., $m/V = 3$ g/liter, and $m_w/V = 3$ g/liter (see Table 5.) So corrected[18] the values become

	Int. kj. per g
Fischer and Wrede	26. 440
Dickinson	26. 439
Jaeger-v. Steinwehr	26. 427
Roth, Doepke, Banse	26. 430

The agreement is now not so good, but the average of all four is still 26.434 with an apparent uncertainty of not more than 7 joules. There is, therefore, no reason at the present time for changing the value adopted by the International Chemical Union, provided the standard conditions assumed above are also adopted. There is, however, need for new determinations of this important quantity under more exactly controlled conditions than have prevailed heretofore.

If now we assume the value 26.434 kj/g for $-\Delta U_B$ when $p_1 = 30$ atm., $m/V = 3$ g/liter, and $m_w/V = 3$ g/liter, then the value of $-\Delta U_R$ for the pure reaction

$$C_7H_6O_2\,_{(s),\ 1\ \mathrm{atm.}} + 7\tfrac{1}{2}\ O_2\,_{(g),\ 1\ \mathrm{atm.}} = 7CO_2\,_{(g),\ 1\ \mathrm{atm.}} + 3H_2O\,_{(l),\ 1\ \mathrm{atm.}}$$

will be 0.08 per cent less (see Table 3) or 26.413 × 122.05 kj. per gram-formula-weight.

It is, of course, this latter value (or rather the corresponding one for $-Q_p$, the heat of the pure reaction under a constant pressure of 1 atmosphere) which would appear for benzoic acid in tables of heats of combustion of chemical substances. The former value $-\Delta U_B$ is applicable only to the use of benzoic acid as a standardizing substance for bomb calorimetry.

APPENDIX I. CONCENTRATION OF SATURATED WATER VAPOR IN GASES AT VARIOUS PRESSURES

Within the pressure range involved in bomb calorimetry the concentration of saturated water vapor varies with the temperature according to the equation

$$\log_{10} C_w = \frac{A}{T} + I \qquad (101)$$

A is a constant characteristic of water and independent of the composition and pressure of the gas phase. (See fig. 2.) I is a function of the composition and pressure of the gas phase.

For water at 25° C. and under its own vapor pressure, we have

$$C_w = \frac{m}{V} = 0.02302 \text{ g/liter} \qquad (102)$$

and for 70°

$$C_w = 0.1967 \text{ g/liter} \qquad (103)$$

Hence for equation (101) we find

$$\log_{10} C_{w(\mathrm{g/liter})} = \frac{-2{,}117}{T} + (I = 5.465) \qquad (104)$$

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[18] An additional correction for temperature has been applied to the Dickinson value since the writer is advised by Doctor Dickinson that this value is for 25° C. (approx.) instead of 20° C.

Within the range of pressures and gas compositions met with in bomb calorimetry the concentration of saturated water vapor varies with the pressure according to the equation

$$C_w = C_0 + \alpha P \tag{105}$$

C_0 is a temperature function only and α varies with the nature of the gas phase. Combining this equation with the preceding one we have

$$\log_{10}(C_0 + \alpha P) = \frac{-2{,}117}{T} + I \tag{106}$$

For N_2 at 50° C. Bartlett [19] found $C_0 + \alpha P = 0.095$ g/liter for $P = 50$ atmospheres

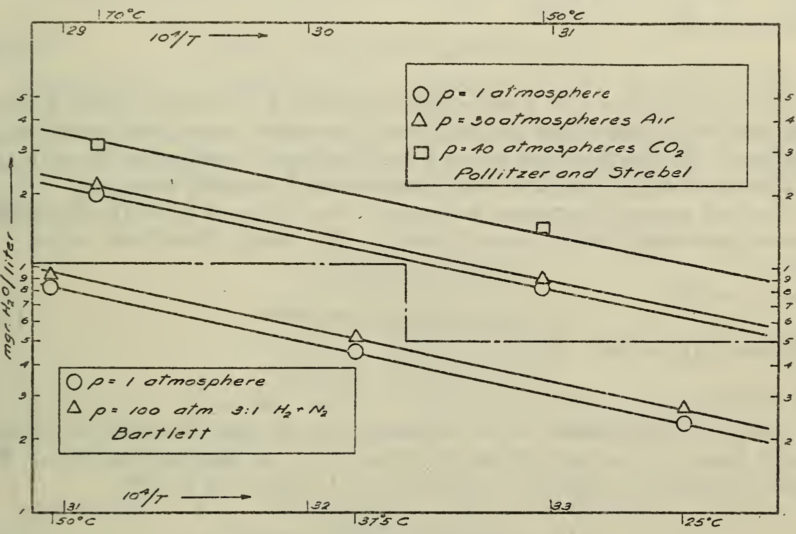

FIGURE 2.—*Temperature variation of the concentration of saturated water vapor in the presence of various gases*

Hence

$$I = 5.530 \tag{107}$$

and at 20° C. and 50 atmospheres

$$\log_{10}(C_0 + \alpha P) = \frac{-2{,}117}{293.1} + 5.530 \tag{108}$$

$$\log_{10} C_0 = \frac{-2{,}117}{293.1} + 5.465 \tag{109}$$

$$C_0 + \alpha P = 1.161 C_0 \tag{110}$$

$$C_0 = 0.01728 \tag{111}$$

$$\alpha = 0.0_4 56 \tag{112}$$

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[19] F. P. Bartlett, J. Am. Chem. Soc., vol. 49, p. 65, 1927.

and

$$C_w = (0.01728 + 0.0_456P), \text{ g/liter for } P \text{ in atm.} \tag{113}$$

For air at 49.9° C. Pollitzer and Strebel[20] found

$$C_0 + \alpha P = 0.099, \text{ g/liter for } P = 72.5 \text{ atm.}$$

accuracy about 1 per cent. These data yield

$$C_w = (0.01728 + 0.0_450\ P), \text{ g/liter at } 20° \text{ C.} \tag{114}$$

For CO_2 at 49.9° C., Pollitzer and Strebel found

$$C_0 + \alpha P = 0.1443, \text{ g/liter for } P = 38.7_2 \text{ atm.}$$

Hence at 20°

$$C_w = (0.01728 + 0.0_334P), \text{ g/liter} \tag{115}$$

Bartlett considers that the experimental data of Pollitzer and Strebel are somewhat too high on account of certain errors in experimental technic. We notice that the α from Bartlett's results for N_2 is 0.0_456 while the data of Pollitzer and Strebel yield 0.0_450 for air.

For our present purposes we require the value of α for O_2, for which no experimental data are available. We shall, therefore, write

for O_2 at 20°

$$C_w = 0.0173 + 0.0_455P \tag{116}$$

and for CO_2 at 20°

$$C_w = 0.0173 + 0.0_334P \tag{117}$$

Bartlett found that C_w for mixtures of H_2 and N_2 could be calculated from the values for the pure gases by the law of mixtures. We shall, therefore, write for mixtures of O_2 and CO_2 at 20°.

$$C_w = C_0 + [\alpha_{O_2}(1-x) + \alpha_{CO_2}x]P \tag{118}$$

$$= 0.0173 + (0.0_455 + 0.0_328x)P \tag{119}$$

The quantity C_0 can be obtained from the expression

$$\log_{10} C_0 = \frac{-2{,}113}{T} + 5.453 \tag{120}$$

which is valid for room temperatures, 16° to 30°.

If C_w is the value for O_2 at the pressure p_1 and C'_w the value for an $O_2 - CO_2$ mixture at the pressure $p_2 = p_1 + \Delta p$, then

$$\Delta C_w = C'_w - C_w = \alpha_{CO_2} p_2 x - \alpha_{O_2}(-\Delta p + x p_2) \tag{121}$$

$$= p_2 x\left[0.0_334 - 0.0_305_5\left(1 - \frac{\Delta p}{p_2 x}\right)\right], \text{ g/liter} \tag{122}$$

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[20] F. Pollitzer and E. Strebel, Z. physik. Chem., vol. 110, p. 708, 1924.

For $p_2=22$ atm., $-\Delta p=3$ atm., and $x=0.3$, this being the most unfavorable case which could occur in bomb calorimetry when $\phi=0$, we have

$$C'_w-C_w=0.00171\pm 3 \text{ per cent} \tag{123}$$

the uncertainty of 3 per cent arising from an estimated uncertainty of 10 per cent in the value assumed for α_{O_2}. From this it may be seen (p. 540) that the uncertainty in the value of α_{O2} is of no practical importance.

Since (see equation (36))

$$p_2x=\frac{RT}{V}(1-0.03)\mathrm{a}n \text{ (approx.)}$$

$$V\Delta C_w=0.080T\times \mathrm{a}n\left[0.0_334-0.0_305_5\left(1-\frac{\Delta p}{p_2x}\right)\right], \text{g; (approx.)} \tag{124}$$

at T°K.

APPENDIX II. EMPIRICAL FORMULA OF A MIXTURE

If two substances or materials containing no elements other than C, H, and O are mixed together in the proportions, m grams of the one and m' grams of the other, the empirical formula of the mixture is CH_bO_c

$$\mathrm{c}=\frac{3(P_Om+P'_Om')}{4(P_Cm+P'_Cm')} \tag{125}$$

$$\mathrm{b}=\frac{12}{1.008}\ \frac{(P_Hm+P'_Hm')}{(P_Cm+P'_Cm')} \tag{126}$$

in which 100 P is the per cent by weight of the element (indicated by the subscript) in the one material and P' is the corresponding quantity for the other material.

APPENDIX III. SUMMARY OF NUMERICAL DATA EMPLOYED

1. Atomic weights—
   C = 12.000.
   H = 1.0078.
   O = 16.

2. Coefficient μ in the equation $p=\dfrac{nRT(1-\mu p)}{V}$—

   For O_2 at 20° C, $\mu=0.0_3664$.
   For O_2-CO_2 mixtures at 20°C., $\mu=0.0_3664[1+3.21x(1+1.33x)]$ where x is the mole fraction of CO_2.

3. Fractional vapor pressure lowering for aqueous solutions of strong electrolytes at 20° C. and N equivalents per liter

$$\frac{-\Delta p}{p}=0.03N$$

4. Concentration of saturated water vapor in contact with gases at various pressures. (See Appendix I, p. 555.)

Total energy of vaporization at 20° C.—

$H_2O = 22.82$ liter-atm/g.

Dissolved gases from an aqueous solution at 20° C.—

CO_2—181 liter-atm/mole.
O_2—115 liter-atm/mole.

5. Total energy of compression as a function of the pressure (in atmospheres), at 20° C.

Units, liter-atm/mole.

O_2, $\Delta U]^p_0 = 0.0663p$.
CO_2, $\Delta U]^p_0 = 0.287p$.
$O_2 - CO_2$ mixtures, $\Delta U]^p_0 = 0.0663[1 + 1.70x(1+x)]p$, where x is the mole fraction of CO_2.

For solids and liquids. (See Table 1, p. 543.)

6. Total energy of formation at 20° C.—

$Fe_2O_{3(s)}$ from its elements = 190 kg-cal.$_{15}$/mole.

$\frac{1}{4}N$ $HNO_3aq.$ from $O_{2(g)}$, $N_{2(g)}$, and $H_2O_{(l)} = 14.55$ kg-cal.$_{15}$/mole.

7. Heat capacity at constant volume and 30 atm.

O_2 at 25° C.—

$C_v = 5.01$ g-cal.$_{15}$/mole.

8. Solubility in water at 20° and a pressure of p atm.—

For O_2, $S_{O_2} = 1.2 \times 10^{-6} p$, mole/cm^3.
For CO_2, $S_{CO_2} = 0.0_3038_2 p$, mole/cm^3.

WASHINGTON, February 13, 1933.