

Thermodynamics of Difference between Gross and Net Heating Values, Solid and Liquid Fuels¹

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THE heating value of a fuel is the heat liberated by the union of the fuel with sufficient oxygen to oxidize it completely. The heat is usually measured by determining the heat given up by the products of combustion in being cooled to the temperature of the original mixture. To make the heating value more definite, it is customary to make these determinations either under constant-volume or constant-pressure conditions.

When fuels containing hydrogen or hydrocarbons are burned, it often occurs that the partial pressure of the water vapor existing in the products is greater than can be maintained by the final temperature of the products which are being cooled to temperature conditions of the initial mixture. This results in enough condensation of water vapor to reduce its partial pressure to that corresponding to the temperature. The heat given up by the water vapor in condensing is greater than the heat which would be given up if the water vapor cooled without condensing, and the difference of these two heats, one from the actual process and the other from a purely hypothetical one, is the difference between the gross and net heating value of a fuel.

When a fuel is burned, the products rise to a maximum temperature and then fall to the final temperature to which the products are cooled. This process is shown on a temperature-volume or -pressure diagram (Figure 1), point 1 representing the initial condition, 2 the maximum temperature, 3 the point at which condensation of water vapor begins, 4 the actual final condition, and 5 the hypothetical final condition assuming cooling of the water vapor without condensation.

Obviously, the heat given up by the products is the same for the noncondensable gases regardless of which path is followed, and from this it follows that the difference between gross and net is merely the difference between dQ_4 and dQ_5 for the water vapor.

If the constant-volume process of combustion is used,

$$dQ = du \quad (1)$$

where dQ is the heat given up in the cooling process and du is the change of intrinsic energy.

For the constant-pressure process,

The thermodynamic principles involved in the determination of the difference between gross and net heating values for both constant-volume and constant-pressure combustion of solid and liquid fuels are discussed. A temperature-volume or -pressure diagram is shown representing the burning and cooling processes, which illustrates the reason for and fixes the definition of the difference between gross and net values.

Differences have been computed for the constant-volume bomb determinations, and a mean value of 970 B. t. u. per pound of water vapor formed is suggested.

Differences have been computed for the constant-pressure combustion process in air for 100 per cent humidity and less. At 100 per cent humidity the difference is practically 1070 B. t. u. per pound of water vapor formed, regardless of the fuel or temperature at which it is burned. For other than 100 per cent humidity, the difference may be anything from 1070 to 0 B. t. u.

During the computations it was observed that the difference between gross and net heating values for the constant-pressure process per pound of water vapor condensed was equal to the latent heat of the water at the final temperature. Thermodynamic proof of this generalization is included.

$$dQ = di \quad (2)$$

where di is the change in thermodynamic potential i , which is defined as the sum of the intrinsic energy and the product of pressure and volume.

$$i = u + pv \quad (3)$$

Constant-Volume Determinations

The bomb is saturated with water vapor before combustion takes place so that all water vapor formed will be condensed during the cooling process. The temperature at which condensation begins (t_c) is fixed by the partial pressure of the water vapor ($p.p.w.v.$). From Dalton's law

$$p.p.w.v. = \frac{\text{moles}_{w.v.}}{\text{moles}_{prod.}} \times P_c \quad (4)$$

where P_c is the total pressure in the bomb when t_c is reached during the cooling process. However, P_c is decreasing with temperature and is therefore unknown unless the corresponding temperature is known. But when the condensation temperature is reached,

$$P_c V = m_p RT_c \quad (5)$$

and at the initial temperature

$$P_1 V = m_1 RT_1 \quad (6)$$

Dividing Equation 5 by Equation 6 and solving for P_c ,

$$P_c = P_1 \frac{m_p}{m_1} \times \frac{T_c}{T_1} \quad (7)$$

Substituting Equation 7 in Equation 4,

$$\begin{aligned} p.p.w.v. &= \frac{m_{w.v.}}{m_p} \times \frac{m_p}{m_1} \times \frac{T_c}{T_1} \times P_1 \\ &= \frac{m_{w.v.}}{m_1} \times \frac{T_c}{T_1} \times P_1 \end{aligned} \quad (8)$$

or since the initial temperature, T_1 , initial pressure, P_1 , the moles of water vapor, $m_{w.v.}$, and moles of mixture, m_1 , are known for a given composition of fuel,

$$p.p.w.v. = K T_c \quad (9)$$

The correct value of T_c must satisfy not only Equation 9 but also the saturated pressure-temperature relationship of steam. Obviously, the solution becomes one of choosing values of T_c , solving Equation 9 for $p.p.w.v.$, and comparing this partial pressure with the saturated pressure found in the steam tables for the assumed values of T_c , until the correct value is found.

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Having determined T_c ,

$$_s dQ_4 = _s dU_4 = (\mu''_c - \mu'_1) \text{ heat units per mole of water vapor} \quad (10)$$

The values of μ are obtained from the steam tables, double prime indicating saturated vapor and single prime the liquid.

The energy given up by the water vapor acting as a perfect gas can be determined from the following energy equation for water vapor:

$$\phi_T = T(6.345 - 0.138 \times 10^{-3} T + 0.141 \times 10^{-6} T^2) \quad (2) \quad (11)$$

which will give the energy at any temperature, T , per mole of water vapor. Thus

$$_s dQ_8 = \phi\mu_8 - \phi\mu_1 = _s d\mu_1 \quad (12)$$

Then

$$\frac{(_s dQ_4 - _s dQ_8)m_{w.v.}}{\text{unit wt. of fuel}} \quad (13)$$

which is the difference between gross and net heating value per pound of fuel.

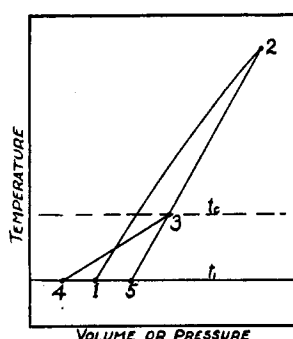


Figure 1—Combustion and Cooling Process

In actual bomb calorific determinations, the final temperature is usually about 3° C. (5° F.) above the initial temperature. Some of the water vapor formed in the products will not be condensed because of the higher final temperature. The amount not condensed can readily be determined from the difference in the amounts of water vapor to saturate the bomb volume at the final and initial temperatures. Knowing this, the quality, x , of the mixture of

water and water vapor can be determined in the usual manner. The energy of this mixture is equal to

$$\mu' + x\rho$$

where μ' is the energy of water at the final temperature and ρ is the internal energy of vaporization at the final temperature.

The energy of the foregoing mixture replaces the value μ'_1 in Equation 10 and reduces the difference between gross and net heating value a small amount.

Values of the differences between gross and net heating values have been computed for various values of C to $(C + H_2)$ ratios, the ratios being made on the molal basis, and are given in Table I and plotted in Figure 2. The two temperatures chosen represent the probable limits of initial temperatures used in calorific determinations.

Table I—Differences between Gross and Net Heating Values per Unit Weight of Water Vapor Formed

$\frac{C}{C + H_2}$	0.60	0.80	0.90	0.974
	CAL. PER KG.			
$t_1 = 20^\circ \text{C.}$	545	547	546	535
$t_1 = 38^\circ \text{C.}$	532	533	530	513
	B. T. U.			
$t_1 = 68^\circ \text{F.}$	981	984	982	963
$t_1 = 100^\circ \text{F.}$	958	959	953	923

Inspection of Table I and Figure 2 will show that a value of about 539 Cal. per kg. (970 B. t. u. per pound) of water vapor formed represents the mean value for most of the range, the deviation from this at high carbon content fuels representing insignificant errors due to very small amounts of water vapor formed per pound of fuel.

Constant-Pressure Combustion Differences

HUMIDITY 100 PER CENT—It is well known that fuels containing carbon and hydrogen show a decrease in products

volume compared to mixture volume provided the water vapor formed is condensed. Then, when fuels are burned at constant pressure in air with 100 per cent humidity and the products cooled to the initial temperature, part of the water vapor in the air will be condensed along with the water vapor formed in the products.

It will be shown later that the difference between the heat given up by water vapor in condensing and cooling at constant pressure from t_c to t_1 , and the heat being cooled at a perfect gas is equal to the latent heat at t_1 . Thus, at 68° C. (100° F.) the difference between the gross and net heating values per kilogram of water vapor condensed is equal to 576 Cal. (1036.6 B. t. u. per pound). However, owing to the condensing of part of the water vapor in the air, mentioned above, the difference per kilogram of water vapor formed in the products is 596 Cal. (1.035×1036.6 B. t. u. = 1073 B. t. u. per pound) over the entire range of C to $(C + H_2)$ ratio. For a temperature of 20° C. (68° F.) this value becomes 593 Cal. (1068.0 B. t. u.), also, for the entire range of fuels. Thus, the difference between gross and net heating values of liquid or solid fuels burned at atmospheric pressure in air saturated with water vapor is approximately 595 Cal. per kg. (1070 B. t. u. per pound) of water vapor formed, regardless of fuel or temperature at which the fuel is burned. This means that the gross heating value per pound of the fuel when burned at atmospheric pressure in air with 100 per cent humidity is higher than that obtained in the bomb by 56 Cal. per kg. (100 B. t. u. per pound) of water vapor formed in products per unit weight of fuel.

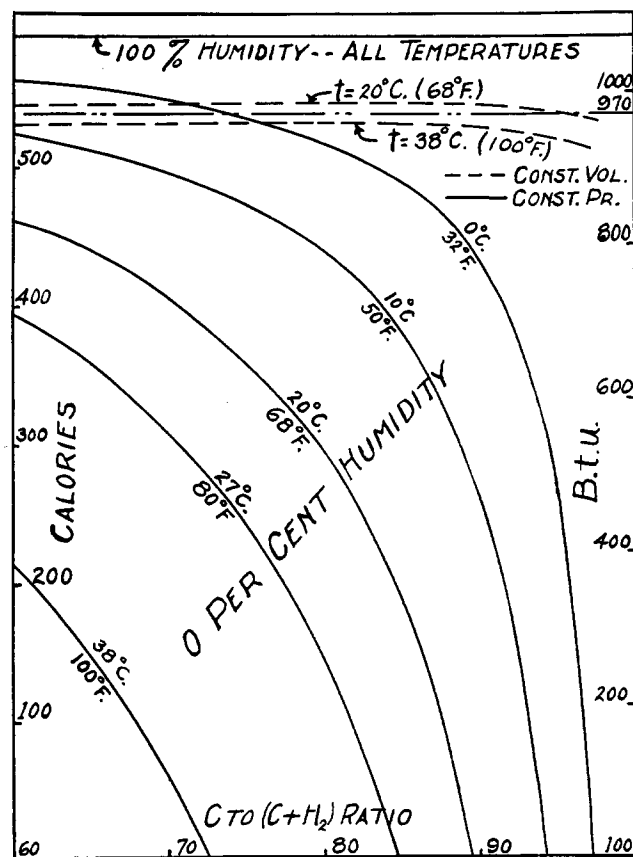


Figure 2—Gross-Net Heating Value per Unit Weight of Water Vapor Formed

HUMIDITY LESS THAN 100 PER CENT—Following the method outlined in "Principles of Thermodynamics" (1) differences between gross and net have been computed for the same C to $(C + H_2)$ ratios and for various humidities and tem-

peratures, some of the results being shown graphically in Figure 2. It is seen that for various combinations of fuel, temperature, and humidity, the difference in gross and net heating values per kilogram of water formed may be anything from 0 to 595 Cal. per kg. (0 to 1070 B. t. u. per pound).

Thermodynamic Proof of Difference

In making the foregoing computations it was observed that the difference between gross and net heating values, at constant pressure, per pound of water vapor condensed was equal to the latent heat of water at the final temperature. The proof that this is true is as follows:

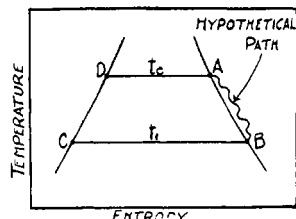


Figure 3—T-E Diagram for Water Vapor

It has already been shown that the difference between gross and net heating values is equal to the difference between the decrease in thermodynamic potential, i , for the actual path and the decrease for the hypothetical path. In the actual cooling process the water vapor becomes saturated at A (Figure 3). An infinitesimal drop in temperature will cause an infinitesimal mass of vapor to condense and in so doing move across the diagram to D. Further cooling will cause more vapor to condense and cause the liquid already at D to be cooled. The first particle cooling will follow the path A-D-C; the last particle will follow the path B-C. However, since i is a point function

$$di = i''_A - i'_c$$

regardless of the path.

For the purely hypothetical process of cooling the vapor from t_2 to t_1 without condensing, which is a constant-pressure process, any path may be drawn. However, the specific

heat of saturated vapor at constant pressure for this range is about constant, and the decrease in i will be equal to

$$dQ = di = c_p (t_2 - t_1)$$

since $dQ = di$ for a constant-pressure process.

It remains to be proved that the end of the hypothetical path is at B. The water vapor at B is at a low pressure corresponding to the temperature t_1 , whereas at the end of the hypothetical path the pressure corresponds to that at t_2 . However, the product of PV for both cases is practically the same, owing to the low pressures involved, which makes the value of i the same and fixes the end of the hypothetical path at B. Then since the di , following any path between two points, must be the same,

$$i''_A - i'_c = c_p (t_2 - t_1) + r_1$$

when r is the latent heat at t_1 , and also represents di from B to C. Rearranging the expression, we have

$$(i''_A - i'_c) - c_p (t_2 - t_1) = r_1$$

the left side being by definition the difference between the gross and net heating values. This has been checked and found true for various conditions, so that the following general rule can be accepted: The difference between the gross and net heating values of a fuel burned at constant atmospheric pressure is equal to the weight of water vapor actually condensed multiplied by the latent heat of steam at the initial temperature of the mixture, which is also the temperature to which the products are cooled.

Literature Cited

- (1) Goodenough, "Principles of Thermodynamics," pp. 294-5, Henry Holt 1927.
- (2) Goodenough and Felbeck, Univ. of Ill. Eng. Expt. Sta., *Bull.* 139, 138 (1924).

Chemical Composition of Avocado Seed¹

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IN RECENT years the large increase of avocado production and the rapid growth of the industry have stimulated search for by-products to utilize the culls. Avocado dehydration, preservation in freezing storage, canning, use in ice cream, cocktail, mayonnaise, and sandwich spreads have been investigated (4). Methods of extraction and refining, and possible uses of the oil are being studied.² All of these, however, have to do with the pulp, while the seed, comprising from 8 to 25 per cent of the fruit, apparently has never been considered. In attacking the problem of preparing by-products from the seed, it was considered that a knowledge of the chemical composition would properly serve as a basis.

Quantitative determinations have been made of the composition of the seed of the avocado (both Mexican and Fuerte varieties), including moisture, ash, acidity, nitrogen, protein, reducing sugars, sucrose, starch, pentosans, crude fiber, and ether extract.

α -D-Mannoheptite was prepared from the seed and identified.

A flour consisting largely of starch was prepared and identified as amyllum.

Very early in the history of organic chemistry, Avequin (2) in 1831 and Melsens (8) in 1839 found avocado seed to be the source of *d*-perseitol. So far as is known, no mention was made of any of the other constituents until 1920 when a report (9) of various oil-yielding seeds was made by the food-testing laboratory of the Surinam. This report states that the seed of *Persea gratissima* contains only 8 per cent fat and 2 per cent saponin, to which the poisonous character is ascribed. Jamieson et al. (7) found but 2.2 per cent oil in an air-dried crushed sample.

Quantitative Determinations

The seeds available for the work here reported were from varieties of *Persea drymifolia* of the Mexican race of horticulture, and the Fuerte was classed as a hybrid of *P. drymifolia* and *P. americana* of the Guatemalan race (11). The varieties of these two races are not always separated into two species, as some authorities list them all as belonging to *P.*

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² Work on the oil is being carried on in the laboratories of the University of Southern California.