Thermochimica Acta
Elsevier Publishing Company, Amsterdam
Printed in Belgium

THE EFFECT OF EMISSIVITY ON HEAT TRANSFER

D. J. DAVID
Columbia Scientific Industries, P. O. Box 6190, Austin, Texas 78762 (U. S. A.)
(Received November 22nd, 1971)

ABSTRACT

Emissivity has been found to play a key role in heat transfer even at relatively low temperatures. Two general equations have been derived which allow one to estimate the emissivity of different materials for this system.

INTRODUCTION

Many studies have appeared which have examined the heat transfer effects upon the differential thermocouple[1-8]. While this is of prime importance, it is not the only aspect of heat transfer to be considered, since the entire sample holder must be heated by a suitable source in order that the experiment may be carried out in the first place.

In examining furnace and sample holder design, it became apparent that the emissivity of the sample holder plays a key and vital role in overall instrument performance in affecting the efficiency of heat transfer to the immediate sample area. For this reason, we wished to examine the effect of emissivity using a more quantitative approach.

Theoretical considerations

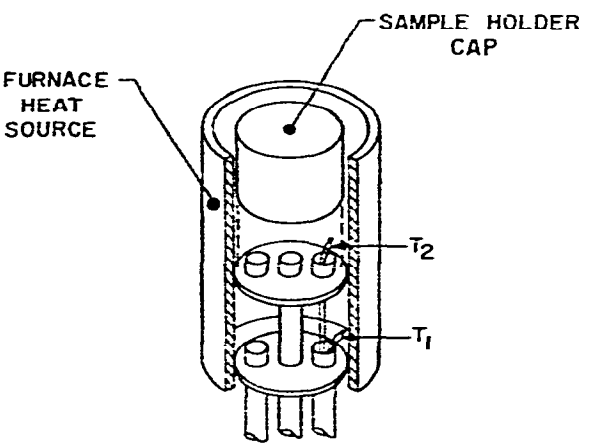

Fig. 1. Representation of sample holder used to study heat transfer effects.

Considering a heat source normal to a sample holder such as that shown in Fig. 1, allows us to use simplified equations associated with heat transfer to the sample holder and its contents. The sample holder will normally contain a sensor such as a differential thermocouple pair which in this instance is not present in Fig. 1 for consideration.

Heat is transferred by three mechanisms which may be operating singly or in combination.

(1) Conduction, which may be represented as

$$q_1 = \frac{k(T_1 - T_2)}{L} \tag{1}$$

(2) Convection, which may be represented as

$$q_2 = h(T_1 - T_2) \tag{2}$$

(3) Radiation, which may be represented as

$$q_3 = F \times \sigma \times \varepsilon (T_1^4 - T_2^4) \tag{3}$$

where q_1, q_2, q_3 = heat transfer rate by each mechanism (cal/cm^2/sec), k = thermal conductivity of sample holder (cal/sec/cm/°K), h = thermal conductivity of medium or convective heat transfer coefficient (cal/sec/cm/°K), L = thickness of sample holder cap (cm), F = geometric factor between source and receiver (dimensionless), σ = Stephen–Boltzmann constant (cal/cm^2/°K^4/sec), ε = total emissivity (dimensionless), T_1 = considered to be temperature of source or furnace, T_1 (°K), T_2 = temperature of receiver, T_2, (°K).

The total heat transferred through the wall of the sample holder from the source or furnace (See Fig. 1) to the receiver, T_2, is given by:

$$q_{total} = \frac{k(T_1 - T_2)}{L} + h(T_1 - T_2) + F \times \sigma \times \varepsilon (T_1^4 - T_2^4) \tag{4}$$

EXPERIMENTAL

The apparatus configuration shown in Fig. 1 was used to obtain all data. The device was programmed with a CSI-Stone Model 500 Programmer. The lower thermocouple T_1, is the programming thermocouple, and furnished the control signal to the temperature programmer. The upper thermocouple, T_2, is positioned in the same vertical plane as that of T_1, so that the thermocouples are the same distance from the furnace element. However, T_2 is positioned a distance above T_1, and is capable of being enclosed by selected materials which would normally act as sample holder caps.

Arrangements were made so that the output of each thermocouple could be monitored. Both T_1 and T_2 are chromel–alumel thermocouples. The full span of the recorder was calibrated to cover the range from 0 to 1000°C, and all programmed

runs were made at a rate of 10°C/min, with room temperature or 25°C corresponding to chart "zero", under static air environmental conditions.

RESULTS AND DISCUSSION

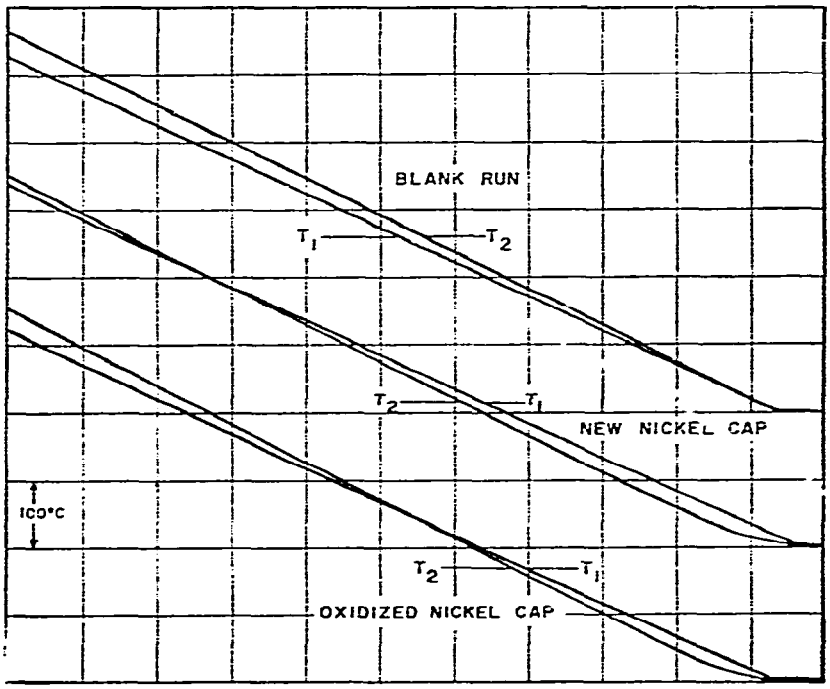

Fig. 2. Program profiles showing temperature differences ($T_1 - T_2$) of blank run and condition of nickel sample holder cap.

A run was made without a cover, of a selected material, in place. This blank run is shown in Fig. 2, from which it can be seen that the gradient within the furnace produces a temperature difference between thermocouples, the extent of which increases as the thermocouples are moved apart in a vertical plane. The higher positioned thermocouple (T_2) will always be exposed to the hotter part of the furnace using the configuration shown in Fig. 1. The blank differences between T_1 and T_2 were used to correct subsequent runs at the same source temperature (T_1). (See Table I, corrected data.)

Several materials were selected for evaluation based upon their variations in emissivity values before and after oxidation. Aluminum was also selected, since its low emissivity value provides a comparison with the higher values of the oxidizable materials.

Fig. 2 also shows a run using a newly fabricated nickel cap, and a subsequent run using the same identical nickel cap, except, after it had been oxidized. Two factors should be noted: (*1*) the ($T_1 - T_2$) difference between each run with the nickel

cap and the original blank run, and (2) the $(T_1 - T_2)$ differences between the unoxidized (new) and the oxidized nickel cap runs. These runs are representative of the differences observed between copper (unoxidized) and copper (oxidized). Aluminum produced a run similar to that of unoxidized or new nickel. These data are listed in Table I, and were used in Eqn. 4.

TABLE I

EXPERIMENTAL RESULTS OF $T_1 - T_2$ VALUES (°C) FOR VARIOUS SAMPLE HOLDER CAP MATERIALS

T_1 (°C)	*Cu (New)*	*Cu (Oxidized)*	*Ni (New)*	*Ni (Oxidized)*	*Al*	*No cap*
	Raw data					
100	20	17	25	18	18	−2
200	16	11	24	7	9	−11
300	7	−2	15	−3	7	−20
400	−6	−7	6	−7	−1	−25
	Corrected data					
100	22	19	27	20	20	0
200	27	22	35	18	20	0
300	27	18	35	17	27	0
400	19	18	31	18	24	0

Eqn. 4 was utilized using the data for nickel, new and oxidized, from Table I, in order to evaluate the geometric factor, F. Since both q_{total} and F are unknown, two equations are required. The two simultaneous equations were obtained by evaluating Ni (new) and Ni (oxidized), at the same temperature, using handbook thermal conductivity values and emissivity values for nickel as follows

$$\mathrm{Ni}^{new}_{300\,^\circ C} \text{ for } q = \frac{0.13\,(473-438)}{0.158} + 5.68\times10^{-5}\,(473-438) + F\times13.5\times10^{-13}\times0.07\,(473^4-438^4) \quad (5)$$

$$\mathrm{Ni}^{ox.}_{300\,^\circ C} \text{ for } q = 0.13\,(473-456) + 5.68\times10^{-5}\,(473-456) + F\times13.5\times10^{-13}\times0.37\,(473^4-456^4) \quad (6)$$

Since the heat transfer rates, q, should be equal when the source temperatures are identical for both runs, we can set the equations equal to each other and solve for F, obtaining

$$F = 7.05\times10^{3} \quad (7)$$

It is interesting to note the contribution of the thermal conductivity and radiation terms. In the case of the new nickel cap, the contribution of the thermal conductivity term was about 1.7 times as great as the radiation term, while for the oxidized sample, this situation was reversed. Thus even at relatively low temperatures the

character of the heat transfer can change entirely and the change is governed by the emissivity of the sample cell material. As the emissivity of the sample cell material increases, the radiation term predominates, although heat is transferred by all three mechanisms. The magnitude of the convection term is so small that it can be neglected for all practical purposes in this system.

A knowledge of F permits an evaluation of ε at different temperatures from experimental data, so long as the same sample cap material is used, since Eqns. 5 and 6 are particular, and not general, solutions.

The data for copper was used to independently evaluate F. A value of

$$F = 7.74 \times 10^3 \tag{8}$$

was obtained. This is considered to be within the error of the method.

The data obtained for nickel or copper could not be used to estimate the emissivity of aluminum since the solution to Eqn. 4 was a particular one only. An assumption was made that this is so because a second geometric factor is involved, say F^*, which affects both the conductivity term and the radiation term. This should be the case because of the physical sample cap mounting and its conduction of heat through the base plate, by virtue of its contact, and the radiation from other parts of the holder to the receiver (T_2). This factor could be neglected when identical materials were used, but must not be ignored in the case of different materials.

For two different metals, say m_1 and m_2, the factor f was related to

$$\frac{k_{m_1}}{k_{m_2}} \times \frac{C_{p_{m_1}}}{C_{p_{m_2}}} \times \frac{\text{Wt.}_{m_1}}{\text{Wt.}_{m_2}} = f \tag{9}$$

where k = thermal conductivity and C_p = specific heat. For Cu and Ni, Eqn. 9 becomes

$$\frac{k_{Cu}}{k_{Ni}} \times \frac{C_{pCu}}{C_{pNi}} \times \frac{\text{Wt.}_{Cu}}{\text{Wt.}_{Ni}} = f \tag{10}$$

An evaluation of Eqn. 4 for Cu (oxidized) emissivity, based upon Ni, showed that

$$f_{m_1/m_2} \times 0.75 = F^* \tag{11}$$

In estimating the emissivity of Cu based upon Ni, we have

$$\text{Ni}_q \times f_{\text{Cu/Ni}} \times 0.75 = \text{Cu}_q \tag{12}$$

In estimating the emissivity of Cu based upon Al, we have

$$\text{Cu}_q = \text{Al}_q \times f_{\text{Cu/Al}} \tag{13}$$

But in this instance, we are unable to use the value $F^*/f_{m_1/m_2}$, since F^* was determined from Cu/Ni, which must be translated into the equivalent Cu/Al.
Therefore, combining

$$\text{Cu}_q = \text{Ni}_q \times f_{\text{Cu/Ni}} \times 0.75$$

and

$$Cu_q = Al_q \times f_{Cu/Al}$$

gives

$$Ni_q \times f_{Cu/Ni} \times 0.75 = Al_q \times f_{Cu/Al} \tag{14}$$

In relating this equation to Ni, we have

$$Ni_q \times f_{Cu/Ni} = \frac{Al_q \times f_{Cu/Al}}{0.75}$$

or

$$Cu_q = Al_q \times f_{Cu/Al} \times 1.33 = Al_q \times F^* \tag{15}$$

TABLE II
CALCULATED "f" VALUES

Material	f
Cu/Ni	6.15
Cu/Al	2.08
Ni/Al	0.334
Al/Ni	2.97

The factor F^* affects all three terms of Eqn. 4 since the conduction and radiation terms also affect the entire holder, and the general equations for this system become

$$m_{1q} = \frac{k(T_1 - T_2)}{L} + h(T_1 - T_2) + 7.35 \times 10^3 \times 13.5 \times 10^{-13} \times \varepsilon_{m_1}(T_1^4 - T_2^4) \tag{16}$$

$$m_{2q} = F^*\left[\frac{k(T_1 - T_2)}{L} + h(T_1 - T_2) + 7.35 \times 10^3 \times 13.5 \times 10^{-3} \times \varepsilon_{m_2}(T_1^4 - T_2^4)\right] \tag{17}$$

Using these equations, Table III shows the results obtained.

TABLE III
EMISSIVITY COMPARISONS AND f FUNCTIONS USED AT 300°C

Experimentally determined	*Literature values*	"f" *function*
$\varepsilon_{Ni}^{ox.}$ 0.31	$\varepsilon_{Ni}^{ox.}$ 0.37	Ni/Al
ε_{Ni}^{occ} 0.068	ε_{Ni}^{occ} 0.01–0.10	Cu/Ni
$\varepsilon_{Cu}^{ox.}$ 0.98	$\varepsilon_{Cu}^{ox.}$ 0.78	Cu/Al
$\varepsilon_{Cu}^{ox.}$ 0.84	$\varepsilon_{Cu}^{ox.}$ 0.78	Cu/Ni
ε_{Al}^{occ} 0.09	ε_{Al}^{occ} 0.05 (approx.)	Al/Ni
ε_{Cu}^{occ} 0.13	ε_{Ni}^{occ} 0.03–0.17	Cu/Ni

REFERENCES

1 D. J. DAVID, *Anal. Chem.*, 36 (1964) 2162.
2 S. L. Boersma, *J. Am. Ceram. Soc.*, 38 (1955) 281.
3 S. L. Boersma, *J. Am. Ceram. Soc.*, 40 (1957) 42.
4 L. G. Berg and V. P. Equnov, *J. Therm. Anal.*, 1 (1969) 5.
5 L. G. Berg and V. P. Equnov, *J. Therm. Anal.*, 1 (1969) 44.
6 L. G. Berg and V. P. Equnov, *J. Therm. Anal.*, 2 (1970) 53.
7 A. P. Gray, *A Simple Generalized Theory for the Analysis of Dynamic Thermal Measurements*, in R. Porter and J. F. Johnson (Eds.), *Analytical Calorimetry*, Vol. I., Plenum Publishing Company, New York (1968).
8 D. J. David, *J. Therm. Anal.*, 3 (1971) 247.