

APPENDIX

CALCULATION OF A SMALL ($\approx 10^{-3}$ K) CORRECTED TEMPERATURE CHANGE

Hubbard et al. [2] have outlined how the corrected temperature change $\Delta\theta_c$ in a reaction calorimetric experiment should be calculated. The applicable equations are:

$$\Delta\theta_{\text{corr}} = r_f(t_f - t_{\text{mp}}) + r_i(t_{\text{mp}} - t_i), \quad (\text{A})$$

$$r_i = \alpha(\theta_{\text{conv}} - \theta_i), \quad (\text{B})$$

$$r_f = \alpha(\theta_{\text{conv}} - \theta_f), \quad (\text{C})$$

$$\Delta\theta_c = \theta_f - \theta_i - \Delta\theta_{\text{corr}}, \quad (\text{D})$$

where $\Delta\theta_{\text{corr}}$ is the correction applied to the observed temperature change of the calorimeter to allow for heat exchange with the environment; r_i and r_f are, respectively, the rates of change with time of the calorimetric temperature at the end of the fore-period and the beginning of the after-period of the experiment; t_i , t_f , and t_{mp} are, respectively, the initial, final, and mid-point times of the experiment, t_{mp} being defined in such a way that it delineates two equal areas A associated with the temperature against time curve; θ_i , θ_f , and θ_{conv} are, respectively, the initial, final, and convergence temperatures of the experiment (θ_{conv} is the calorimetric temperature reached after an indefinitely long time); and α is the rate of temperature change due to heat exchange with the environment. Each individual calorimetric system has a characteristic α which should be reproduced to within a few percent for each experiment.

Throughout this book, the "blank" has been referred to on numerous occasions when two-chambered reaction vessels have been employed. This quantity allows for reactions of the expanding F_2 with minute traces of H_2O or other impurities on the interior surfaces of the reaction vessel. It is, essentially, an empirical correction determined by expanding F_2 into the bomb section of the reaction vessel; experimental conditions duplicate as far as possible those of an energy of combustion measurement, only the calorimetric sample is omitted. Typically, the corrected temperature change in such an experiment is $\approx 10^{-3}$ K or less. We note, in passing, that such temperature changes are not rare in solution calorimetry either where, in practice, the thermal effect of an endothermic reaction may be cancelled approximately by an input of predetermined electrical energy from the heater with the result that the corrected temperature change is very small, just as in the "blank" experiments of fluorine bomb calorimetry.

In a typical "blank" experiment, the duration of the fore-rating period is about 600 s after which the valve on the storage tank is opened, a temporary dip in the calorimetric temperature occurs as the F_2 expands, and approximately 800 s later an essentially constant drift rate of the calorimetric temperature is re-established. In practice, that drift rate is almost always greater than the initial rate, even though the temperature may have risen slightly in the interim, and that leads to an anomalous value for α .

This phenomenon has always been a puzzle. Apparently, the performance of the calorimeter changes once the tank is opened and prevails until the end of the experiment. It has been speculated that such behavior was due to an alteration in the position of the reaction vessel in the calorimeter once the valve is opened or to a change in the stirring pattern of the water in the calorimeter. Whatever happens, it is assumed that the effect lasts throughout the experiment. Thus, the calculation of $\Delta\theta_{\text{corr}}$ is based on the final drift rate; the initial drift rate is used solely to deduce t_i . (It is instructive to recall that combustion calorimeters of the type discussed here were originally designed to measure temperature changes of the order of 1 K.)

By substituting the values of r_i and r_f from equations (B) and (C) into equation (A) one obtains:

$$\Delta\theta_{\text{corr}} = \alpha\{\theta_{\text{conv}}(t_f - t_i) - \theta_i(t_f - t_{\text{mp}}) - \theta_i(t_{\text{mp}} - t_i)\}. \quad (\text{E})$$

The two rightmost quantities in equation (E) give $-A$, the negative of the area to which we referred earlier. Thus,

$$\Delta\theta_{\text{corr}} = \alpha\{\theta_{\text{conv}}(t_f - t_i) - A\}. \quad (\text{F})$$

Next, θ_{conv} is calculated from equation (C):

$$\theta_{\text{conv}} = \theta_f + r_f/\alpha. \quad (\text{G})$$

Values for A , θ_i , r_f , and $(t_f - t_i)$ from the computed output and the value of α characteristic of the calorimeter (for experiments at NIST, $\alpha = 4 \cdot 10^{-5} \text{ s}^{-1}$ is taken) are combined to give a new $\Delta\theta_{\text{corr}}$. This result, along with θ_i and θ_f , yields the corrected temperature rise θ_c which is then multiplied by the energy equivalent of the calorimetric system to give the value of the “blank” correction.