# On the Accuracy of Moving-Bomb Calorimetry

## III. The Accuracy of Heat of Combustion Data of Sulfur Compounds

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The method of moving-bomb calorimetry has been shown to give highly reproducible results for sulfur compounds [1]. It has been more difficult, however, to assess the absolute accuracy of the bomb calorimetric data since there may be systematic errors present that defy detection. A reliable check can only be ascertained by a comparison of results obtained with the bomb calorimetric method with those determined in an independent way.

Hubbard and Waddington [2] compared the heat of formation value of propanethiol-2, obtained from heat of combustion experiments with that derived from equilibrium measurements. They found an excellent agreement, indicating the absence of systematic errors in the moving-bomb technique.

Sunner and Wadsö published a check based purely on thermochemical measurements [3]. They took advantage of the fact that thiolacetic acid can be quantitatively hydrolyzed to acetic acid. The heat of hydrolysis was determined as well as appropriate heats of solution and dilution of reactants and reaction products. Thus, the enthalpy change accompanying the idealized reaction

$$CH_3{\cdot}COSH(l) + H_2O(l) \rightarrow CH_3{\cdot}COOH(l) + H_2S(g)$$

was determined to $-0.64 \pm 0.07$ kcal.mole$^{-1}$.

By combining this value with heat of formation data of water, acetic acid and hydrogen sulfide, a value for the heat of formation of thiolacetic acid could be derived and compared with that obtained from combustion experiments [4]. Unfortunately, the heat of formation of acetic acid was not unambiguously known at the time when Ref.[3] was published. A precise check of the moving-bomb technique by this method had therefore to await an accurate redetermination of the heat of combustion of acetic acid.

Recently, Evans and Skinner have determined the heat of combustion of acetic acid accurately [5]. They calculated therefrom the heat of formation of acetic acid to $\Delta Hf^\circ_{298.16} = -115.72 \pm 0.1$ kcal.mole$^{-1}$. Using this value, the well-known heat of formation data of water and hydrogen sulfide and the heat of hydrolysis value given above, the heat of formation of thiolacetic acid is found to be

$$\Delta Hf^\circ_{298.16} = -51.58 \pm 0.1 \text{ kcal.mole}^{-1}.$$

This datum has to be compared with the heat of formation of thiolacetic acid obtained from combustion calorimetry:

$$\Delta Hf^\circ_{298.16} = -51.5 \pm 0.2 \text{ * kcal.mole}^{-1}.$$

The close agreement between the two results is additional strong evidence to support the contention that the moving-bomb calorimetric method as used for sulfur compounds does not involve significant, systematic errors.

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* The overall standard deviation of the mean.

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