LETTERS TO THE EDITOR

THE RELATIVE IMPACT OF THERMAL STRATIFICATION OF THE AIR SURROUNDING A CALORIMETER

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Last month there were several responses to the paper entitled "Potential for Positional Variation in Flow Calorimetric Systems" which discussed a theoretical examination [1] of heat and mass flow [2] with inclusion of the Bernard instability [3].

"I've been thinking about another problem that could be plaguing the Cravens-style vertical flow calorimetry ... thermal stratification in the air space outside the cell. In at least one of the public demos Cravens put on, he enclosed the cell in an insulated chamber made with two Dewars placed mouth-to-mouth. This created a more-or-less dead airspace around the cell and, since the cell was operated at a temperature significantly above ambient, I would expect a considerable temperature gradient to exist in this air space, hottest at the top and cool at the bottom. With the very slow flows he used (14 ml/min is ~0.7cm/sec flow velocity in 1/4" ID tubing), the temperature sensors could be significantly affected by simple conduction through the walls of his fittings. Such a problem would cause the upper temp sensor, which is the outlet sensor, to be hotter than the lower sensor ... resulting in a false positive indication. Because the airspace stratification is "driven" by the heat of the cell, this false positive indication should become larger when the cell temperature is raised...."

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Several issues appear to be involved.
1) Could thermal stratification of the air physically located outside of the electrolytic cell influence the thermal leakage from the cell by changes in the net thermal conductance?
2) Does thermal conduction through mechanical fittings effect the reading of a temperature sensor?
3) Could such a thermal air thermal stratification effect also alter the temperature sensors through the fitting effect (described at #2)?

The following is the semiquantitative estimate of the impact of the phenomenon discussed in question #1. Instead of a simple mean temperature of outside air of 30°C, in this gendanken experiment assume the air is varied over the temperature range from 20 to 40°Centigrade. Assume there does not exist any variation in the air or calorimeter conditions with respect to time or external mass transport. The enthalpic losses to the local "ambient" environment from the cell include conduction, radiation (with the 4th power temperature term in the Stefan-Boltzmann equation), and convection losses of two types — both flow incurred and thermal induced [4,5]. To qualitatively determine the impact, let us model the calorimeter in a single dimension and as a linear system. We will ignore for simplicity spatial- or time-variation of the material factors, boundary effects [6], and other isothermal effects.

Changing the air by thermal stratification probably would mainly alter the thermal conduction term. That thermal conduction loss is in "series" with the thermal conduction term through the calorimeter wall itself. The thermal conductance of the two compartments — consisting of the air and the outer wall of the calorimeter — could be modeled as

$$K_{equiv} = \frac{K_{wall} * K_{air}}{K_{wall} + K_{air}} \quad [\ \text{cal/(sec-cm}^2\text{)(degC/cm)}\ ].$$

The equation is derived similar to the corresponding electrical system with the thermal resistances added in series, after converting the thermal barriers (resistances such as R_{wall}) to thermal conductance ($R_{wall} = 1/K_{wall}$).

How much could such thermal stratification — physically located outside of the electrolytic cell — influence the net thermal conductance loss of the calorimeter and thus alter the measured result of a calorimeter? These thermal

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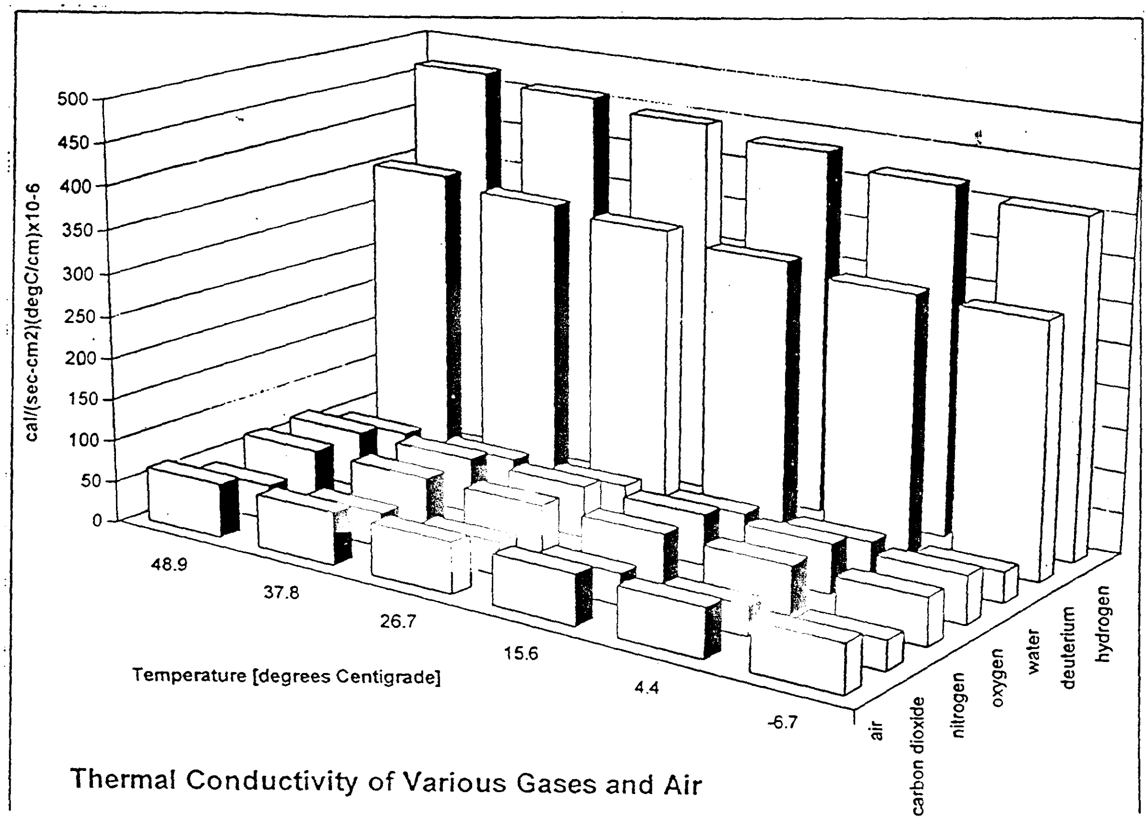

Temp. (C)	air	carbon dioxide	nitrogen	oxygen	water	deuterium
-6.7	56.2	33.7	56.2	57.2	36.8	305.8
4.4	58.3	35.6	58.3	59.4	38.9	310
15.6	60.3	37.6	60.3	61.6	40.5	322.3
26.7	62.2	39.7	62.4	63.6	42.6	334.7
37.8	64.2	41.7	64.1	65.9	44.6	343
48.9	66	43.8	65.7	68.2	46.7	355.4

Fig. 1 — Thermal Conductivity of Gases
The hydrogen isotopes show markedly greater thermal conductivity than other, higher molecular weight, gases. This 3D bar graph demonstrates thermal conductivity (cal/(sec-cm^2)(degC/cm) x 10^{-6} as a function of temperature (-7 to 49 degrees Centigrade) for air, carbon dioxide, deuterium (D_2), hydrogen (H_2), nitrogen (N_2), oxygen (O_2), and water (data after Handbook of Chemistry and Physics (Chemical Rubber Co., 1973).

conduction changes are based upon relatively small differences in thermal conductivity of the gases surrounding the calorimeter. The thermal conductivity of air varies from 42 to 45 cal/(sec-cm^2)(degC/cm) x 10^{-6} between 20 and 40°C. In this example, this difference in thermal conductivity amounts to a 6% change, ± 3% around the mean. Furthermore, the variation's impact might, if it varies linearly with temperature, just balance when integrated over the entire wall. The impact, based upon convention models of heat and mass transfer [4,5,6], is that if the spatial distribution of temperature is even and linearly distributed, there will be no significant changes upon calorimeter calibration. It appears that only when there is a nonlinear variation of the air's thermal conductance-temperature curve, that there accrues significant deviation from the calibration. To calculate the impact of the effect, let us assume the nonlinear asymmetry is quite significant and results in a 2% variation. With equation (1), it is possible to actually substitute number. If K_{air} is a tenth that of the wall, $K_{air} = 0.1\ K_{wall}$, then a hypothetical 2% asymmetric stratification change in air conductivity will alter the total conductivity by about ± 1.8%. If K_{air} is $\sim K_{wall}$ (10 K_{wall}), a hypothetical 2% asymmetric stratification change in air conductivity will alter the total conductivity by about ± 1.0% (± 0.2% respectively).

Most importantly, as shown in Fig. 1, the thermal conductivity effects generated by the stratification are quantitatively small, compared to the impact of the "hydrogen gas displacement effect" which might exist in some electrolysis systems. So what is the impact of possible thermal stratification of gas external to a calorimeter? The overall impact of such a distribution upon the overall system thermal conductance is small. This is reasonable because it must be less than a few % change from expected, and furthermore — only those changes deviating from linearity will produce a net change. Finally, any putative change from such thermal stratification is insignificant compared to the "hydrogen gas airspace effect" which occurs when the air around the electrochemical cell is replaced by hydrogen (or deuterium in heavy water experiments) which thereby markedly increase the thermal conductance of the system (Fig. 1). Most significantly, the hydrogen gas effect has the impact of making calculations of putative excess energy a lower limit to that which may have actually occurred if such systems have such an unanticipated hydrogen volume in the gas space.

In summary, temperature gradients in the vicinal air surrounding a calorimeter can exist for several reasons. For this to be significant there must be either a nonlinear or an asymmetric thermal air stratification. Even then the impact is small and probably not significant when compared to the quantitatively larger hydrogen gas airspace effect.

REFERENCES

1. M. Swartz, "Potential for Positional Variation in Flow Calorimetric Systems," *J. New Energy*, vol. 1, no 1, pp 126-130 (1996).
2. J. Melcher, Continuum Electromechanics, MIT Press, Cambridge, 10.13-10.18 (1981).
3. S. Chandrasekhar, Hydrodynamic and Hydromagnetic Stability, Clarendon Press, Oxford, 9-75 (1961).
4. M. Jakob, , G.A. Hawkins, Elements of Heat Transfer and Insulation, John Wiley, New York, (1950).
5. A.I. Brown, S.M. Marco, Introduction to Heat Transfer, McGraw-Hill Book Co (1958).
6. H. Schlichting, D.J. Kestin, Boundary Layer Theory, Pergamon Press, New York (1951).