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The Ideal Gas–Calorimetric Thermometer

A thermometer that is sensitive to differences between temperature scales is proposed.

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The ability to assign unique values of temperature is a fundamental requirement in modern science and technology. It is also important that these values be consistent with the values on a (theoretical) thermodynamic temperature scale. This is necessary because the values of thermodynamic properties are sensitive to the temperature scale on which they are determined, and, in fact, a small difference between temperature scales can be appreciably amplified in its effect on some of these properties. Moreover, thermodynamic relations between such properties (relations which are basic tools in science and technology) are strictly true only for thermodynamic temperatures. Over the years extensive measurements have been made to determine the values of the thermodynamic temperatures at which certain well-known phase transitions occur (the fixed points), so that the practical temperature scale would be in close agreement with the thermodynamic temperature scale.

Recent measurements by Guildner (*1*) suggest that the present International Practical Temperature Scale, IPTS-1968 (*2*), has serious deficiencies near the steam point. Using a gas thermometer, Guildner obtained a value at the steam point on the thermodynamic scale that differs from the value on IPTS-1968 by an amount which is more than five times larger than the assigned uncertainty (*2*) for the IPTS-1968 value. Guildner suggested that sorption effects had significantly compromised the accuracy of earlier gas thermometry measurements and may have contributed to the large variations in the values at the steam point. Other types of thermometers have been used to measure the values on the thermodynamic scale, such as those based on the speed of sound (acoustic thermometers) and those associated with measuring total or spectral radiation. However, each of these has special limitations (*3*; *4*, pp. 385 and 432), so that over its working range the (equation of state) gas thermometer is still the general standard for approximating the thermodynamic temperature scale.

It is my purpose in this article to illustrate a method for measuring thermodynamic temperatures which offers the advantage of enhanced sensitivity to differences between a practical scale d the thermodynamic scale (*5*). The physical basis for this thermometer rests on two facts:

1) Differences between temperature scales can be determined from a comparison of thermodynamic properties measured on these scales.

2) Thermodynamic properties for simple substances as a function of the thermodynamic temperature can be accurately calculated for the ideal gas by the methods of statistical mechanics.

Douglas has shown (*6*) that the temperature derivative of the difference between two temperature scales is approximately equal to the fractional difference between the heat capacities on these scales. I propose to use the ideal gas heat capacities for a substance calculated from the known molecular structure by the methods of statistical mechanics as the thermodynamic scale reference. (The ideal gas heat capacity is, ipso facto, the heat capacity on the thermodynamic scale.) The ideal gas heat capacity is then compared with the heat capacity of the substance measured calorimetrically and extrapolated to zero pressure. If other systematic errors have been rendered relatively small, the integration over the temperature range of the fractional difference in the heat capacities yields directly the temperature scale differences, that is, the difference between the thermodynamic scale and the practical scale. To illustrate the method, I shall use existing data for gaseous ammonia (*7*, *8*).

Heat Capacity of Gaseous Ammonia

The data for the calorimetric measurements of the heat capacity at constant pressure for ammonia (*7*) were obtained at the National Bureau of Standards about 50 years ago. The experimental data extend from about $-15°C$ to $+150°C$ and from about ½ atmosphere to about 20 atmospheres, except at the lower temperatures where they extend to within a few degrees of the saturation curve. The data were smoothed and tabulated for temperatures in the range $-30°C \leqslant t \leqslant 150°C$ and for pressures in the range $0 \leqslant P \leqslant 20$ atmospheres. A comparison of the smoothed results with the experimental data indicates a maximum deviation of 0.26 percent, but about half scatter within ±0.05 percent.

The ideal gas calculation (*8*) for ammonia includes a term-by-term sum-

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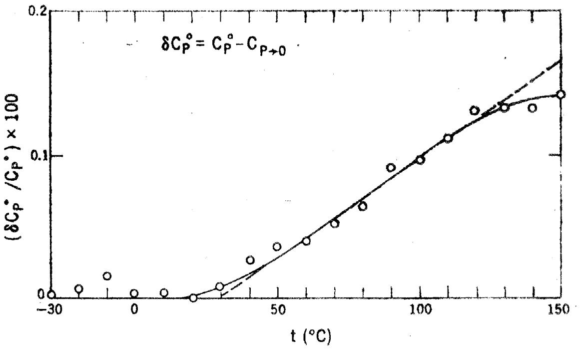
Fig. 1. The fractional difference (in percent) in the heat capacity versus values of temperature for ammonia. The $C_P{}^0$ values are the ideal gas values (*8*). The $C_{P\rightarrow0}$ values are experimental values extrapolated to zero pressure from (*7*).



mation of the rotational-vibrational structure of the highly anharmonic out-of-plane vibrational mode. In the region −30°C to +150°C the principal uncertainty in the tabulated ideal gas heat capacities arises from the gas constant, so that the accuracy in this region is better than 1 part in 10,000. Thus it is thought that the major part of the differences between the ideal gas heat capacity and that obtained calorimetrically (as extrapolated to zero pressure) can be ascribed to errors in the calorimetric values.

Fortunately, the calorimetric work done one-half century ago was reported in sufficient detail that we can interpret these measurements in terms of standard units in use today. However, it should be realized that uncertainties from the conversion can never be completely removed. This is so because the instruments that were used then are no longer available for direct calibration, and, even if they were, there would still be an uncertainty due to aging effects. For this analysis I employ the conversion factor between the international joule and the absolute (mechanical) joule then used (1923) by the experimenters. There is an uncertainty of about 1 part in 10,000 in the conversion from this source.

In Fig. 1 the fractional difference (in percent) in the constant pressure heat capacities is plotted versus values of temperature. At each point shown in Fig. 1 the difference between the heat capacities $\delta C_P{}^0$ refers to the calculated ideal gas value $C_P{}^0$ at a particular value of the temperature on the *thermodynamic* scale minus the analogous calorimetric value extrapolated to zero pressure $C_{P\rightarrow0}$ at the same numerical value of temperature on the *practical* scale used in the laboratory experiment. The smooth curve was drawn through the plotted points.

At the lower temperatures, from −30°C to +30°C, the experimental $C_{P\rightarrow0}$ results agree with those for the ideal gas to within 2 parts in 10,000, that is, to nearly the accuracy of the ideal gas calculation. However, below −10°C the experimental results include extrapolations in regions where the experimental C_P isotherms exhibit sharp curvature, so that the agreement below −10°C is clearly fortuitous. As the temperature increases from +30°C to +150°C, it is apparent that a small systematic difference exists which is monotonic in temperature, with a maximum difference of 15 parts in 10,000 at +150°C. As discussed above, this systematic difference is ascribed to error in the calorimetrically obtained values. It is this systematic difference that I would like to consider in this article.

Ideal Gas–Calorimetric Thermometer

I pose the following question: Can the small systematic difference indicated in Fig. 1 be ascribed to differences between the thermodynamic scale and the practical scale used by the experimenters? It has been ascertained (*9*) that in the temperature range of the experiments the laboratory scale used was essentially identical to the International Temperature Scale, ITS-1927 (*10*); this scale is nearly identical to ITS-1948 (*11*). In 1968 the present practical scale (*2*), IPTS-1968, was adopted. It included significant revisions. [The differences between the practical scales, IPTS-1968 and ITS-1948, as tabulated in (*6*), are illustrated in Fig. 2.] However, at the steam point IPTS-1968 and ITS-1948 have the same value, and at the triple point they are constrained to be identical by definition. Thus we conclude that at the ice point and at the steam point the values of temperature on the practical scale as realized at the National Bureau of Standards in 1923 agree with the values on IPTS-1968 as realized today (*12*).

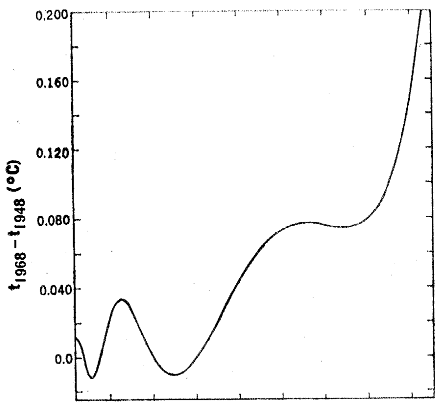


Fig. 2. Relative difference between IPTS-1968 and ITS-1948 versus values of temperature.

In (*6*) the relation between the thermodynamic functions as measured on different scales was obtained by means of Taylor series expansions. In the present application the practical and thermodynamic scales are very close, so that only the lead terms in such expansions need be retained. Figure 3 is a schematic drawing depicting the relation between two scales which are assumed to be in close agreement with each other and with the thermodynamic scale. The ordinate θ refers to the thermodynamic temperature scale. The abscissa t refers to numerical values of temperature for thermometers that reproduce the individual scales. Thus, if a substance is observed by someone using scale 1, the numerical value A for this scale corresponds to the value of thermodynamic temperature $\theta(A)_1$ in Fig. 3. If the same substance is observed by one using a thermometer based on scale 2, it would have a value on the ordinate of Fig. 3 given by $\theta(A)_2$ at A on the scale 2 thermometer. I define μ to be the difference in thermodynamic temperature at the same numerical value of temperature, that is,

$$\mu(A) \equiv \theta(A)_1 - \theta(A)_2 \qquad (1)$$

Obviously, in the schematic drawing (Fig. 3) $\mu(A)$ is positive; that is, A on scale 1 represents a hotter state than A on scale 2. For this numerical value of temperature the difference in enthalpy of a substance measured on these scales is given by

$$\delta H_A \equiv H(A)_1 - H(A)_2 \cong \mu(A) C_P(A)_1 \qquad (2)$$

The relation for the heat capacity difference for the substance is then

$$\delta C_P(A) \equiv C_P(A)_1 - C_P(A)_2 = \frac{d}{dt}\delta H_A \qquad (3)$$

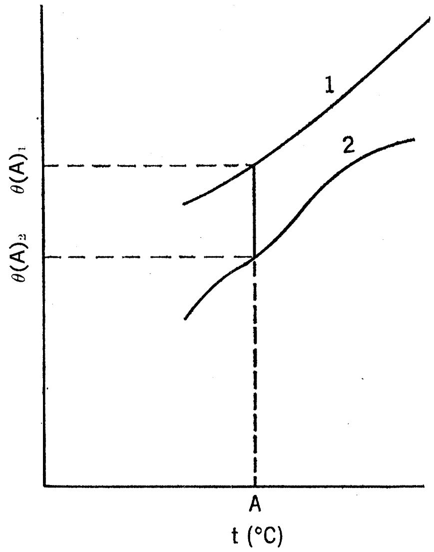


Fig. 3. Schematic comparison of two temperature scales. The ordinate refers to thermodynamic temperatures, and the abscissa refers to the values of temperature.

which with Eq. 2 yields the relation

$$\delta C_P \cong \frac{d}{dt}[\mu(C_P)_1] = \mu\frac{d}{dt}(C_P)_1 + (C_P)_1\frac{d}{dt}\mu \qquad (4)$$

In Eq. 4 $\mu\, dC_P/dt$ is negligibly small (except in a small region near the critical point), so that we obtain the relation

$$\frac{\delta C_P}{(C_P)_1} \cong \frac{d}{dt}\mu \qquad (5)$$

Now let us consider the situation in which scale 1 in Fig. 3 refers to the thermodynamic temperature scale and scale 2 refers to the practical temperature scale in use at the National Bureau of Standards in 1923. Then in the limit of zero pressure the δC_P in Eqs. 3–5 reduce to $\delta C_P{}^0$, where

$$\delta C_P{}^0 \equiv C_P{}^0 - C_{P\rightarrow 0} \qquad (6)$$

where $C_P{}^0$ and $C_{P\rightarrow 0}$ refer, respectively, to the ideal gas value and the experimental value extrapolated to zero pressure, as described above and compared in Fig. 1. The quantity μ now refers to the difference between the thermodynamic scale and the practical scale, and a positive value of μ means that the thermodynamic scale is hotter. If Eq. 5 is rewritten in integral form for the interval 0° to 100°C, we obtain the relation

$$\mu(100) - \mu(0) = \int_0^{100} \frac{\delta C_P{}^0}{C_P{}^0}\, dt \qquad (7)$$

It may be seen (Fig. 1) that $\delta C_P{}^0/C_P{}^0$ in the region from 30° to 100°C is approximately a straight line, with a value of zero at about 30°C and very nearly 0.001 at 100°C, and with a value of zero for $0° \leqslant t \leqslant 30°C$. Thus we obtain

$$\frac{\delta C_P{}^0}{C_P{}^0} \cong \alpha x \qquad (8)$$

where $\alpha = 10^{-3}/70$, $x = t - 30$ for $t \geqslant 30°C$, and $x = 0$ for $t < 30°C$. Equation 7 then yields

$$\mu(100) - \mu(0) \cong 0.035°C \qquad (9)$$

Since the scales are in agreement at the ice point, $\mu(0) = 0$. Thus, Eq. 9 indicates that at 100°C the thermodynamic scale is hotter by 0.035°C than the practical scale of 1923. By the arguments above, it is hotter by this amount than the practical scale in current use, IPTS-1968.

The value of temperature on the thermodynamic scale corresponding to the steam point, as implied by this analysis, is given by

$$\theta_{\text{steam}}\ (\text{thermo}) = 99.965°C \qquad (10)$$

The value reported by Guildner (*1*) is

$$\theta_{\text{steam}}\ (\text{thermo}) = 99.973°C \qquad (11)$$

The agreement is within the uncertainty of our ability to interpret the 50-year-old calorimetric data.

Sensitivity and Accuracy

Let us now investigate the sensitivity of the proposed thermometer and the accuracy required of the calorimetry. Consider the situation for which the difference between the practical scale and the thermodynamic scale in the temperature interval τ may be represented by

$$\mu = \gamma t^n,\ 0 \leqq t \leqq \tau \qquad (12)$$

where γ and n are constants. If the absolute temperature in degrees Kelvin is written

$$T = T_0 + t$$

the ratio of the fractional difference in heat capacity to the fractional difference between the scales is obtained from Eqs. 5 and 12, namely,

$$\frac{\delta C_P{}^0}{C_P{}^0} \Big/ \frac{\mu}{T} = \frac{T}{t}\, n \qquad (13)$$

In the region near 100°C Fig. 1 yields the value $n = 2$. If T_0 refers to the ice point, Eq. 13 yields a value for the ratio of about 7 at 100°C. This result is consistent with data in (*6*), from which a ratio of about a factor of 10 in the region 0° to 100°C is obtained for the special situation considered therein (*13*).

Now let us consider the extent to which systematic errors in the calorimetric measurements affect the accuracy of the temperature determination. The calorimetric errors degrade the result by the extent to which they alter the area under the curve in Fig. 1. Let us for this exercise assume that an accuracy of measurement is achieved such that we can assign an uncertainty of 1 part in 10^4 to the experimental heat capacity data points. Let us first consider the most unfavorable situation for which each data point is taken to be in error by this amount and the bias is all in the same direction. In this case the error in the value of temperature at 100°C would be $10^{-4} \times 100 = 0.01°C$. For this case the error would increase with the interval from the ice point, so that at 200°C it would be double that at 100°C, but at 50°C it would be only half as much. If we assume a less severe form of the bias for the experimental data points, the accuracy would be improved; for example, an improvement of a factor of 2 over the above would result if the systematic bias in the data points were all in the same direction but increased linearly with temperature. An accuracy of 1 part in 10,000 in the calorimetry might, therefore, be expected to result in an accuracy for the temperature of the steam point of ±0.005°C.

In recent years there has been a paucity of accurate calorimetric measurements for dilute gases. However, a precision of measurement approaching 1 part in 10^4 was achieved nearly 20 years ago (*14*). Advances in instrumentation since that time could be expected to render the calorimetric requirements more tractable. The data for ammonia (*7*) taken nearly one-half century ago are also suggestive of the feasibility, although we should not rule out the possibility that the agreement achieved for these data was fortuitous. The accuracy of the thermometer could be enhanced by judicious choice of the working fluid. For example, if one of the noble gases were to be used, the experimental C_P versus pressure isotherms would have little curvature at low pressures. Extrapolations to zero pressure for these gases would be more accurate than those for ammonia. Also the ideal gas $C_P{}^0$ values are practically constant for the noble gases.

References and Notes

1. L. A. Guildner, paper presented at the Fifth Symposium on Temperature, Its Measurement and Control in Science and Industry, Washington, D.C., 21 to 24 June 1971.
2. Comité International des Poids et Mesures, *Metrologia* **5**, 35 (1969).
3. H. Plumb and G. Cataland, *Int. J. Sci. Metrol.* **2**, 127 (1966) (see appendix).
4. J. F. Swindells, Ed., *Precision Measurement and Calibration, Selected NBS Papers on Temperature* (National Bureau of Standards Special Publication 300, Washington, D.C., 1968), vol. 2.
5. L. Haar, paper presented at the Second International Conference on Calorimetry and Thermodynamics, Orono, Maine, 12 to 14 July 1971.
6. T. B. Douglas, *J. Res. Nat. Bur. Stand. Sect. A* **73**, 451 (1969).
7. N. S. Osborne, H. F. Stimson, T. S. Sligh, Jr., C. S. Cragoe, *Bur. Stand. U.S. Sci. Pap. No. 501* (1925).
8. L. Haar, *J. Res. Nat. Bur. Stand. Sect. A* **72**, 207 (1967).
9. H. F. Stimson, personal communication.
10. K. Burgess, *J. Res. Nat. Bur. Stand.* **1**, 635 (1928).
11. H. F. Stimson, *ibid.* **42**, 209 (1949).
12. The very small temperature difference, about 0.010°C, between the triple point and the ice point is readily calculated, and for my purposes I assume that the thermodynamic scale and the practical scale are in agreement at the ice point.
13. Table 4 of (*6*) includes data for the difference between thermodynamic properties on IPTS-1968 and ITS-1948. Consider the range 0° to 100°C. From column 3 the maximum value of $\delta C_p/C_p$ in the range is about 4×10^{-4}. From column 2 the maximum value in this range for μ yields $(\mu/T)_{\max} \sim 3 \times 10^{-5}$. The ratio is about 10.
14. J. F. Masi, H. W. Flieger, J. S. Wicklund, *J. Res. Nat. Bur. Stand.* **52**, 275 (1954).
15. Supported in part by the Office of Standard Reference Data.

Predicting Attitudes toward Violence

Monica D. Blumenthal

Violence has been a conspicuous part of American life during the last few years (*1*). Assassinations (*2*), riots (*3*), student disruption (*4*), and violent crime, which is increasing in proportion to the population (*5*), have all contributed to the aura of violence in this decade. Moreover, there has historically been a great deal of violence in American life (*6*). Indeed, some authors contend that most major social movements in the United States have been accompanied by violence. When violence is considered in its historical perspective, it is clearly of the utmost importance to develop and test a theoretical model capable of predicting violent behaviors.

As a first step in this quest, a model designed to predict attitudes toward violence was developed and tested. It was assumed that attitudes are likely to be reflected by behaviors, and that a model capable of predicting attitudes toward violence could later be modified to explain part of the variance in predicting behavior. To test this model, a survey was taken of attitudes toward violence in a representative random sample of 1374 American men between the ages of 16 and 64 (*7*). The men were interviewed in the coterminous United States in the summer of 1969, and the final response rate was 80 percent. Black men were sampled at a higher rate than others, thus the final sample included 303 blacks.

Measuring attitudes toward violence is an important venture in its own right. One of the characteristics of contemporary American life is the extent to which the mass media expose us to violence. For example, the question of whether or not television increases aggressive and violent behaviors was considered so crucial by the surgeon general that he established a major committee to investigate the problem (*8*), even though the staff of the National Commission on the Causes and Prevention of Violence had already published an extensive monograph on the subject (*9*). If the mass media can influence people to act more aggressively and violently, as may be the case, one must ask how such influence is exerted. Do the media simply serve as a model for imitation (*10*), or do the messages they project modify fundamental social values that inhibit or facilitate violent behaviors?

Many people think of violence as primarily expressive actions generated by frustration and fueled by anger, possibly because much of the work on aggression by social psychologists has developed along this line, beginning with the studies of Dollard *et al.* (*11*). These studies served as the foundation for the work of many others (*12*). However, as Berkowitz (*13*) points out, violence may be primarily instrumental—neither directly related to frustration, nor accompanied by anger. Instrumental violence can be used as a tool for achieving a variety of goals, some of which are political (*14*). For example, it may be used to force a change in the distribution of power in situations where persuasion and influence cannot be used successfully (*15*), or it may be used as a tool to maintain the status quo. Instrumental violence can also be used for purely individual purposes, such as gaining money by committing robbery.

Clearly, individuals might hold quite different attitudes toward different kinds of violence. One would not expect the same person to approve of both violence to maintain the status quo and violence to produce revolutionary change. Consequently, the model developed to explain attitudes toward violence specified that types of violence must be differentiated. The survey focused mainly on measuring attitudes toward violence for social change and violence for social control.

The Model

For any particular set of circumstances and for any particular person, the level of violence considered to be justifiable may be regarded as the resultant of opposing forces, some of which tend to drive the level down until no violent act is perceived as justifiable and others of which tend to drive the level up until acts of extreme violence become justifiable. Among these forces are the following.

1) *Basic cultural values against violence.* The Judeo-Christian ethic, which is widely espoused in this country, states that "Thou shalt not kill." In addition, a prominent theme in the New Testament is the notion of the golden rule—that is, that one ought to treat one's neighbors as one would like to be treated oneself. Both of these

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