ChE views and opinions

HOT LIPS, A COLD HEART AND THERMOMOMETRY

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THE ORIGIN OF THE THERMOMETER, a device with some sort of scale for measuring the hotness or coldness of objects, is obscure. However, the climate in Europe in the beginning 1600's was hot for it, it had to be invented at that time, and so it was . . . but by whom? In Italy Galileo had his champions, and so had Santorio, Professor of Medicine at Padua. Then there was the Welsh doctor and religious nut Fludd; also the gadgeteer, inventor, and perpetual-motion-machine-maker, Drebbel of Holland. But who was first? Since people in those days didn't much care about getting into the Guinness Book of Records we probably will never satisfactorily resolve this question. It seems that this sort of immortality was not the passion then that it is today.

In any case, by the middle of the 1600's the thermometer was widely known in Europe, each maker having his own scale of measurement. A popular design started with "1" in the middle of the device to represent everyday comfort. It then indicated 8 degrees of coldness and 8 degrees of hotness, each degree in turn divided into as many as 60 minutes. Other makers were more descriptive, viz

Extream Hott
Very Hott
Sultry
Hott
Warm
Temperate
Cold
Frost
Hard Frost
Great Frost
Extream Frost

Even as late as the middle 1800's one could buy a thermometer having 18 different marked scales.

The development of a standarized temperature scale was a long and bumbling process. About 100 years after the invention of the thermometer enter Daniel Gabriel Fahrenheit, Danzig born, Dutch adopted, master instrument maker, and traveller. While in Copenhagen in 1704 or 5 (or maybe 6) he visited Ole Rφmer, Danish astronomer, where he observed him busily calibrating thermometers. Struck by the elegant simplicity of Rφmer's choice of calibration points . . . 7½° for the ice-water and 22½° for body temperature, Gabe immediately adopted these for his own. But since fractions always bothered him he eventually multiplied everything by 4 to get rid of the two halves, fudged upward a bit, and ended up with 32° and 96° for these calibration points. On this scale a mixture of sea salt and ice melted at about 0° and water boiled somewhere between 200° and 240° (say 212° as a good average). Because humans are somewhat unreliable, some hot blooded, others questionable, before long the freezing point (32°) and the boiling point of water (212°) became the accepted calibration points. Since Fahrenheit's thermometers sold well this scale soon became widely adopted.

The temperature measures the "quantity of heat" in a body, or in today's language, "thermal energy." So "why not measure temperature directly." Georgian, an American engineer, strongly urges we adopt such a scale choosing the ideal gas as measuring instrument.

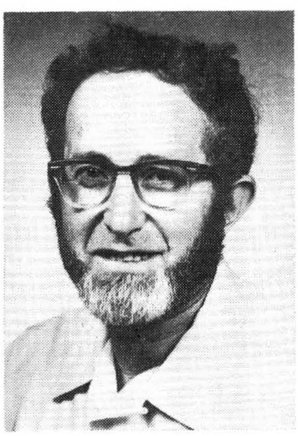
PARTY PLEASER

IT WAS QUITE A MARVEL in those days to put ice and a liberal helping of salt in a pan, insert a thermometer and see it zonk down to 0°F and stubbornly refuse to budge . . . even with the pan on a hot stove! But in our age of TV marvels we may have to dress up this experiment to catch anyone's attention. Here is one way, best done at a large party or gathering. Bet a particularly obnoxious fellow $10 that he cannot keep his foot in a pan of salt and ice for 10 minutes.

Sit him down and while his foot is freezing solid get hold of a hammer. After 10 minutes his pain is gone and you are ready for the finale to this demonstration. Remove his foot from the pan and strike his big toe firmly with the hammer. The brittle toe will snap off and fly across the room. Accompanied by "ooohs" and "aaahs" retrive this toe and in a matter-of-fact way return it with $10 to the surprised owner. This spectacular ending will guarantee that you and thermometers will be the talk of the town for a long time to come.

To return to the thermometer, while Gabe's came into wide use in England and Holland, the French completely ignored this Northern development. Their man was Réaumur who after 1731 vigorously championed a spirits of wine thermometer . . . French wine, of course, and red for easy reading. His scale went from 0° for ice water to 80° for boiling water. Unfortunately, however, among other things Réaumur's insistence on a one-point calibration and the fact that the quality of French wine varied from year to year, led to all sorts of complications. So although the French gave this thermometer a good try for over a century, they eventually gave it up; and drank their wine instead.

While these developments were taking place in warmer climes Swedish astronomer Anders Celsius tramped his snowy land with 10 cold fingers and 10 cold toes advocating a 100 division scale (centigrade) by continually proclaiming "water boils at 0°, water freezes at 100°, boils at 0°,



Octave Levenspiel, professor at OSU, is primarily interested in problems of chemical reactors. He has written a text on this subject, and has won the ASEE Lectureship Award for his early visions in this field.

His weakness for scientific curiosities has led to flirtations with 4-colorologers, 2nd law repealers, Fibonacciics, boomerologists, topolographers, and other such. He is also 1975 president of the Northwest Neothermo Society.

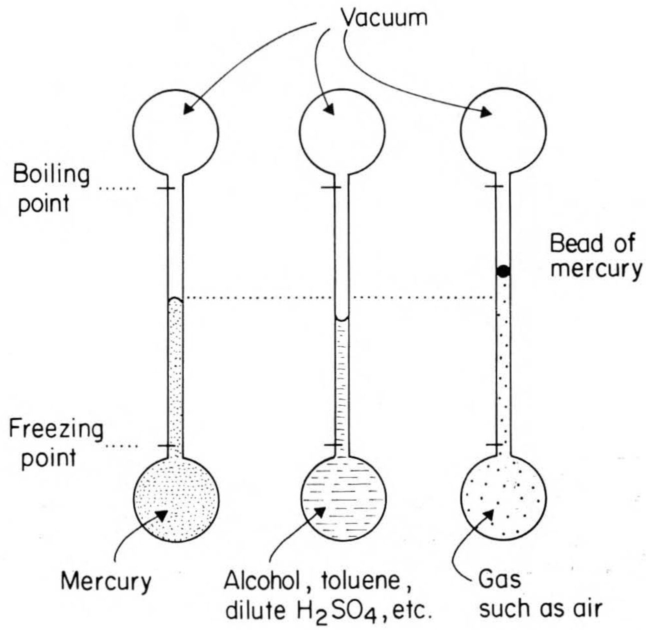


FIGURE 1.

freezes at 100." By happenstance however, Anders' intimate friend, Linnaeus, the great botanist, was left-handed. Because of this he kept snatching the wrong end of the instrument and using it upside down, and kept reading 0° for the freezing point and 100 for the boiling point, and thus recommended this scale.

To confuse the issue further there were other strong claimants for the honor of inventing this scale; nevertheless, in 1948 the 9th General Conference of Weights and Measures decided that it knew enough, it dismissed all the others, and ruled that what had been known as °Centigrade should henceforth and forever more be known as °Celsius. And so Celsius' name will be with us forever, and all because he chose his parents wisely. Had Linnaeus' name been Clinnaeus we might today be talking of °Clinnaeus instead of degrees Celsius.

CALIBRATION CONFUSION

THERMOMETERS EVOLVED into three broad types, as shown in Fig. 1, and as users became fussier and demanded more precision all sorts of problems cropped up. For example, should melting ice or freezing water be one of the calibration points? In practice they differ! Should boiling water or condensing steam be the other? The zero point also slowly and continually changed with time. In mercury thermometers it crept upward, in alcohol thermometers it slid downward.

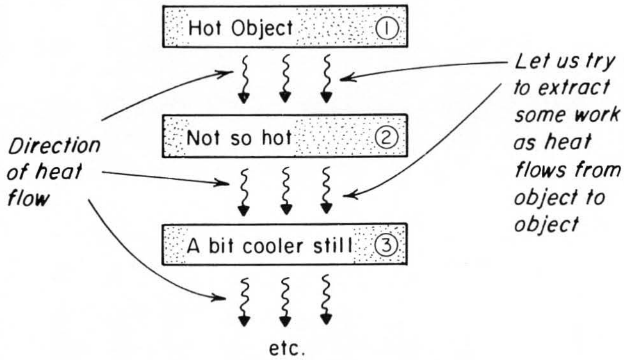


FIGURE 2.

Was this due to the aging of glass, the slow decomposition of the fluids, or what? And these changes continued for 10, 20, 30 years!! Also, how did these scientists explain the small periodic variations according to season!!?

Probably the most serious problem was that when one type of thermometer read a temperature halfway between calibration points the others did not because of changing coefficients of expansion of fluids. This is illustrated in Figure 1. In this case which thermometer read the true midpoint temperature—which to trust? Was the selection of equal intervals of temperature an arbitrary matter, or was there a rational way for doing this? These difficulties kept scientists out of mischief for quite a while.

In the 1800's there was much concern about developing a rational temperature scale. In 1847 Regnault pinpointed the problem by stating:

> **"We give the name *thermometer* to instruments intended to measure the variation of the quantity of heat in a body . . . A perfect thermometer would be one whose indications are always proportional to the quantity of heat absorbed, or, in other words, one in which the addition of equal quantities of heat always produces equal expansions . . . Unfortunately this is not so for real substances."**

Just a year later William Thomson, later Lord Kelvin, magically devised just such a temperature scale based upon the concept of the ideal reversible heat engine of Sadi Carnot. To illustrate its basis, imagine a number of objects or heat reservoirs arranged from hot to cold as shown in Fig. 2, and let heat flow from one to the other while doing as much work as possible.

Suppose that 100 units of heat leave reservoir 1 for reservoir 2, and in the process are able to do 10 units of work in the most efficient engine conceivable. Then 90 units of heat reach reservoir 2. Suppose these 90 flow on, doing 10 more units of work before reaching the next reservoir, and so on.

Kelvin argued that we should choose a temperature scale which is proportional to this heat flow. Any proportionality would do, thus 100, 90, 80°, etc. or 250, 225, 200°, etc., for the sketch shown in Fig. 3. Scales such as these are now called Absolute temperature scales.

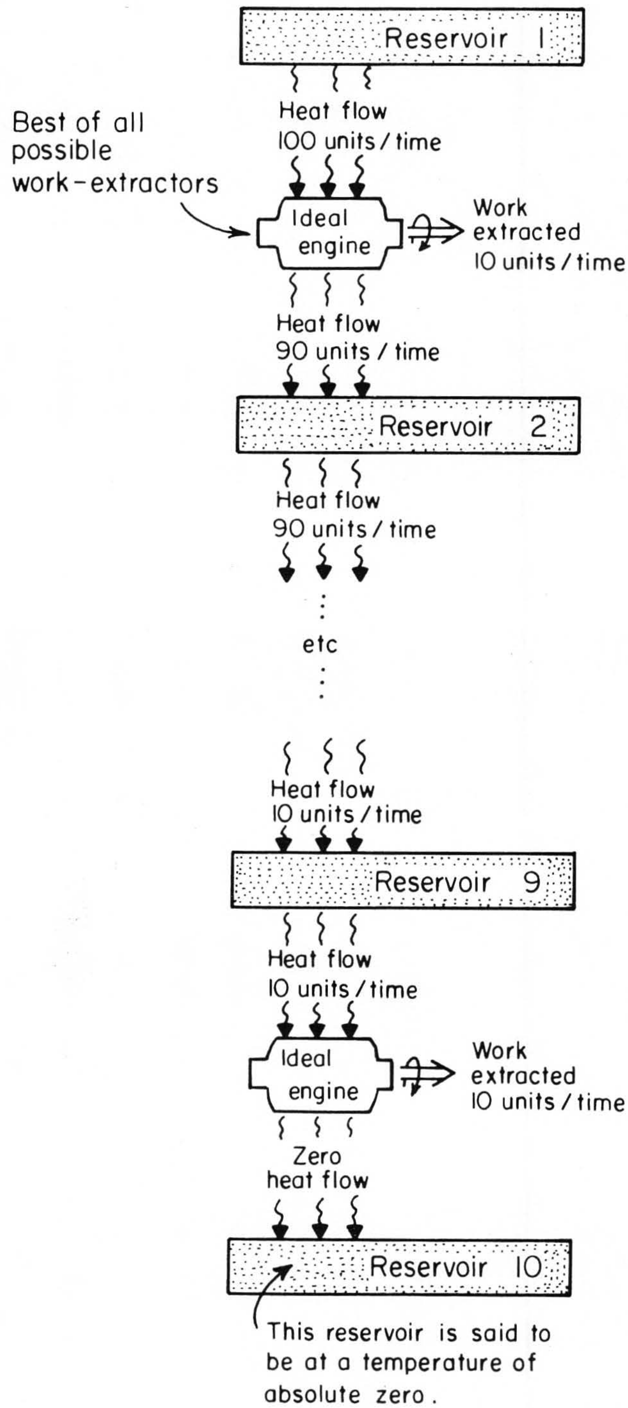


FIGURE 3.

An interesting bonus to this argument of Kelvin's is that since no heat enters the lowest reservoir of Fig. 3 none can leave it to flow to an even colder one. Thus this bottom reservoir in the sketch must be the lowest imaginable of temperatures, the ABSOLUTE ZERO of temperature. What a jewel of an idea this turned out to be.

On this basis we now commonly use two scales; the Kelvin scale corresponding to degrees Celcius and the Rankine scale corresponding to degrees Fahrenheit. These are sketched in Fig. 4.

Today, more than 100 years later, how pure do we find his conclusions? Giant refrigeration machines fueled by Nobel prizes help us freeze our way even closer to this "THOU SHALT NOT TRESPASS" limit, yea, within a thousandth of a degree, but Kelvin's limit still stands unshaken and confident.

Finally Kelvin found that simple gases at very low and constant pressures occupied volumes proportional to their absolute temperature, and therefore provided a practical way for accurately calibrating thermometers.

TEMPERATURE TODAY

SO HERE IS HOW THINGS stand today. First of all the lowest possible temperature imaginable, the absolute zero, has been invented. This is where our temperature scales should start from, and this is where our absolute scales (°Kelvin and °Rankine) in fact do. Secondly, we have a rational way for choosing equal intervals of temperature.

We just have one question left. Starting from this cold cold zero point, why pick our unit of temperature the way we do? Why base it on 100 intervals or 180 intervals between the freezing and boiling point of water? Why pick water, why not googliox? Isn't there a more reasonable way of selecting our unit of temperature?

As Regnault long ago pointed out, the temperature measures the "quantity of heat" in a body, or in today's language, its "thermal energy". So why not measure temperature directly as energy per unit quantity of material. Georgian, an American engineer, strongly urges that we adopt such a scale choosing the ideal gas as measuring instrument. The reason for this is that the energy of any ideal gas is proportional to its absolute temperature. So measure its energy and you've got its temperature.

The sketches in Fig. 5 compare various possible absolute temperature scales following this

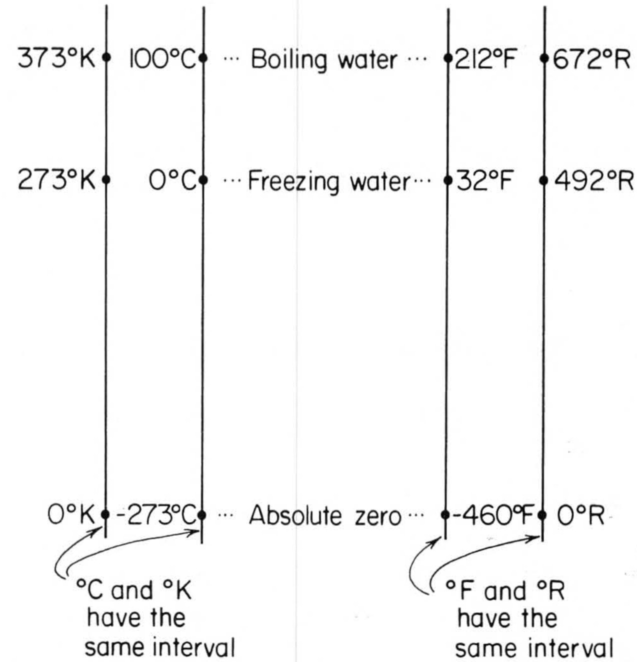


FIGURE 4.

proposal. Because of its compatibility with the SI units Georgian particularly favors the last of these scales, or joules/kmol.

It may seem awkward and foreign to talk of water freezing at 2270°X, boiling at 3100°X, and of having a mild fever of 2600°X (where X would then honor some famous scientist whose name does not start with the letters C, F. K or R). However, you must admit that it would be a smashing bit of one-upmanship to sprinkle one's talk this way. But more seriously, with such a scale a number of simplifications occur naturally. In particular it would forever banish one conversion

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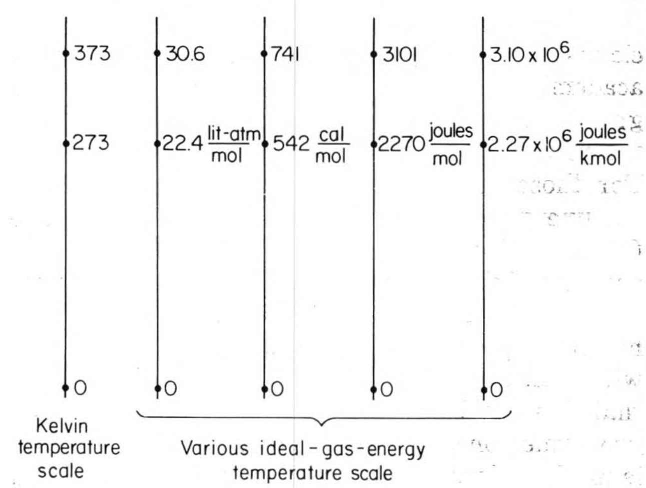

FIGURE 5.

other than flow rate may also be easily investigated.

CONCLUSION

OBVIOUSLY MANY OTHER applications of CSSL may be envisioned, not only in kinetics and reactor engineering, but in other areas of chemical engineering and other engineering and scientific disciplines as well. These languages should be used as instructional aids in the investigation of advanced dynamic systems on the undergraduate level. They allow considerable ease of analysis such that the student may devote his attention to a detailed study of system mechanics. This does not constitute much of a compromise in the education process since the details of numerical analysis are normally covered in other, more basic, applied math courses. Digital simulation is fast replacing analog simulation and the modern CSSL represents an exteremely high level, user oriented simulation package. □

```
LFN = INPUT
  $D1
      C1 = Q/V
      C2 = —DHRXN/(RO*AA*CP)
      C3 = US/(V*RO*CP)
      RA = —RKO*EXP (—E/(R*TEMP))*CA
      CA. = C1* (CAO-CA) +RA
      CB = CAO-CA
      TEMP. = C1*(TF-TEMP) + C2*RA+C3* (TC-TEMP)
  7/8/9
  7/8/9
    $SYSTEM TMAX = 5000., DT = 0.01, DIMIN=0.01, NPOINT =
      51$
    $ST1 CA = 0.002, TEMP = 318.5$
    $UND RO=1., CP=1., Q=8.0, V=2000., US = 1.356, DHRXN
      = —10000., TF = 300., CAO = 0.005, RKO=7.86E+12, R=
      1.9872, TC=305., AA=—1.$, E=22500.$
  7/8/9
  LIST, CA, CB, TEMP
  PLOTXY, TEMP, CA
  PLOT, CA, CB
  PLOT, TEMP
  7/8/9
  6/7/8/9
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FIGURE 6: Program used in solving Example 2.

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NOMENCLATURE

a_i	Stoichiometric coefficient, dimensionless.
C_i, C_{iF}	Reactant concentration in reactor and reactor feed respectively, moles/cc.
C_p	Reacting fluid heat capacity, cal./(gm.)(°C.).
E	Activation energy, cal./mole.
ΔH_R	Energy of reaction, cal./mole.
k,k_o	First order reaction rate constant and pre-exponential factor respectively, sec^{-1}.
k_1, k_2, k_3	Second order reaction rate constants, liter/(mole)(sec.).
q	Volumetric flow rate, cc./sec.
r_i	Reaction rate, mole/(cc.) (sec.).
R	Gas law constant, cal./(mole)(°K).
S	Heat exchange surface area, $cm.^2$.
t	Time, sec.
T,T_F,T_c	Temperature in reactor, reactor feed, and to heat exchange coil respectively, °C.
U	Overall heat transfer coefficient, cal./($cm.^2$)(°C.)(sec.).
V	Reactor volume, cc.
ρ	Reacting fluid density, gm./cc.
[ ]	Denote molar concentration of enclosed species.

THERMOMOMETRY: Levenspiel

Continued from page 105.

factor from our lives (all thermo students would cheer this), that miserable gas constant. Thus, for a mole of ideal gas

$$pV = RT \text{ would become } pV = T$$

$$C_p - C_v = R \text{ would become } C_p - C_v = 1,$$

for one mole of any substance

$$C_p \text{ and S would be dimensionless}$$

and the gas constant R, the Boltzman constant k, and Avogadro's number A would be related as follows:

$$R = \frac{k}{A} = 1 \quad \text{or} \quad k = \frac{1}{A}$$

Imagine, the letter R would be free forever more to play new roles. In fact so would the Boltzman constant k. With all the new concepts of science crying for symbols what a boon this would be.

I wonder whether a change to so pure and rational a temperature scale could receive serious consideration today, or is science too big, with too much inertia? We'll see. □