Priestley Medal Address

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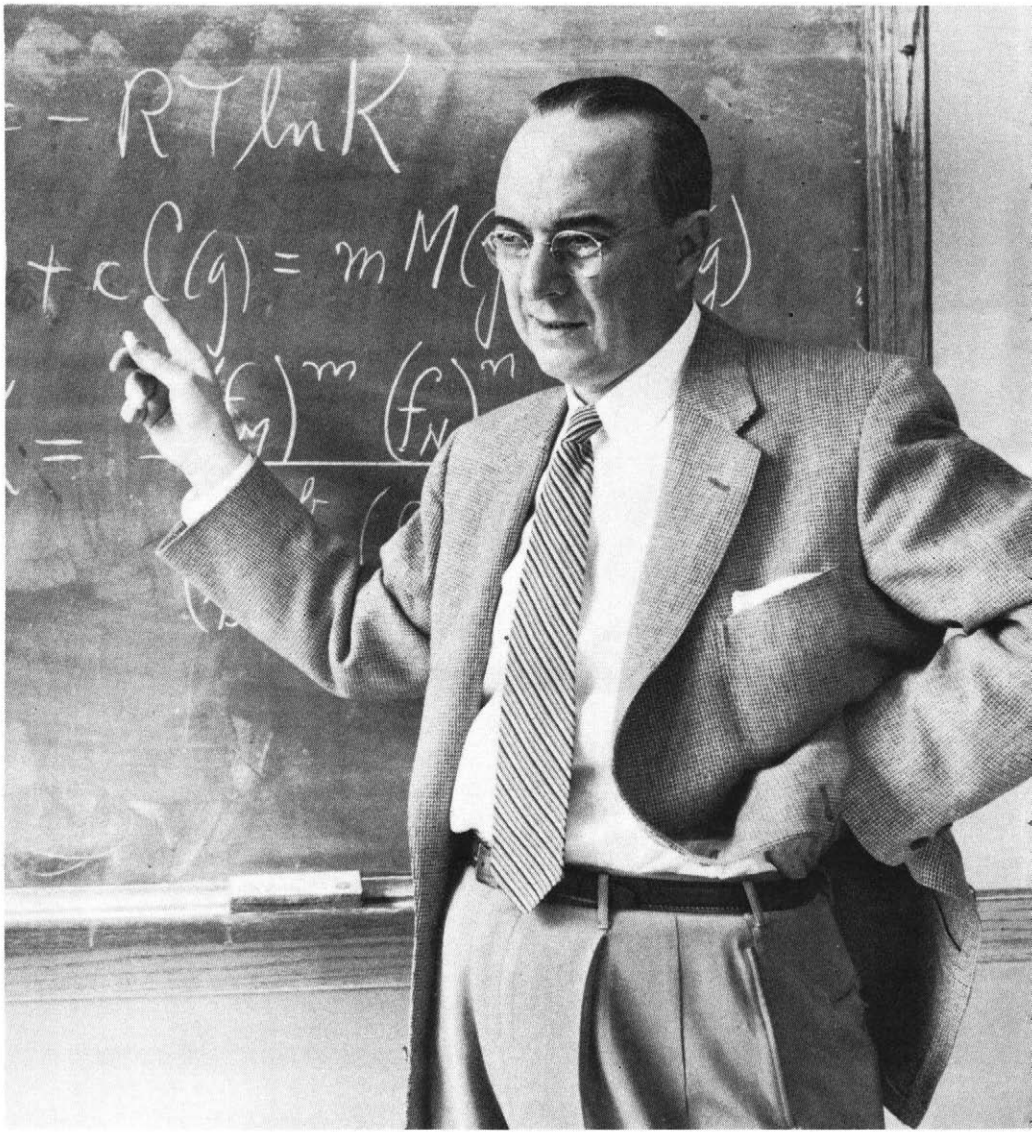
Chemical thermodynamics in the real world



When Dr. Milton Harris, then Chairman of the Board of Directors of the Society, telephoned me one day last June with the message that I had been chosen to receive the Priestley Medal, I was most happily taken by surprise. This award, commemorating one of the world's early great experimental chemists, is a high honor and I accept it most humbly. To be listed in the company of all the preceding Priestley Medalists is a great privilege, and one which I take much to heart.

For my talk this evening, I have selected the subject "Chemical Thermodynamics in the Real World," because it represents an area in which I have worked a great deal and because it relates to present-day problems of our society. I will try to show that thermodynamics is a discipline highly relevant to the real world in which we live and that its fundamental laws may be related to human experience.

First, let me make the point that science and technology have done wonders for the human person. In his primitive days, man devoted all his efforts to the sheer business of eking out an existence and staying alive—getting food and shelter and protecting himself from animal and man predators. As science and technology developed, with work machines of all kinds, man found himself in the new situation of having time to ponder about natural phenomena and the world in which he lived.

In the United States today, we find that science and technology have given man such a high capability for producing goods and services that we are now approaching a four-day workweek. This will give man even more time to read and think, and to enjoy nature, the cultural arts, and recreation. Further, advances in the science and technology of health and medicine have extended the average lifetime of our people, providing still more days to enjoy life on earth.

Beginning with his cave-man days, man's existence has always been accompanied by pollution. In the early days, pollution was easily disposed of in the natural environment. Later, it became necessary to arrange for the specific disposal of the more detrimental wastes produced by man in homes, in manufacturing, and in recreation. Until recently, this appeared to be reasonably satisfactory.

There are two ways of reducing pollution of any particular kind: One way is to destroy or eliminate the process that causes the given pollution and do without the goods and services produced by that process.

Dr. Frederick D. Rossini delivered his Priestley Medal address March 29 at the national ACS meeting in Los Angeles, Calif. The Priestley Medal was established in 1922 by ACS to recognize distinguished services to chemistry. The award consists of a gold medal designed to commemorate the work of Joseph Priestley and a bronze replica of the medal. It is awarded to members and nonmembers of ACS; medalists are selected by the Board of Directors.

Carried on without limit, this procedure would, in time, have us revert to primitive cave-man existence. The other way is to call on science and technology to refine and refashion the given process so as to reduce the amount of pollution associated with it down to limits which can be easily tolerated by man.

Reversion to nature and the primitive life does not automatically bring us pure water and pure food. Depending on the location and the proximity of other substances, the water and the food may have natural contaminants of various amounts, some of which can be very harmful to humans. There is nothing that is absolutely pure, nor can man ever make it so. Even with the best equipment, all we can do is reduce the amount of impurity in any given substance to lesser and lesser amounts. Nothing in the world has absolutely zero amount of impurity—the case is similar to the unattainability of the absolute zero of temperature.

With these views, I take as a basic assumption that science and technology are a great good for mankind, and that all the machines and devices created by science and technology can, with proper development and use, bring great advantage and much benefit to all humanity.

Science is based upon observation and measurement. The ability to measure is one of man's great capabilities. Thermodynamics involves accurate measurements. Thermodynamics deals with all forms of energy and matter and with their transformations. Every process or reaction that occurs can be subjected to the powerful scrutiny of thermodynamics. Therefore, the more expert we become in thermodynamics the more we can develop increasingly greater control over the energy and the matter of the world in which we live.

Throughout all history, man's material development has gone hand in hand with his ability to develop and control sources of power and energy. The technological advancement of a country may be measured in terms of its production and consumption of energy. It follows, then, that we need to understand this science that deals with energy, "thermodynamics."

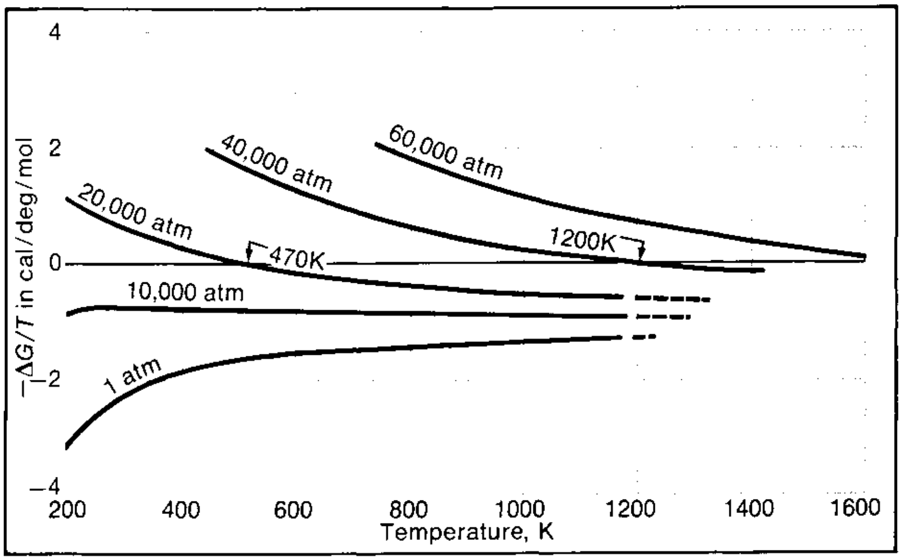
Synthetic diamonds. One example of the role of thermodynamics in technological advancement is the production of synthetic diamonds. In 1938, we published a report on the thermodynamics of the conversion of graphite into diamond. The making of synthetic diamonds has been a fascinating prospect ever since 1797, when diamond was first shown to be a form of carbon. Though many investigators in different countries tried to produce synthetic diamonds, and a number of them claimed success, it was generally agreed that, as of 1938, no synthetic diamonds had ever actually been produced. What we wanted to do then was to calculate the pressures and temperatures necessary for the conversion of graphite into diamond, the hardest material known to man.

For these calculations, we needed data on the difference, between graphite and diamond, of the values of the following properties: energy, entropy, density, change of energy with temperature, change of density with temperature, and change of density with pressure. With these data, and the first and second laws of thermodynamics, we made the calculations. The results of those calculations are shown below. We have plotted on the vertical axis $-\Delta G/T$, the negative of the change in free energy divided by the absolute temperature, and on the horizontal axis the absolute temperature in Kelvins. The dashed lines represent extrapolation of the data. Thermodynamically, the conversion of graphite into diamond is possible anywhere in the region above the horizontal zero line, the conversion being favored at lower temperatures and higher pressures. But a high temperature is required to have the reaction proceed.

From this chart, one sees that the pressures required are very high:

Temperature, K	Pressure, atm
1200	40,000
1600	60,000

About 1956, after a few years of work by a high-powered team of its scientists and engineers, one of the big industrial research laboratories of the U.S. succeeded in producing real synthetic diamonds of small size, suitable for important industrial uses. This was a great breakthrough and has since been accomplished in several laboratories in the U.S. and other countries. These experiments were carried out in the general area of the temperatures and pressures predicted by our calculations.



In my opinion, the actual production of synthetic diamonds succeeded because of several things: The availability of reliable thermodynamic calculations on the conversion of graphite into diamonds; the discovery of a suitable catalyst and solvent; and the development of an apparatus capable of sustained use at high temperatures and high pressures.

Fuel cells. Fuel cells are another example of the importance of thermodynamics in man's control of energy. In 1967, we published a report on the thermodynamics of fossil fuel cells. During the past 50 years, the total quantity of energy consumed in the U.S. per year has about tripled. Today, all fossil fuels—natural gas, petroleum, and coal—account for about 95% of the energy produced in the U.S. The natural supply of petroleum and natural gas may last another 50 to 100 years. The natural supply of coal may last another 500 to 1000 years.

The conventional combustion of fossil fuels for power may take place in a steam-turbine-generator system to produce useful energy for electricity or in an automotive engine to produce useful energy for transportation. In both of these cases, the conversion of the heat energy into useful energy is severely limited by the second law of thermodynamics, through the Carnot factor. On the average, only about

35%, or less, of the heat energy is actually converted into useful energy.

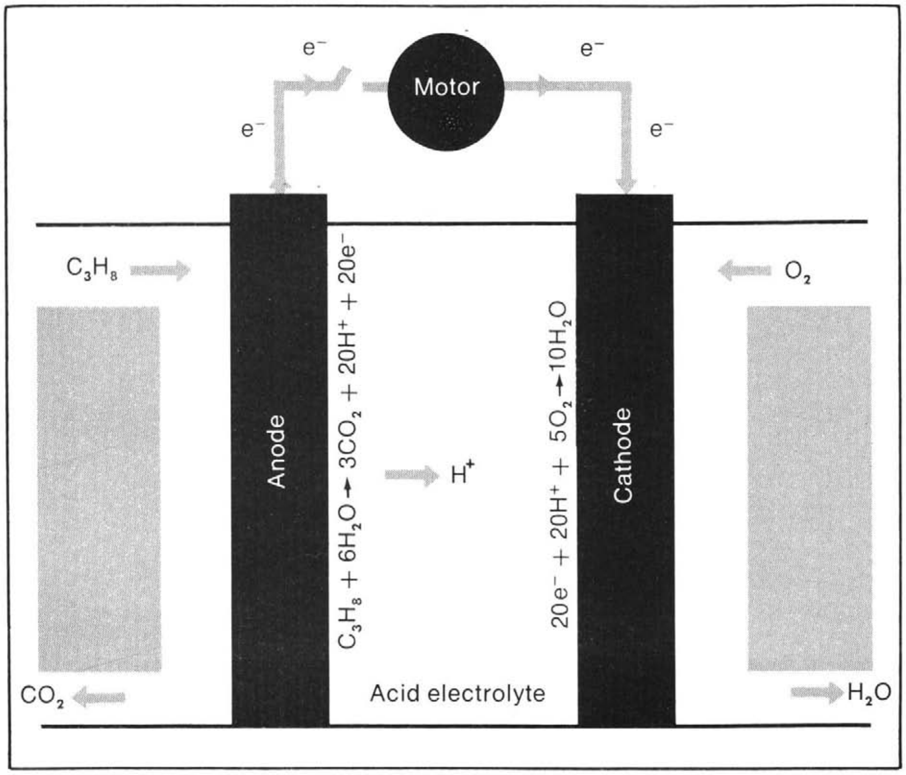
The conventional combustion of a fossil fuel is a thermodynamically irreversible process. However, it is possible, by means of a device called the fuel cell, to carry out the process of combustion in a thermodynamically reversible manner. In this case, theoretically, 100% of the energy is convertible into useful energy. Even allowing for a 30% loss, we could thus obtain with the fuel cell twice as much energy from the same amount of fuel as with the conventional process.

The schematic, below, gives a diagram of an ideal hydrocarbon fuel cell, using propane. In this ideal picture, the fuel enters at the upper left, the oxygen enters at the upper right, the produced carbon dioxide is discharged at the lower left, and the produced water is discharged at the lower right. At the anode, propane reacts with water to form carbon dioxide plus hydrogen ions and electrons. The hydrogen ions produced pass from the anode through the electrolyte to the cathode. The electrons pass from the anode into the external circuit through the work machine and return to the system at the cathode. At the cathode, the oxygen molecules combine with hydrogen ions and electrons to form water molecules. The sum of the electrode reactions is simply the combustion of propane in oxygen to form water and carbon dioxide.

The fossil fuel cell power plant has many attractive possibilities. As previously mentioned, a given amount of fuel in it should produce about twice as much energy as in a conventional power plant. Other possible advantages of the fossil fuel cell power plant are summarized as follows: No noise; no vibration or moving parts; no mechanical generating problem; no heat transfer problem; no starting problem; minimal maintenance; no dirt or other local pollution; no atmospheric pollution; completely self-contained; and can be coupled directly to a direct current motor.

Fossil fuel cell power plants could be used in many different places, such as trucks and passenger vehicles for city driving; industrial plant trucks; locomotives; marine installations; standby power generators; portable power plants; a central generating plant for isolated areas; and small power installations in isolated areas. When the fossil fuel cell power plant is part of a mobile vehicle, the fuel is carried in a suitable container aboard the vehicle. When the fossil fuel cell power plant is stationary, the fossil fuel can be fed into it as a gas, liquid, or pulverized solid, through a pipeline from a nearby or a remote source.

The possible advantages and uses of the fossil fuel cell power plant appear so attractive as to warrant the considerable amount of research and development work still required before a fully operational and practical everyday device becomes available. We hope that this may come in the not too distant future.



Societal problems. So far, I have cited two examples to show how fundamentally important thermodynamics is to all of us in the real world. Now, without going into detail let me simply say that there are many problems of our present-day society of which thermodynamics can make significant contributions toward solutions. Here are listed some of the problems to which I refer:

- Maintenance of the quality of the air we breathe and the water we drink.
- Maintenance of the quality of our natural resources of land and water.
- Production, distribution, and consumption of food.
- Production, distribution, and consumption of energy.
- Proper disposition of waste produced by man in the home, in factories, on the farm, and in recreation.
- Proper recovery and use of our mineral resources, and their recycling, wherever possible.
- Proper disposition of the thermal discharge from fossil fuel and nuclear power plants.
- Problems of local, national, and international transportation, by land, water, and air.
- Problems of local, national, and international communication.

In all of these problems, thermodynamics enters to a greater or lesser extent, either directly or indirectly, through its relation to the various areas of chemistry, physics, biology, geology, and the various branches of engineering.

For the last part of my discussion, I want to put before you an exercise in chemical thermodynamics. In thermodynamics, we have two important properties, energy and entropy, and two important laws, the first law and the second law. The first law expresses the conservation of energy for any process that occurs. The second law expresses the conservation of entropy for any reversible process—for all other processes there is an increase in entropy.

A simple description of energy is that the energy of a system arises from the binding forces that hold together the elementary particles—nuclei, ions, atoms, molecules, and macromolecules—constituting the system. The greater the binding forces, the more tightly bound is the system, and the lower is its energy. This corresponds to a state of greater security. The smaller the binding forces, the less tightly bound is the system, and the higher is its energy. This corresponds to a system of lesser security.

The sketch, below left, shows two hydrogen atoms unattached, at the upper level, and attached to form the hydrogen molecule, at the lower level. Taking the energy of the hydrogen molecule as zero, we see that the energy of the two unattached hydrogen atoms is greater by 104,000 calories per mole. We see this easily since we know that to dissociate the hydrogen molecule into its atoms we have to add a great deal of energy to it.

Here is a simple description of entropy: The entropy of a system arises from the number of states of existence available to it. The number of states increases with increase in the randomness of a system and decreases with increase in the degree of order of a system. The greater the number of states, the greater is the entropy. This corresponds to a system of greater randomness and greater freedom. The smaller the number of states, the smaller the entropy. This corresponds to a system of lesser randomness, more order, and lesser freedom. In the limit, with only one state available, the system is completely ordered and the entropy of the system is zero.

The sketch, below right, shows again the two unattached hydrogen atoms and the hydrogen molecule. It is seen that at 25°C the entropy of the two free atoms is greater than the entropy of the two bound atoms by 75% or about 24 calories per degree mole. Clearly the two unattached atoms, which can move independently of one another, have much more freedom than the two atoms bound together in the molecule.

Let us look at the equilibrium constant, K, for the reaction of dissociating the hydrogen molecules into their atoms:

$$(\mathrm{H{:}H})\ \text{gas} = \mathrm{H}\ (\text{gas}) + \mathrm{H}\ (\text{gas})$$

$$K = (P_{\mathrm{H}})^2/(P_{\mathrm{H_2}})$$

For any given reaction, we are interested in as large a value of K as possible, in order to obtain greater amounts of the products. In this example, the larger the value of K, the larger the concentration of hydrogen atoms that are in equilibrium with hydrogen molecules.

With the first and second laws of thermodynamics we can derive two important equations:

$$\Delta G^\circ = -RT \log_e K$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

Here ΔG° is the standard change in free energy, R is the gas constant, T is the absolute temperature, K is the equilibrium constant, ΔS° is the standard change in entropy, and ΔH° is the standard change in heat content, very nearly the same as the change in energy. Since the term on the left side is the same in the two equations, the quantities on the right side are equal to one another. Hence we can write

$$-RT \log_e K = \Delta H^\circ - T\Delta S^\circ$$

or

$$\log_e K = \Delta S^\circ/R - \Delta H^\circ/RT$$

From this equation, K increases with increase in ΔS°; and K increases with decrease in ΔH°. Increase in ΔS° comes with increase in the number of states of existence available, leading to greater "freedom" in the system. Decrease in ΔH° comes with increase in the energy of binding of the atoms in the molecular structure, leading to greater "security" in the system. These are opposing factors in the evaluation of K, and hence, for a given temperature, the final state of equilibrium is a compromise between the "freedom" term, $\Delta S^\circ/R$, and the security term, $-\Delta H^\circ/RT$.

To repeat this, the final state of equilibrium, then, is a compromise between two more or less opposing factors: greater freedom or greater entropy, as measured by $\Delta S/R$; and greater security or lesser energy, as measured by $-\Delta H^\circ/RT$.

Here we have an interesting picture derived from our science of thermodynamics—equilibrium or stability is a compromise between freedom and security. In terms of human experience, the meaning of security can be interpreted to mean that one is secure and safe in his person, in his family, in his home, in control of his property, on the streets, and on his travels. The meaning of freedom is quite clear—the privilege of doing whatever one wants to do. However, in our civilized society, we have come to believe in behavior according to natural law—that one can do whatever he wishes so long as he does not abridge or infringe upon the rights and privileges of others. To me, all this means living with some rational kind of law and order.

The picture we have developed from thermodynamics is very simple: One cannot have a maximum of freedom and a maximum of security at the same time. If there is a maximum of freedom, there will be zero security. I interpret this to mean that if we have total freedom, everyone can do whatever he wishes, including the injuring of others, the stealing of property, and the like. On the other hand, if there is a maximum of security, there will be zero freedom. I take this to mean that if we have total security, we will be constrained at every step and have a virtual strait-jacket life.

One sees that there is a trade-off between freedom and security. In a state of total freedom, we can afford to give up some freedom to obtain some security. The ideal situation would appear to be one in which we have established that amount of security necessary to have human beings live happily and in harmony with one another, through observance of an appropriate amount of law and order, and then to have as large an amount of freedom as can be accommodated in this situation.

The point of all this is that our creator has fashioned laws that are deep seated and broadly applicable, that science is heavily interwined in our everyday life, frequently without our realization, that we need to break down the compartmentalization of knowledge, that we need to work for a unification of learning, and that we need to understand better the meaning and purpose of life.