

Chemical transformations are brought about by the transfer of energy from a source to a sink, the latter being the chemical system of interest. Strictly speaking, energy is that which diminishes when work is done and is equivalent to the work done. The dimensional units of energy and work,  $\text{ml}^2/\text{t}^2$ , are identical. Energy is also defined as the capacity for producing effects, said effects being of widely differing character.

Energy may be classified as being stored or in transition. Examples of stored energy are (1) mechanical, as in a flywheel, where the stored energy is given by  $E = \frac{1}{2}mv^2$  for each particle of mass  $m$  and velocity  $v$ ; (2) geopotential, due to gravity, where  $E = mGh$ ,  $G$  being a gravitational constant and  $h$  being the height above some frame of reference; and (3) internal energy stored within matter, such energy being a function of the state of the elementary particles comprising the matter. This includes strain energy as stored in a spring, chemical energy, and energy stored by virtue of temperature.

The following are examples of energy in transition. (1) One is mechanical, a situation in which a force moves its point of application. Mechanical work is defined as  $W = \int F \cos \mathbf{q} ds$ , where  $F$  is the force applied and  $s$  represents the course followed. In the field of high pressure (a special form of mechanical energy), the work done is expressed as  $W = \int P dV$ , where  $P$  is the pressure and  $dV$  is the change in volume. (2) Electrical work or energy due to a potential difference  $\Delta E$  under which a current flows is another example. The potential  $E$  is measured in volts, the current flow in amperes, and the energy (product of current flow and potential difference) is measured in joules. (3) Another is heat, that enigmatic form of energy in transit because of a temperature difference. This energy is not called heat before it starts to flow or after it has ceased to flow. Heat is unidirectional. It only flows from a higher to a lower temperature, and the source and the sink, in an isolated system, will eventually attain the same intermediate temperature.

Energy in transition can often be expressed as the product of two factors: a capacitive or extensive factor and an intensive factor. Some examples are shown below.

Type of Energy	Extensive Factor	x	Intensive Factor	= Energy, Commonly Measured in
Electrical	Coulombs		Potential	Joules
Heat	Heat Capacity		Temperature	Calories
Radiation	Planck's constant		Frequency	Ergs
Kinetic	Mass		$\frac{1}{2}(\text{Velocity})^2$	Ergs
Pressure	Volume		Pressure	Liter-atmospheres
Chemical	Moles		Chemical Potential	Calories

The intensive factor associated with energy is usually responsible for inducing phenomenologic changes in matter. Such changes often occur when a certain threshold value of the intensive factor is attained. In connection with electrical energy, we observe ionization potentials, deposition potentials, decomposition potentials, and so on. With heat energy there are melting points, boiling points, triple points, and all kinds of critical points. In the case of pressure energy there are solidification pressures, a large variety of phase transformation pressures, electronic transition pressures, and various types of critical point pressures. Because intensive factors bring about such changes in matter, it is important to vary this parameter over as large a range as possible. By so doing new phenomena are invariably discovered.

It is worthwhile to reflect on how extreme values of intensive properties may be obtained. As I see it, there are three general methods to employ: (1) disproportionation, (2) gathering or focusing, and (3) in situ energy transformation.

An electrical transformer by having a high turns ratio between primary and secondary windings can take a given amount of low voltage/high current energy at the primary terminals and by disproportionation provide high voltage/low current energy at the secondary terminals, or vice versa. Similarly a lever can disproportionate a given amount of energy as a small force operating through a large distance to yield a tremendous force available over a small distance. "Give me a place to stand and, with lever, I will move the

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world," said Archimedes. Hydraulic pumps and rams operate on similar principles to those used by levers and make it possible to exert very large forces on small areas, thus giving rise to high pressures.

Each of the above disproportionators has theoretical capabilities for raising the intensive property to infinitely large values. Practically, however, each is restricted by limitations in the properties of materials of construction. Voltages obtainable with transformers are limited by breakdown of the electrical insulation. Forces obtained with a lever are limited by the tensile strength of the material of which the lever is constructed, and pressures derived by transferring the large thrust of a hydraulic ram to a small area (to generate high pressure) are limited by the compressive strength of the transferring material. Limitation imposed by the strengths of materials can sometimes be circumvented by inventive design. Thus the maximum voltage obtainable from a transformer can be increased considerably by certain spacing and placement of the windings. Similarly geometrical considerations, to be discussed in the chapter on high-pressure techniques, increase the pressures obtainable from high-pressure devices.

The second law of thermodynamics apparently precludes disproportionation as a means for increasing the temperature of a system. Thus in an isolated system of initial temperature  $T_0$  and heat capacity  $C_0$ , it would not be possible to increase the temperature to a high value  $T_h$  by causing the heat capacity to decrease to a low value  $C_l$  such that  $T_0C_0 = T_hC_l$ .

An example of a gathering or focusing process to obtain practical use of an already high intensive property is the use of parabolic mirrors or lenses to concentrate radiant energy from the sun. An example of a gathering or focusing process to obtain practical use of an already high intensive property is the use of parabolic mirrors or lenses to concentrate radiant energy from the sun. The energy coming from sun to earth arrives in a very diffuse but undegraded state; that is, the radiation spectrum is about the same as that emanating from a blackbody at the same temperature as the sun's surface. In order to make it possible for this energy to interact with a useful quantity of matter, it must be concentrated by some kind of gathering process. Incidentally, it is interesting that the capacitive factor for radiant energy is invariant; namely, it is Planck's constant, the quantum of action.

In situ energy transformation is the most widely used method for obtaining a high value of an intensive property. For example, high temperatures are obtained in an electrical resistance furnace by the in situ transformation of electrical energy into heat. In a particle accelerator, tremendous velocity is imparted to electrically charged particles by extraction of energy from electromagnetic fields. At extremely high velocity, relativistic phenomena come into play, and there is an in situ transformation of kinetic energy into mass. The kinetic energy of a high-speed electron is transformed into radiant energy as the electron impinges on a metallic target, and so on.

In the field of high pressure, the use of disproportionation to obtain high pressures has given the most satisfactory results. However there are some in situ energy transformations that have been used. It is possible to generate a pressure in a fixed volume by increasing the temperature of a material within this confined space. Chemical energy may be utilized to generate pressure by employing a chemical reaction or phase change in which the products of the reaction or the new phase normally occupy a larger volume than that to which they are confined.

So far this discussion has centered around means for obtaining high values of intensive properties. Low values are also important, particularly low values of pressure (high vacuum) and low temperature. One of the most exciting discoveries of all time is the phenomenon of electrical superconductivity at low temperature, discovered by Kamerlingh Onnes in the Netherlands in 1911. The attainment of high vacuum is a necessity for all the achievements of high-energy physics and for a great deal of the modern solid-state technology.

To obtain low temperatures, two items are important: (1) thermal insulation, to prevent heat leak from ambient conditions into the system, and (2) means for extracting heat from the system (refrigeration). The attainment of high vacuum is also anticipatory: means must be provided (1) for preventing leak of gaseous substances into the system and (2) for extracting gases from the system. Materials science and inventiveness, particularly in the mechanical area, have been necessary for the advancement of these fields.

Aside from the general requirements briefly considered herein for attaining extreme conditions and the significance of the intensive factor of energy in transition, there are ancillary items important to chemical experimentation. One is the efficiency with which energy is transferred from the source to the sink. I will illustrate this with a story. During the period 1927 to 1933, I was a skinny, underweight farm boy attending school (grades 1 through 9) at a four-room building in Marriott, Utah. We played baseball (hardball) during lunch hour and two recesses every day, weather permitting. It was fashionable to use the heaviest bat available (an ego-building show of strength). But I could hardly hold such a bat. However, while

enduring taunts from my muscular peers, I could handily knock a home run with a small girl's softball bat. It didn't know it then, but it was all a matter of  $E = \frac{1}{2}mv^2$  and matching the energy available at the source (myself) to the sink or load (the ball). A heavy bat swung slowly could contain less energy than a light, fast swinging bat because energy increases with the square of the velocity but only linearly with the mass. Only recently have the major baseball leagues recognized this.

In an automobile, the necessity of matching the energy available at the source (the engine) to the sink (the wheels) is manifest by the gear-shift box or automatic transmission. In the field of electricity, the efficient coupling of an energy source to a sink is known as impedance matching. Gears, levers, pulleys, coaxial cables, and parallel twin-lead TV wires all serve the same purpose—the effective transfer of energy from source to sink.

There are parallels for chemistry. All chemical reactions, including phase changes, are connected with the repositioning of atoms relative to other atoms. Thermodynamics gives us a nonmechanistic criterion for ascertaining that rearrangements may or may not occur given  $P$ ,  $V$ ,  $T$ ,  $n$ , and  $C$  (pressure, volume, temperature, number of moles, and heat capacity) for all substances in the system. But it does not tell us the time it will take. Chemical kinetics, at its present state of development, can predict reaction time in only a few instances. But experimental studies in this field are very valuable for eliciting mechanisms by which reactions take place. Chemical reactions are much more complex than mechanical or electrical systems; but, in the gross, inducing a reaction to proceed in a reasonable length of time (assuming favorable thermodynamics) is an impedance-matching problem. That is, energy from a source must be channeled through an interface matched to the sink for energy in transit to flow freely and rapidly into the system. Often a chemical reaction is "broad band." It will accept energy (heat or otherwise) without benefit of a specific impedance-matching interface. But many reactions, while highly favorable from a thermodynamic standpoint, will not proceed without a catalyst. The catalyst may be regarded as the impedance-matching device—the bat between the boy and the ball. In order to match a source to a sink, something must be known about the characteristics of each. This is easy in electronics and mechanics but difficult in chemistry. Hence choosing a catalyst is often done by trial and error. Exploring under extreme conditions will discover only the broad-band reaction products. Catalysts will be needed to find the diamonds.

Kinetic studies are often directed toward understanding chemical reactions at the atomic and molecular level. At this level, reactions proceed very fast, sometimes in  $10^{-15}$  sec. Since the Greeks, we have wondered what matter was like if we divided and divided it into ever smaller pieces. Fortunately for chemists, it need only be divided into neutrons, protons, and electrons. Physicists, with their greater dividing power, are currently having Technicolor migraines.

Troubled by the increasing complexities of divided matter, some have turned to dividing time, but this presents perplexities also, even for chemists. Time can be divided and measured by means of waves. Useful waves for chemical experimentation are electromagnetic and ultrasound, for which the corresponding particles are photons and phonons. When the energy of waves is high, the uncertainty principle may limit the information obtainable from fast reactions in chemistry. The uncertainty principle states that  $\Delta E \Delta t \geq h$ , where  $\Delta E$  is the uncertainty in the range of the energy and  $\Delta t$  is the uncertainty in measurement of the time. Planck's constant is represented by  $h$ . For a time interval of a femtosecond ( $10^{-15}$  sec), the uncertainty of an energy measurement would be at least 10 kcal/mole. Since chemical bond energies lie in the range of 5 to 200 kcal/mole, the uncertainty principle will frustrate accurate measurement of energy parameters in times less than about a femtosecond. Interestingly, time itself may be quantized. The smallest unit of time is the chronon, which is about  $4.5 \times 10^{-24}$  sec. This corresponds to a frequency of  $2.2 \times 10^{23}$  sec<sup>-1</sup> and a wavelength of  $1.4 \times 10^{-23}$  cm.

Since there is a lower time limit in which chemists can do their kinetics and an upper limit (for the laboratory) based on man's patience and lifetime, it is interesting to ask questions concerning upper and lower limits for pressure and temperature. For temperature, we speak of absolute zero as the theoretical lower limit. Nevertheless, energy content at absolute zero, while a minimum, is not zero and is so expressed by the uncertainty principle. Chemical synthesis near absolute zero would ordinarily be restricted by slow reaction rates, at least in the gross. An insufficient number of molecules would have enough energy to transcend the kinetic barrier. However it seems possible that the order characteristic of systems at low temperature might, through quantum effects or for other reasons, change the nature of the activated state for a chemical reaction. There may be unexplored territory here.

Physical measurements at low temperature have been very enlightening with respect to theory and fundamental problems of chemistry. For example, specific heat measurements have been made to temperatures as low as  $0.001^\circ$  K, and it has been possible to sort out contributions due to the lattice, the

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electrons, and the nuclei. In these measurements investigators have "seen" energy of the nucleus equilibrate with the electrons. This transfer of energy can occur because of the finite possibility that an electron will, in due time, pass through the nucleus.

At extremely low temperatures, radioactive nuclei have been aligned in a magnetic field such that particles or radiation resulting from nuclear disintegration are emitted in preferred directions. Can this order be used to advantage in nuclear fusion? Extremely high temperature (the sledgehammer approach) is the current mode for attempts at sustained nuclear fusion. Are we overlooking an ultralow-temperature finesse.

The upper theoretical temperature limit for chemical experimentation is set only by the fact that chemistry, as ordinarily perceived, ceases to exist. At a sufficiently high temperature, all molecules will become mon-atomic ions and form a plasma.

Very low pressures (high vacuum) offer opportunity for chemical experimentation with atomic, molecular, and ion beams and for the study of surfaces and other things. There is not intrinsic property of high vacuum, per se, that should limit chemical experimentation in the sense that low temperature does. The practical limit for vacuum may be set, considering perfect pumps and no leaks, by contamination from the ever-present high-energy rays and particles from outer space.

The theoretical limit for high-pressure chemical experimentation is similar to the case of high temperature. For any system there will be a pressure where ordinary chemistry will not be known. Sufficient pressure will make metals of all nonmetallic elements. Regular chemistry will prevail at pressures as high as  $10^7$  atm. the ultimate galactic pressure is thought to exist in the recently postulated black holes.