

The Conversion of Chemical Energy

Part 1. Technological Examples

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Chemical energy is energy that is either stored or can be released through a distinct chemical reaction. As such, it appears in many forms (Table 1), always in the form of some kind of potential energy. When a chemical reaction occurs, the energy of the chemical species may change and energy can be released to or absorbed from the surroundings. This can involve the exchange of chemical energy with another kind of energy or with another chemical system.

Table 1. Types of Chemical Energy

Type	Examples
Chemical Bonding	Connections between atoms
Electronic Energy Levels	Molecules after absorption of visible or ultraviolet radiation
Vibrational/Rotational Energy Levels	Thermally excited molecules or after absorption of infrared or microwave radiation
Osmotic Energy	Membrane separated concentration differences*
Electrochemical Energy	Elements capable of transferring electrons

*Especially interesting in the context of biological chemistry.

Chemists commonly characterize changes in the chemical energy of a system through changes in the Gibbs free energy, ΔG , which is appropriate for reactions run at constant pressure. If $\Delta G < 0$ for a reaction, then the reaction is spontaneous and energy is released to the surroundings. If $\Delta G > 0$ then the reaction will not proceed spontaneously, though it can be "forced" through the appropriate input of energy from the surroundings. This transfer of energy between a reacting chemical system and its surroundings involves the coupling of the two forms of energy. This article discusses such energy couplings through examples from contemporary technological problems. A second article discusses examples from bioenergetics, the study of energy transfers in biological systems.

Heat and Work in Chemical Energy Conversion

A chemical reaction, defined as a change in the chemical state of the system, is typically accompanied by a release or an uptake of energy from the surroundings. This energy transfer typically involves another form of energy, in patterns sketched in Figure 1. Some reactions involve the transfer of *heat*, which means that thermal energy—the energy associated with the temperature of a system—is generated or consumed. But other forms of energy can be coupled to chemical energy changes and in those cases the performance of *work* on or by the chemi-

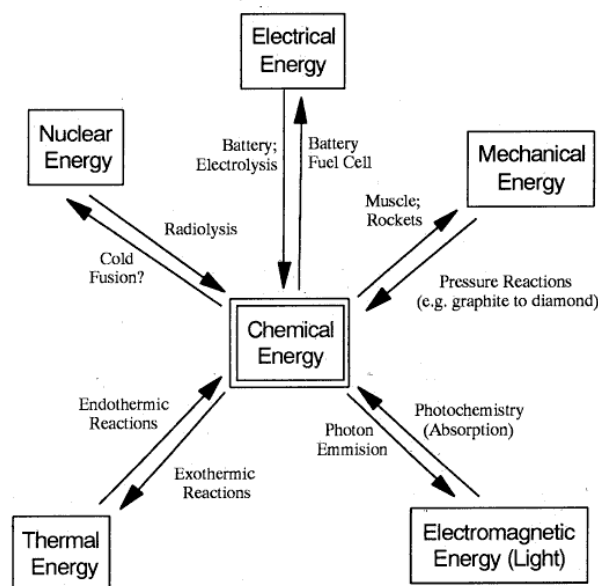


Figure 1. The relationship between chemical energy and other forms of energy, with examples. Note that a reaction can have energy transferred to or from several types of energy, as in the conversion of chemical energy into electrical energy and thermal energy.

cal system occurs. Examples of work involve the generation or consumption of mechanical energy (moving masses around), electrical energy (causing charged particles to move in an electric field), or electromagnetic energy (the transmission of photons of a variety of frequencies). Most practical processes involve the coupling of a chemical energy change to the transfer of heat and the performance of work and, as we shall see, the efficiency of a process can be dependent of the relative amount of associated work and heat.

The official energy unit in all kinds of energy is the joule, but historically and practically, other units, some peculiar

Table 2. Converting Units of Energy (1a)

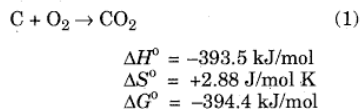
	Converting To:				
	Joule	Calorie	Btu	kWh	eV
Joule	1	0.2390	9.478×10^{-4}	2.778×10^{-7}	6.242×10^{18}
Calorie	4.184	1	3.967×10^{-3}	1.162×10^{-6}	2.614×10^{19}
Btu	1.055×10^3	2.520×10^2	1	2.931×10^{-4}	6.586×10^{21}
kWh	3.600×10^6	8.596×10^5	3.412×10^3	1	2.247×10^{25}
eV	1.602×10^{-19}	3.826×10^{-20}	1.518×10^{-22}	4.450×10^{-26}	1

Note also that relationship between the wavelength of each photon of light required for a reaction requiring E_n in energy is: λ (nm) = $1.20 \times 10^5 / E_n$ (kJ/mol).

to a given kind of energy, are used as well. It is important to be able to convert other units to joules, and vice versa. Table 2 provides conversion factors among the most common units.

Combustion: Chemical to Thermal Energy

In many reactions that are permitted to proceed "spontaneously" the energy that is emitted becomes thermal energy in the system and, eventually, its surroundings. This is what happens in the combustion of a fuel, such as coal, in a burner to heat a substance, such as water, for use in a turbine or engine (1). The efficient harnessing of chemical energy as thermal energy is, therefore, a critical part of the design of a combustion system. Let us consider the combustion of coal, which involves, approximately, the oxidation of carbon to carbon dioxide (eq 1).



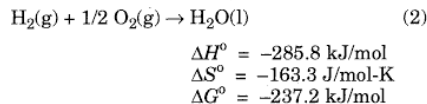
The heat liberated in the combustion reaction is used to heat water vapor to produce high temperature steam, which is then led into a turbine that, in turn, drives a magnet in a generator. There are, then, three energy conversion steps: (1) from chemical to thermal, (2) from thermal to mechanical, and (3) from mechanical to electrical. In the combustion reaction, the chemical system of coal plus oxygen is converted into another chemical system, carbon dioxide, plus heat. Ideally, all the heat is captured in the thermal energy of the steam. But the exhaust gases from the burner are very hot and remove heat to the atmosphere. Heat is also diverted to the vaporization of any noncombustible material in the fuel, especially moisture, and to bring the air used in combustion to the correct temperature. Energy is also released into the environment in the form of radiation, mostly in the infrared, from the hot surfaces of the equipment. The best that is done practically is to convert about 80% of the available chemical energy into actual thermal energy in the steam.

The next step in electricity generation is the conversion of the thermal energy of the steam to the mechanical energy of a turbine. The efficiency of this step is limited by absolute thermodynamic constraints as described classically through an ideal heat cycle such as the Carnot cycle. Practical machines achieve efficiencies on the order of 45%. Finally, the actual electrical generation step captures the mechanical energy of the turbine with over 95% efficiency. Overall, the three-step electricity generation process yields about 33% of the chemical energy in the starting coal and oxygen as electrical energy.

Chemical Energy Coupling: Direct Production of Electrical Work

There are occasions when considerations of efficiency and cleanliness make the large-scale burning of a fossil fuel and indirect electricity generation very unfavorable. In such cases it is worthwhile to invest in more complicated technologies so that the chemical energy is directly converted into some other form of energy—particularly electrical energy. This is exemplified in the coupling of the energy released in an oxidation–reduction reaction with electrical energy, as in the operation of a fuel cell.

In contrast to traditional batteries, which contain a certain amount of chemical substance that is ultimately exhausted, fuel cells get their energy from substances that are continuously supplied to the unit (2). The only fuel cells that come close to economic viability today all rely on a single reaction, the reaction of the chemical system hydrogen plus oxygen to make water plus energy (eq 2).



This reaction involves the net transfer of electrons from hydrogen to oxygen. Direct reaction releases the chemical energy as thermal energy (and some light). But the reaction can be coupled to electrical energy generation—the production of electrical work—by forcing the electrons transferred from hydrogen to oxygen to go through a wire. How is this electrical energy related to the chemical energy change? That is described by the simple relation between electrical potential (in volts) and chemical potential (in J):

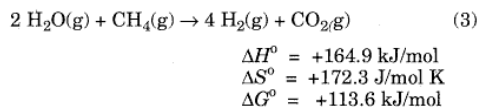
$$\Delta E = -\Delta G/nF$$

Where n is the number of moles of electrons transferred in the reaction as written ($n = 2$ for eq 2) and F is the Faraday, which is a constant with a value of 96,485 coulomb mol^{-1} . The Faraday serves to relate chemical amounts (moles) and electrical amounts (Coulombs). For the above reaction, the theoretical potential for each electron is $\Delta E^\circ = +1.23\text{V}$. This is the largest potential that can be achieved per hydrogen fuel cell.

Many early fuel cells run with aqueous potassium hydroxide as the electrolyte; such alkaline fuel cells (AFCs) were used with great success in special applications such as the early American space program. But on a larger scale a better technology today is the phosphoric acid fuel cell (PAFC) that uses H_3PO_4 as the electrolyte. In the coming decade PAFC technology may become competitive with traditional generation strategies while, over the longer term, more emphasis will be placed on the use of the molten carbonate fuel cell (MCFC, operated at $\sim 1000^\circ\text{C}$ with pure Na_2CO_3 as the electrolyte) and a one of several types of solid oxide fuel cell (SOFC) designs. Both are more tolerant of impurities in the hydrogen fuel and, indeed, can complete the oxidation of CO to CO_2 productively.

Theoretically, a fuel cell will make all of the free energy liberated in the oxidation of hydrogen available as electrical energy. But in practice thermal energy is also generated because of resistance to current flow in the cell and the inefficiency of electron transfer at an electrode surface. The best modern fuel cells operate at less than 70% efficiency, giving about 0.85V of electrical power per cell.

Fuel cell technology is also constrained by the purity and source of the hydrogen fuel. Since hydrogen is not a terrestrial substance it must be made from another fuel through a process known as reforming. There are several varieties of reforming; one that has the advantage of being very clean is the reforming of methane with steam to CO_2 and H_2 (eq 3). This endothermic reaction runs most efficiently at $\sim 1000^\circ\text{C}$.

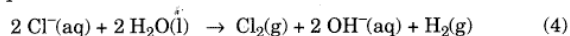


The hydrogen is then consumed in a fuel cell according to eq 2, and we can calculate that a total of $4 \times (-237) = -948$ kJ of energy can be in principle obtained from the indirect combustion of one mole of methane in a fuel cell. There is some wastage because the energy liberated in the reforming process is not converted into electricity. However, most practical reforming designs do capture the heat evolved in reforming for use in steam generation.

Chemical Synthesis: The Storage of Chemical Energy

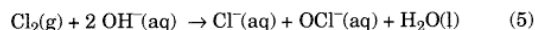
An important part of industrial chemistry is the production of substances with high chemical energy by driving a chemical reaction with a positive ΔG with the input of another kind of energy, especially electrical energy. One

prominent example is the synthesis of chlorine, Cl_2 , which is extremely important as a source of oxidation power, either directly or in the form of chlorine bleaches, and in the synthesis of several important chemicals. Its industrial synthesis is accomplished by the electrolytic conversion of brine (a concentrated solution of sodium chloride in water) to Cl_2 , NaOH , and H_2 in a variety of chlor-alkali processes (eq 4) (3).

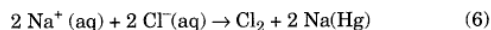


$$\begin{aligned} \Delta H^\circ &= +446.0 \text{ kJ/mol} \\ \Delta S^\circ &= +79.4 \text{ J/mol K} \\ \Delta G^\circ &= +422.4 \text{ kJ/mol} \\ \Delta E^\circ &= -2.18 \text{ V} \end{aligned}$$

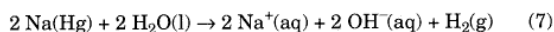
The basis for the chlor-alkali industry was established about a century ago with the development of two methods, the mercury cell and the diaphragm cell. More recently an innovation known as the membrane cell has also been introduced and is becoming increasingly important. A critical engineering problem in any chlor-alkali process is the need to separate the product streams, because aqueous hydroxide and chlorine react rapidly to give chloride and hypochlorite (eq 5).



The mercury cell keeps the product streams apart by producing Cl_2 and NaOH/H_2 in two different steps. An electrolysis reaction is used to split sodium chloride into chlorine gas at the anode and sodium metal as a solution in mercury (known as an amalgam) at the cathode (eq 6). The mercury is present in a pool at the bottom of the reactor and is continuously drained away to react in the second step with water to give hydrogen gas (recovered as fuel) and sodium hydroxide (eq 7).



$$\begin{aligned} \Delta G^\circ &= +604 \text{ kJ/mol} \\ \Delta E^\circ &= -3.13 \text{ V} \end{aligned}$$



$$\Delta G^\circ = -282 \text{ kJ/mol}$$

The advantage of the mercury cell is that the sodium is carried away from the brine and the NaOH that is formed is, therefore, very pure. This saves in the energy required to process the NaOH , but the reaction goes by a high energy route. Compared to the direct reaction (eq 4), the mercury cell requires almost 160 kJ/mol more energy in the electrolysis step and this energy, about 20% more than is thermodynamically required for the products, is lost as heat in the hydrolysis of the amalgam. Also, mercury is a very toxic substance and emissions must be controlled carefully.

The diaphragm cell features the direct production of H_2 , NaOH , and Cl_2 with the product streams separated by a diaphragm made of asbestos (Fig. 2). This diaphragm is permeable to water, sodium ion, and, to a lesser extent, chloride ions but is impermeable to hydroxide. Aqueous sodium chloride enters a compartment containing the anode, where Cl_2 is formed. The solution continues into the other compartment, where the cathode serves to reduce the water to H_2 and where hydroxide and sodium ions accumulate, to be discharged in the effluent. The diaphragm cell involves the direct production of all the chemical products in the initial electrolysis step. No high energy chemical intermediate (the sodium amalgam) is produced and, therefore, the electrical potential is much lower than in the mercury cell. However, the product NaOH from the diaphragm cell contains a lot of unreacted NaCl , and the process of purification—if needed—can consume enough energy so that the mercury and diaphragm cells are about equal in the amount of energy needed in the end.

The last 20 years has seen a revolution in chlor-alkali processes through the introduction of ion-exchange membranes (4). These membranes, with trade names like Nafion (duPont) and Flemion (Asahi Glass) are impermeable to all anions. Only cations flow across them. In principle, they are similar to diaphragm cells, but there is no problem with NaCl contamination of the NaOH . The strength and reliability of the membranes has also permitted the development of so-called zero-gap cells. The anode and cathode lie very close together, separated by the membrane. This greatly decreases the distance current must pass from the anode to the cathode and lowers the actual cell potential for this single stage process to $\sim 2.9 \text{ V}$. Membrane technology represents about 5% of United States capacity (diaphragm cells are about 75%, mercury, 17%). It is dominant in certain other parts of the world, because of political decisions to replace mercury technology early (in Japan, the chlor-alkali plants went from almost 100% mercury cells in 1973 to $\sim 75\%$ membrane, 25% diaphragm today).

The Infinite Energy Source: Chemical Synthesis with Solar Energy

Currently, almost all of the energy used in the world comes from nonrenewable terrestrial sources, mostly fossil and nuclear fuels. There are problems associated with both, however, and these are not answered by fuel cells

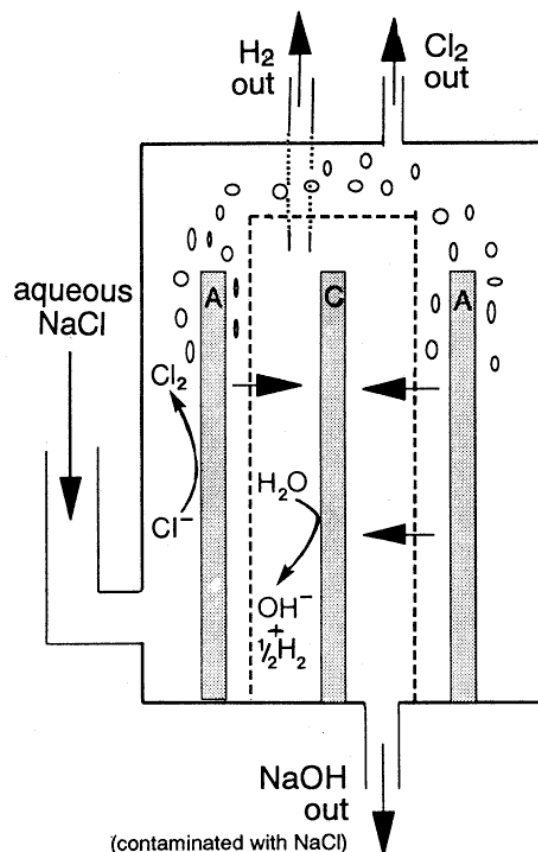
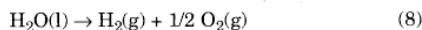


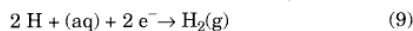
Figure 2. Schematic drawing of the diaphragm cell for the electrolysis of aqueous sodium chloride. Brine enters the cell and chloride ions are oxidized at the anodes A to give chlorine gas, which is removed from the top. The solution then passes through the asbestos diaphragm (dashed line), and then hydrogen ions are reduced at the cathode C to give hydrogen gas, which is released through a separate pipe (shown in part by dotted lines), and sodium hydroxide, which is drained out.

that are ultimately based on reformed methane or petroleum that will someday be depleted and, more importantly in the near term, that always produce carbon dioxide as a by-product. Carbon dioxide pollution is associated with the "greenhouse effect" of global warming and may, therefore, be at least as serious as toxic, noise, or heat pollution. Thus, it would be better if one could use a "clean" fuel, such as hydrogen (5), which gives simple water upon combustion, or could convert CO₂ back into a combustible fuel (6). Either process would have to rely on light from the sun and would be, by definition, a form of artificial photosynthesis.

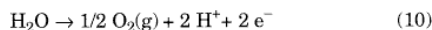
Light interacts with matter by inducing certain transitions, such as those to an electronic excited state in a molecule. This energy must then be used in the work of making higher energy molecules. Consider the best studied reaction for artificial photosynthesis, the splitting of water to hydrogen and oxygen (eq 8). It is just the opposite of the reaction discussed earlier for fuel cells. But it is much harder to accomplish. One cannot just shine visible light on water and split it. (Remember, pure water is colorless.) Instead, water must be oxidized at one site and reduced at another, according to the steps in eqs 9 and 10.



$$\begin{aligned} \Delta H^\circ &= +285.8 \text{ kJ/mol} \\ \Delta S^\circ &= -163.3 \text{ J/mol K} \\ \Delta G^\circ &= +237.2 \text{ kJ/mol} \\ \Delta E^\circ &= -1.23 \text{ V} \end{aligned}$$



$$E^\circ = 0.0 \text{ V}$$



$$E^\circ = -1.23 \text{ V}$$

The multi-electron character of water splitting means oxidation and reduction "power" must be accumulated at separate sites in a way that prevents loss of the energy through the re-emission of light or the chemical "quenching" of the energized system. One must quickly convert the

excited state into some form of chemical or electrical energy before simple emission of a photon and return to the ground state occurs. This is usually done by coupling the excited state to a charge transfer or charge separation event and then permitting the separated charges to reduce and oxidize water molecules at different locations. Unfortunately, all of the current systems for the photochemical splitting of water are rather expensive in terms of materials and technique of construction (but not really in terms of the wastage of light energy that is, after all, very abundant). Economically useful artificial photosynthesis probably will require dramatic advances in the materials used and, perhaps, changes in strategies for photochemical energy separation.

Acknowledgment

This article is dedicated to the memory of Norman H. Nachtrieb.

Literature Cited

- (a) Culp, A. W. Jr. *Principles of Energy Conversion*; McGraw-Hill: New York, 1979. (b) Shepard, M. L.; Chaddock, J. B.; Cocks, F. G.; Harman, C. M. *Introduction to Energy Technology*; Ann Arbor Science: Ann Arbor, 1977. (c) Amr, A. T.; Golden, J.; Oulette, R. P.; Chermisinoff, P. N. *Energy Systems in the United States*; Marcel Dekker: New York, 1981.
- (a) Linström, O. *CHEMTECH* **1988**, 490, 553, 686; *CHEMTECH* **1989**, 44, 122. (b) Linden, D., Ed. *Handbook of Batteries and Fuel Cells*; McGraw-Hill: New York, 1984; (c) Appleby, A. J., Ed. *Fuel Cells, Trends in Research and Application*; Hemisphere: Washington, 1987.
- (a) Brook, W. N. *Chem. Brit.* **1986**, 1096. (b) Leddy, J. J.; Jones, I. C. Jr.; Lowry, B. S.; Spillers, F. W.; Wing, R. E.; Binger, C. D. In *Kirk-Othmer Encyclopedia of Chemical Technology*, 3rd ed.; Mark, H. F.; Othmer, D. F.; Overberger, C. G.; Seaborg, G. T., Eds.; McGraw-Hill: New York, 1978; Vol. 1, p 799. (c) Hardie, D. W. F. *Electrolytic Manufacture of Chemicals from Salt*, 2nd ed., The Chlorine Institute: Washington, 1975. (d) *North American Chlor-Alkali Industry Plants and Production Data Book*; The Chlorine Institute: Washington, 1989. (e) Rudd, E. J.; Savinell, R. F. *J. Electrochem. Soc.* **1989**, 136, 449C. (f) Beck, T. R.; Ruggieri, R. T. *Advances in Electrochemistry and Electrochemical Engineering*, **1981**, 12, 301.
- (a) Sajima, Y.; Sato, K.; Ukihashi, H. *AIChE Symposium Series* **1988**, 82, 108. (b) Brooks, J. D. *Proc. Electrochem. Soc.* **1988**, 88-92, 41. (c) Seko, M.; Ogawa, S.; Ono, H.; Suzuki, O. *Proc. Electrochem. Soc.* **1984**, 84-111, 49.
- Grätzel, M., Ed. *Energy Resources through Photochemistry and Catalysis*; Academic: New York, 1983.
- Meyer, T. J. *Acc. Chem. Res.* **1989**, 22, 163.

Pick Up An Early Issue of the *Journal* and Read ...

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It is quite likely that many readers of the *Journal*, have never consulted the early issues dating from 1924. Even those who have had the opportunity over the years to browse through the yellowing pages, may have their doubts as to the relevance of such old material in today's "hi-tech" society. Early issues of the *Journal* are important though, and serve as a good reminder of the pioneering work of our scientist and educator antecedents.

There are many areas that might be chosen to illustrate the *Journal's* history of chemical education through the early and mid 20th century but none more interesting to the majority than the campaigns for adoption of metric (1) and SI (2, 3) measures. For example, in the mid 1920's a fascinating metric play was written in order to ease the introduction of metrication into schools (4), and the construction of cubic models was proposed as a method of teaching volume relations (5). Although most papers favored conversion from English-derived to metric measure (6-10)—and later still to SI measure (11-14)—voices of dissent were common (15) and led to some interesting correspondence debates (references 7, 8, 16 and 12, 13, 17-21, respectively). Most authors supported the simultaneous teaching of English-derived and metric measures (6) and metric and SI measures (17, 18, 20, 22).

Far from being relegated to the dusty top shelves of our libraries, early issues of the *Journal* deserve our continuing attention for the wealth of ideas they contain. Not only should many articles be of interest to today's generation of chemical educators, but the historical perspective is invaluable.

Literature Cited

- Moreau, H. *J. Chem. Educ.* **1953**, 30, 3.
- Socrates, G. *J. Chem. Educ.* **1969**, 46, 710.
- National Bureau of Standards. *J. Chem. Educ.* **1971**, 48, 569.
- Hall, A. L. *J. Chem. Educ.* **1925**, 2, 600.
- Persing, K. M. *J. Chem. Educ.* **1928**, 5, 725.
- Bingham, E. C. *J. Chem. Educ.* **1925**, 2, 62.
- Neville, H. A. *J. Chem. Educ.* **1925**, 2, 593.
- Neville, H. A. *J. Chem. Educ.* **1926**, 3, 215.
- Lind, S. C. *J. Chem. Educ.* **1943**, 20, 623.
- Wakeham, G. *J. Chem. Educ.* **1946**, 23, 134.
- Davies, W. G.; Moore, J. W.; Collins, R. W. *J. Chem. Educ.* **1976**, 53, 681.
- Heslop, R. B. *J. Chem. Educ.* **1979**, 56, 665.
- Dingley, D. *J. Chem. Educ.* **1979**, 56, 665.
- Davies, W. G.; Moore, J. W. *J. Chem. Educ.* **1980**, 57, 303.
- Audrieth, L. F.; Johnstone, H. F. *J. Chem. Educ.* **1942**, 19, 297.
- Dale, S. S. *J. Chem. Educ.* **1925**, 2, 1064.
- Nelson, R. A. *J. Chem. Educ.* **1979**, 56, 661.
- Lambert, J. L. *J. Chem. Educ.* **1978**, 55, 638.
- Adamson, A. W. *J. Chem. Educ.* **1978**, 55, 638.
- Wright, P. G. *J. Chem. Educ.* **1979**, 56, 663.
- Adamson, A. W. *J. Chem. Educ.* **1979**, 56, 665.
- Grosser, A. E. *J. Chem. Educ.* **1981**, 58, 366.