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Title of Study: A STUDY OF RED-OX REACTIONS AND POTENTIALS
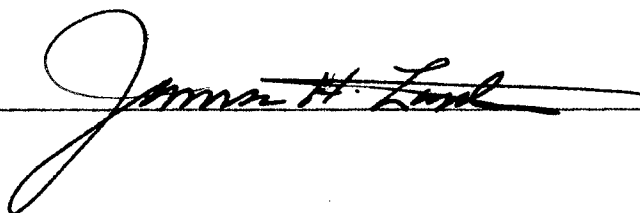
Pages in Study: Candidate for Degree of Master of Science

Major Field: Natural Science

Scope of Study: Study was made in various chemistry reference books
    and selected college texts which serve as references for this
    report. The report consists of a summary of studies related to
    oxidation-reduction reactions and the fundamental behavior of the
    constituents of electrolytic solutions. Examples of calculations
    of certain potentials, their use in predicting the possible course
    of chemical reactions, and the description of some methods for
    obtaining unknown potentials follows. The relation of the oxida-
    tion potential to some thermodynamic properties of chemical re-
    actions is then considered. The theory has been generalized and
    the specific examples of chemical reactions used are those which
    most high-school chemistry teachers will be familiar with. An
    explanation of the arbitrary conventions used in the theory of
    oxidation-reduction reactions is included to aid in the understand-
    ing of this study.

Findings and Conclusions: Unfortunately, the high-school chemistry
    teacher may be poorly acquainted with this unit of chemistry,
    since treatment of it in the conventional courses is often scanty;
    lacking this background, the teacher may not be able to give ade-
    quate explanation of the principles involved. By combining the
    fundamental theory with the study of various reactions and their
    potentials, a better perception of this phase of chemistry may be
    obtained.

ADVISER'S APPROVAL _____

A STUDY OF RED-OX REACTIONS

AND POTENTIALS

BY

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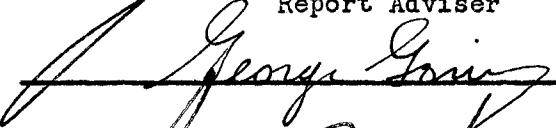
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A STUDY OF RED-OX REACTIONS

AND POTENTIALS

Report Approved:

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Report Adviser

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Dean of the Graduate School

ACKNOWLEDGEMENT

TABLE OF CONTENTS

CHAPTER I

INTRODUCTION

Electron transfer or oxidation-reduction reactions occupy a place
of outstanding importance in chemistry, along-side acid-base reactions.
Both acid-base and oxidation-reduction reactions are intimately involved
in the metabolic processes of cells and both are useful as tools in the
analysis of solutions.[1]

Unfortunately, the high-school chemistry teacher may be poorly
acquainted with this unit of chemistry, since treatment of it in the con-
ventional courses is often scanty; lacking this background, the teacher
may not be able to give adequate explanation of the principles involved.
In most cases, a better understanding of the subject on the teacher's
part will make the presentation of it to students more lucid and more
efficient, and time will be better utilized.

The author's purpose in compiling the material of this report is
to provide a source of reference of the principles involved in the
study of oxidation-reduction reactions and to gain a better understand-
ing of this phase of chemistry.

Study was made in various books and chemistry texts which serve
as references for this report. The primary sources of material were

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[1] Wallace S. Brey, Jr., _Principles of Physical Chemistry_ (New York,
1958), p. 136.

The <u>Oxidation</u> <u>States</u> <u>of</u> <u>the</u> <u>Elements</u> <u>and</u> <u>their</u> <u>Potentials</u> <u>in</u> <u>Aqueous</u>

<u>Solutions</u>, Wendell M. Latimer, (New York, 1951) and <u>Principles</u> <u>of</u>

<u>Physical</u> <u>Chemistry</u>, Wallace S. Brey, Jr., (New York, 1958). The former

is a reference book of thermodynamic data and interpretation of their re-

lation to inorganic chemistry. The latter is a college text for phy-

sical chemistry.

This report begins with a summary of studies related to oxidation-

reduction reactions and the fundamental behavior of the constituents of

electrolytic solutions. Calculations of certain potentials, their use

in predicting the possible course of chemical reactions, and the descrip-

tions of some methods for obtaining unknown potentials follows. The

relation of the oxidation potential to some thermodynamic properties

of chemical reactions is then considered.

All standard values of potentials and constant terms were taken

from the <u>Handbook</u> <u>of</u> <u>Chemistry</u> <u>and</u> <u>Physics</u>, edited by Charles D.

Hodgman, (Cleveland 1956).

For simplicity in preparation of this copy the letter (D) will

be used to represent the symbol (Δ), which indicates change. Also the

Faraday, a unit of electricity, will be represented by the letter (<u>F</u>).

CHAPTER II

A BRIEF HISTORY OF SOME EARLY INVESTIGATIONS LEADING TO THE PRESENT

KNOWLEDGE OF OXIDATION AND REDUCTION.

1. **Examples of reactions explained by the phlogiston theory.**
Iron, in rusting, undergoes a slow combustion and loses phlogiston.
Then, the metal consists of rust plus phlogiston. The theory may also
by applied to reaction in solution. If iron is introduced into a sol-
ution of blue vitriol, it goes into solution while copper is precipit-
ated. The iron gives up its phlogiston to produce the copper; further-
more certain quantitative relationships can be drawn for the iron which
disappeared, and the copper which is precipitated, must contain the same
amount of phlogiston.[2]

2. **Faults of the theory.** In the first place, no one could mention
a single property of phlogiston. Also it had been shown by Rey that when
metals are burned the calx weighs more than the metal, whereas if burn-
ing meant a loss of phlogiston it should weigh less. At that time this
received little attention.[3]

3. **One of the first implications of oxidation and reduction as it
is known today.** When Antoine Lavoisier (1743-1794) substituted reduction

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[2]F. J. Moore, <u>A History of Chemistry</u>, (New York, 1939), p. 53.

[3]Ibid, p. 54.

for phlogistication and oxidation for dephlogistication it was natural that the newly discovered element, oxygen, should usurp the position of exaggerated importance from which phlogiston had just been displaced. This is exactly what happened. Every element found its position in the system of Lavoisier according to its relation toward oxygen. Metals now became elements which united with oxygen to form bases, the metalloids became the elements which united with oxygen to form acids. Lavoisier did not hesitate to draw the conclusion that all acids contain oxygen. If oxygen is an essential component of acids, why do they evolve hydrogen with metals? Lavoisier's explanation was to this effect: water is simultaneously decomposed, the hydrogen is evolved as such while the oxygen unites with the metal to form a base, which now can add an acid to form a salt.[4]

4. _A survey of early electrochemical studies_. One of the earliest recorded observations of the chemical effect of a current was that of Priestley and Cavendish (1775) who noticed that nitric and nitrous acids are formed if moist air is subjected to an electric discharge.

Systematic electrochemical researches were made possible by the discovery by Galvani (1791) of an improved source of current which resulted when two different metals and a liquid were joined together in a circuit.[5]

Volta made a distinction between conductors of the first and

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[4]Ibid, p. 100.

[5]G. Kortum and J. O'M. Bockris, _Textbook of Electrochemistry_, (New York, 1951), p. 1.

second class: in the first class he placed metals, graphite, and certain ores and in the second all aqueous solutions. These two classes are the analogues of similar modern divisions into electric and ionic conductors.

He also set up a "potential series" for conductors of the first class, i.e. he arranged them in such a way that in a circuit made up of two of them and a conductor of the second class, a positive current would pass through the liquid from the higher to the lower one in the series, the potential being the greater the further apart the members were in the series.

Ritter's discovery (1798) that Volta's series was the same as that established from experiments on the power of metals to displace each other from solution first established direct connection between galvanic and chemical processes, and this can be regarded as the beginning of electrochemistry as a systematic science.

The development of electrochemistry was greatly accelerated by the introduction of Volta's pile (1800). The galvanic cells used to this time could provide potentials of little more than one volt, so that chemical changes caused by the passage of current could be observed only inside the cell itself. Volta's pile consisted of a series of zinc and silver plates laid on top of one another and separated by pieces of cardboard wetted with salt solution. The pile thus consisted of a battery of galvanic elements connected together, and Volta recognized that the resultant potential was a simple summation of the potentials produced by a single element of the two metals and the moist conductor.

In 1800, Ritter determined that one pole of the pile had an oxidizing and the other a reducing function, independent of the nature

of the metals concerned.

Particular difficulty was found in explaining the fact that during the electrolysis of water, hydrogen and oxygen appeared at the two poles of the cell respectively, in addition to the production of alkali and acid at these poles. Davy proved by very careful experiments (1807) that chemically pure water is decomposed during electrolysis without the formation of alkali or acid, so that the latter could be attributed to added salts or to impurities which came from the air or the material of the vessel.[6]

General acceptance of the chemical theory of the Voltaic pile was resisted primarily because there was no obvious quantitative connection between chemical and electrical processes. This difficulty was overcome by Faraday who in 1834 established the laws named after him. According to these the masses of electrolytic decomposition products are proportional to the amount of electricity passed, and a given quantity of electricity, are in the ratio of their equivalent weights.

An important spur to further progress was Daniell's work (1836) on the production of cells with a constant potential. The Daniell cell consists of a copper rod in a copper sulfate solution and a zinc rod in a zinc sulfate solution, the solutions being separated by a diaphragm of clay.

5. <u>Correlation of the characteristics of electrolytic solutions to electrical processes.</u> According to Grotthus's theory, ionization in the present sense of the word, i.e. splitting up of molecules into positive and negative carriers of charge, took place only upon passage of current through the solution.

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[6]Ibid, p. 2.

Clausius (1857) contradicted this idea on the ground that a current flows through a solution on the application of very small potentials and conforms to Ohm's law. Hence, the electric field cannot split the molecules into ions because, were this to occur, the relation of the current to the potential would be different at low currents (when the splitting would be in progress) from that at high currents.[7]

Some thirty years later Svante Arrhenius, a Swedish chemist, proposed his theory of ionization, and promoted a better understanding of electrolytic solutions.

Arrhenius's theory consisted essentially of the following points: 1. When an electrolyte is dissolved in water, some of its molecules break down into electrically charged particles, or ions. 2. The conductivity of any solution is due to these ions and is dependent upon the number and kind of ions between the electrodes. 3. In solutions of ordinary concentrations, ions and molecules of the electrolyte are in equilibrium with each other. 4. In solutions of ordinary concentrations not all electrolytes are ionized to the same extent, weak electrolytes being only slightly ionized whereas strong electrolytes are quite highly ionized.

Later experimentation with X-ray analysis of crystals showed that many electrolytes, such as sodium chloride, consist of ions even in the solid state.

There was little reason to expect these ions to combine in solution to form molecules when the behavior of other electrolytes indicate that the tendency for ionization should be greater in solution than

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[7]Ibid, p. 5.

under other conditions, however, the chemical activities and conducti-
vities of concentrated solutions of strong electrolytes are less than
would be expected if ionization were complete, which was one reason for
Arrhenius's belief that their ionization is incomplete.[8] In 1923, Debye
and Huckel succeeded in developing a quantitative treatment of these
deviations, at least for dilute solutions, by considering the electro-
static interactions between ions in the solution. This theory assumes
that strong electrolytes are present in solution entirely in the form of
ions. If a single ion in the solution is considered, it is evident that
ions of the opposite sign, drawn by electrostatic attraction, have a
slightly greater probability of being in the neighborhood of the given
ion than do ions of the same sign. As a result, the given ion is sur-
rounded by an ionic atmosphere, or a region of slight excess of charge of
the opposite sign, and is held more tightly in position than if the ionic
atmosphere were absent. The freedom of motion of the ion is restricted,
and this restriction is greater, the greater the total concentration of
ions in the solution.[9]

6. <u>Summary of fundamental concepts relating to electrolytic oxida-
tion and reduction.</u> An electric current is carried through a solution
of an electrolyte by the motion of its ions; the positive ions move to-
ward the cathode and the negative ions toward the anode. The current
carried by each species of ion is proportional to its concentration and
velocity.

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[8]Paul Arthur and Otto M. Smith, <u>Semimicro Qualitative Analysis</u>,
(New York,1952),p. 40.

[9]Wallace S. Brey, Jr., <u>Principles of Physical Chemistry</u>, (New
York,1958),p. 136.

Electricity is transferred from the electrolyte to the electrodes through the mechanism of chemical reactions at the electrode surfaces, usually referred to as half reactions, which always involve the liberation of electrons at the anode and the taking up of electrons at the cathode. The substances entering into either electrode reaction may be positive ions, negative ions, or neutral molecules.

The sum of the two electrode reactions is the cell reaction. If the cell reaction takes place spontaneously, we have a battery or electric cell capable of doing external work. If this reaction is not spontaneous, and external electromotive force must be used to force electricity through the cell, the process is called electrolysis.[10]

7. Conclusions and objectives set forth. So far only the aspects of electrochemistry that deal with electrolytic solutions have been mentioned. It is necessary that the basic behavior of chemical solutions be kept in mind to understand the reactions that take place within them. The ordinary chemical reaction in a single container involves the direct transfer of electrons between the various ions and molecules present therein as contrasted to the exchange of electrons through an external circuit in the case of the electrolytic cell.

Considering these developments in the area of electrochemistry as a starting point, it shall be the purpose of the following chapters to report findings from the literature of the mechanism or nature of chemical reactions and/or physical actions that occur during the oxidation and reduction processes.

[10] Wendell M. Latimer and Joel H. Hildebrand, Reference Book of Inorganic Chemistry, (New York, 1951), p. 525.

CHAPTER III

OXIDATION POTENTIALS AND VARIOUS METHODS FOR THEIR DETERMINATION

1. <u>Oxidation potentials of some common elements.</u> Electron-trans-
fer reactions involve oxidation-reduction couples, or pairs of species
which differ by the presence or absence of one or more electrons. For
example, if one allows a solution containing ferric ions to react with
a solution containing iodide ions, an electron is removed from each
iodide ion, leaving an iodine atom, whereas the addition of an electron
to each ferric ion converts it to a ferrous ion. The ferric ion is
reduced by the addition of the electron and the iodide ion is oxidized
by the loss of the electron. The ferric ion and the ferrous ion are
the two members of one couple; the iodide ion and the iodine atom form
the two members of a second couple.

The oxidation potential (E), is a "measure of the tendency of the
system to donate electrons to an electron acceptor and is expressed in
volts".[11] The standard oxidation potential (E°) is a constant charact-
eristic of the couple and is equal to (E) when all materials partici-
pating in the reaction are present in unit concentration. The reaction
mentioned above can be considered to be the algebraic sum of two couples:

$$2I^- = I_2 + 2e,$$
$$2Fe^{+++} + 2e = 2Fe^{++},$$
$$\overline{2Fe^{+++} + 2I^- = 2Fe^{++} + I_2}$$

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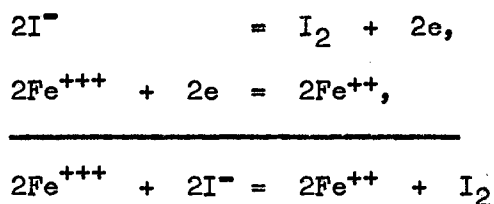
[11] Brey, p. 196.

Their standard oxidation potentials can be added in the same way to give the potential for the total reaction.

$$E^o$$

			E^o
$2I^-$	$= I_2 + 2e$		-0.5356 volts
$2Fe^{+++} + 2e$	$= 2Fe^{++}$		0.7701 volts

$2Fe^{+++} + 2I^- = 2Fe^{++} + I_2$ $\quad$ 0.2345 volts
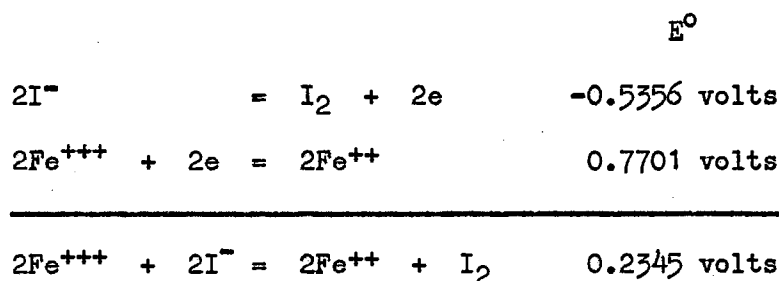
When the resultant oxidation potential for any reaction is positive the reaction will be spontaneous.[12]

It must be remembered that the potential of the reaction which is measured is the resultant of the potentials of both reactants. Only the algebraic difference of the two oxidation potentials is experimentally obtainable.[13] The classical example of the displacement of hydrogen by zinc will be used to illustrate the basis upon which standard oxidation potentials are assigned.

$$E^o$$

			E^o
Zn	$= Zn^{++} + 2e$		0.7628 volts
$2H^+ + 2e$	$= H_2$		0.0000 volts

$Zn + 2H^+ = Zn^{++} + H_2$ $\quad$ 0.7628 volts
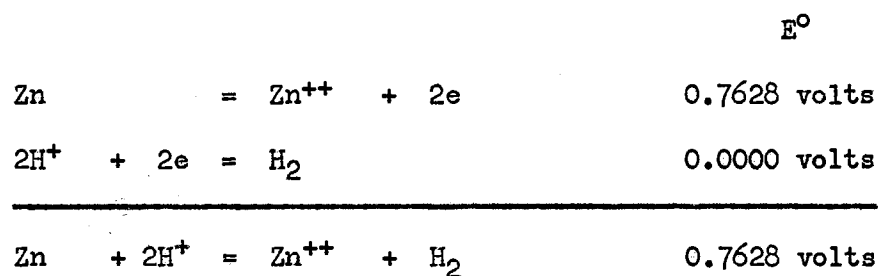
A cell consisting of the above couples develops a potential of 0.7628 volts. In order that any couple may have some assigned numerical value of its potential, the value of zero has been arbitrarily assigned

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[12]Ibid, p. 196.

[13]Ibid, p. 199.

to the hydrogen gas - hydrogen ion couple.[14]

Two conventions have arbitrarily been developed for assigning a potential value for a half-reaction. These conventions differ only by the way the couple reaction is written. If the couple reaction is written with the electrons on the right side of the equation the sign of the potential is positive when the reduced form of the couple (written on the left) is a better reducing agent than hydrogen as in the illustration above.

In the other case the oxidized form is written on the right and the electrons on the left and a negative sign is given to the potential for any couple which is a better reducing agent than hydrogen.

					E^o
Zn^{++}	+ 2e	=	Zn		-0.7628 volts
H_2		=	$2H^+$	+ 2e	0.0000 volts
Zn^{++}	+ H_2	=	Zn	+ $2H^+$	-0.7628 volts
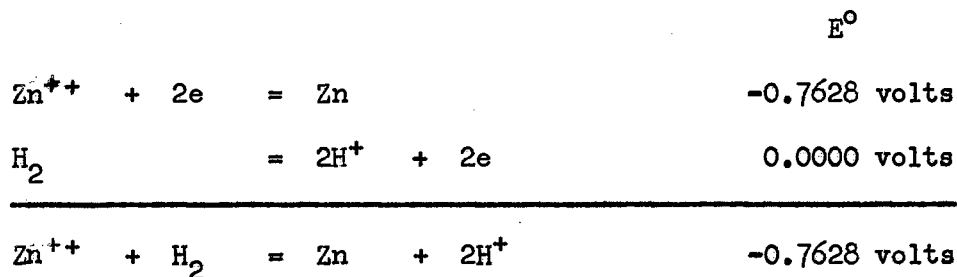
In this case the resultant potential is negative and energy must be supplied to cause hydrogen to reduce zinc ion to metallic zinc.

In either case the difference in potential is the same. The resultant potential differs in sign according to the direction the reaction is to go.

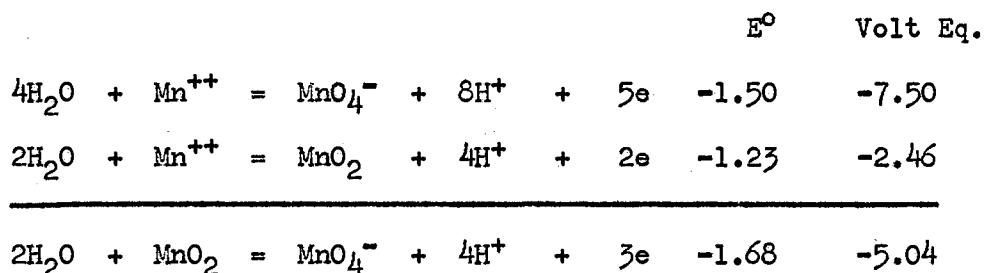|					E^o
Zn	+ $2H^+$	=	H_2	+ Zn^{++}	+
Zn^{++}	+ H_2	=	Zn	+ $2H^+$	-
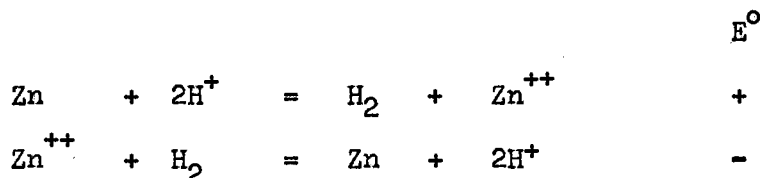
2. Computation of unknown oxidation potentials from obtainable

[14] Wendell M. Latimer, The Oxidation States of the Elements and Their Potentials in Aqueous Solutions, (New York, 1952), p. 5.

<u>values</u>. Sometimes it may be desired to calculate one half-reaction, which is unknown, from two other half-reactions that are known.

It has been determined that when one half-reaction is subtracted from another the difference will be a complete half-reaction. The potential of this new reaction is the algebraic difference in equivalent potentials of the two known reactions.

Care must be taken in this case to subtract the free energies in volt equivalents so that the different numbers of electrons involved are properly accounted for. An example of this calculation is as follows,

								E^o	Volt Eq.
$4H_2O$	+	Mn^{++}	=	MnO_4^-	+	$8H^+$	+	$5e$	-1.50	-7.50
$2H_2O$	+	Mn^{++}	=	MnO_2	+	$4H^+$	+	$2e$	-1.23	-2.46
$2H_2O$	+	MnO_2	=	MnO_4^-	+	$4H^+$	+	$3e$	-1.68	-5.04

The volt equivalent for the first half-reaction is the product of its oxidation potential and the number of electrons given up in the reaction (-1.50 x 5). Similarly the volt equivalent is obtained for the second half-reaction (-1.23 x 2). The difference between the two divided by the difference in the number of electrons yields the E^o value for the new half-reaction (-5.04/3) = -1.68 volts.[15]

3. <u>The experimental determination of oxidation potentials</u>. The most important method of determining the oxidation potential experimentally is the potentiometric determination. As there are no reliable or simple means for measuring the potential of a single electrode, it is always measured against some other standard electrode or half cell. By connecting the two electrodes, an element is built up, the electro-

[15]Walter J. Moore, <u>Physical Chemistry</u>, (New York, 1950), p. 463.

motive force of which can be measured.

If the terminals of the cells were connected with a voltmeter, no exact results could be expected, as the cell would send current through the system resulting in polarization at the electrodes and a change in e.m.f.

The procedure usually employed is the Poggendorf-Du Bois-Reymond method, by which the e.m.f. to be measured is balanced by an opposing but known e.m.f. The described procedure may be represented by the following diagram.[16]
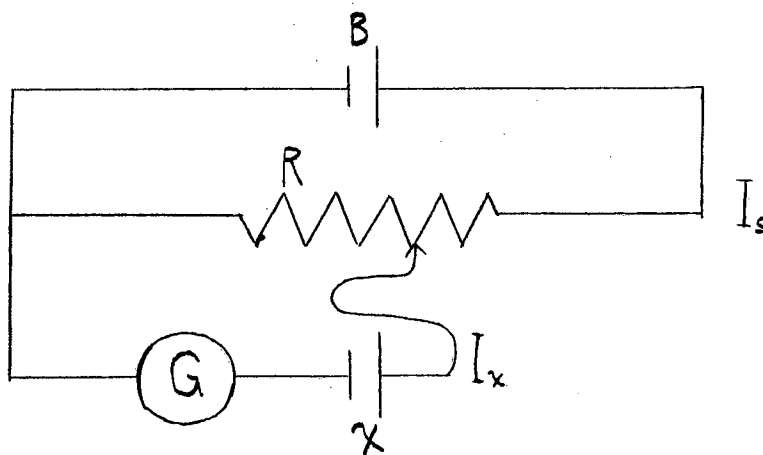
This circuit for measurement of electrical potentials without drawing any current is the potentiometer circuit. The current I_s opposes current I_x. There is a continuous drop in potential along R. When the potentials just balance the galvanometer shows no deflection.

Another method of determining the oxidation potential of reactions from experimental data comes from the relation of the equilibrium constant (K) to the oxidation potential. The equilibrium constant is obtained experimentally and the oxidation potential is then calculated.

The potential of a reaction is a measure of the driving force of

[16] I. M. Kolthoff and H. A. Laitinen, pH and Electro Titrations, (New York, 1941), p. 76.

the reaction. Every reaction is, in some degree, a reversible reaction, and the chemical driving force for a reaction depends upon how far the system is from equilibrium.

The value of the potential under conditions of unit concentration of all reactants and products is the standard potential, E^o, and is related to the equilibrium constant by the equation,

$$E^o = \frac{2.303\ RT}{n\ \underline{F}}\ \log K.$$

R is the universal gas constant (1.987 calories/mole degree), T is the absolute temperature, n is the number of electrons transferred in the reaction, and $\underline{F}$ is Faradays constant (23,060 calories/volt). The numerical correction factor from the natural log to the common log is 2.303.

If the reaction is carried out at 25° C. the constant terms may be combined so that the relation of E^o to the constant K becomes,

$$E^o = \frac{0.0592}{n}\ \log K.$$

CHAPTER IV

THERMODYNAMIC RELATIONSHIPS TO THE OXIDATION POTENTIAL.

1. The meaning of thermodynamics. Thermodynamics, literally

"movement of heat", is concerned with energy in its various forms.

The law of the conservation of energy is sometimes referred to as the

first law of thermodynamics.[17]

Thermodynamics expresses the driving force of a reaction in terms

of change in free energy. In the case of the galvanic cell the change

of free energy is the amount of chemical energy convertible into elect-

rical energy.[18]

2. The thermodynamic entities directly related to the oxidation

potential. a. Free energy: The free energy change (DF) of a chemical

reaction is a measure of the maximum available work which can be obtained

in going from the initial to the final state; it is related to the react-

ion potential by the following equation.

$$DF \text{ (joules)} = -E \text{ n } 96,500 = -\text{Work (max.)}$$
$$DF \text{ (calories)} = -E \text{ n } 23,060 = -\text{Work (max.)}$$

Electrical work equals the amount of electrical charge transported,

multiplied by the potential difference through which the charge moves.

If the amount of charge transferred is nF, where F is the value of the

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[17]Brey, p. 89.

[18]Ibid, p. 202.

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Faraday, which is the number of coulombs of charge corresponding to the oxidation or reduction of one equivalent of material, and E is the oxidation potential for the reaction.

The free energy of a reaction is the sum of the free energies of formation of the products of the reaction, less the sum of the free energies of formation of the reacting substances.[19]

The standard free energy (DF^o) of formation of a substance is the free energy change when one mole of a substance is formed from the elements in their standard states. The element is arbitrarily said to be in its standard state when it is in the physical form which is stable for the element at 25^oC. and under a pressure of one atmosphere. Under these conditions the free energy of formation of the elements is taken as zero.

b. Heat of reaction: The heat of a reaction has a definite relation to the free energy and oxidation potential and since the heat of reaction can be determined experimentally it will be of value.

The standard heat of formation (DH^o) of a compound is the value of the heat of reaction when one mole is formed from the elements in their standard states.[20] The heat of a reaction is calculated on the same basis as was the free energy, i.e., the difference between the heats of formation of the products and the heats of formation of the reactants. The heat of formation of the elements in their standard state is taken as zero. The unit of measure of both is usually kilocalories/mole.

3. <u>The second law of thermodynamics and entropy defined</u>. The Basis of the second law of thermodynamics can be expressed by the follow-

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[19]Latimer, p. 8.

[20]Brey, p. 107.

ing ideas. There is a tendency for the energy of any system to be lost spontaneously, i.e., water will seek the lowest level. The second idea of energy loss is that the system approaches a state of minimum order.

One of the corollaries of the second law is the principle that not all of the energy possessed by a system can be converted into work. For example if one gram of ice melts, there is absorbed by the gram of water 80 calories, but the water has no more capacity for doing work than did the ice. The heat absorbed is equal to a gain in unavailable work. Also it may be noted that the disorder in this system has increased, as the molecules are now free to move about freely.

This then is an example of entropy (S) which is designated as a measure of the unavailable work or disorder. It is usually referred to as irreversible energy. The entropy change (DS) for a chemical reaction may be calculated by subtracting the entropies of the reactants from the entropies of the products.[21]

4. _The relation of these thermodynamic properties to the oxidation potential._ When zinc dissolves in hydrochloric acid the chemical energy is converted to heat. This heat is called the heat of reaction, and differs from the free energy or the reversible energy by the "irreversible energy" which is equal to the entropy times the absolute temperature of the reaction,

$$DF = DH - TDS$$

The DF° and E° may then be calculated if the corresponding DH° and DS° values are known.[22]

There is an extensive section of chemical thermodynamic values
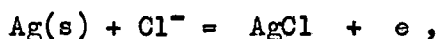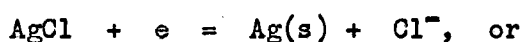

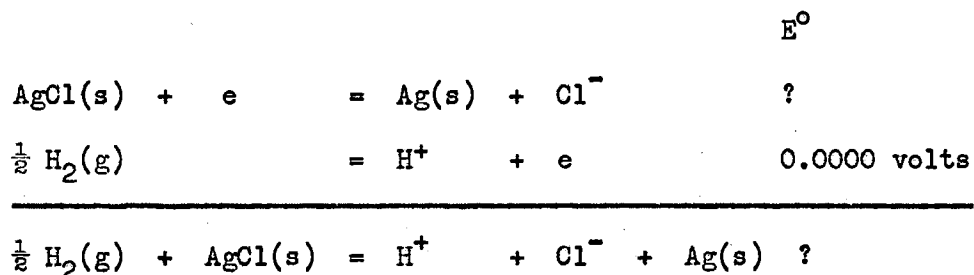[21] Ibid, p. 113.

[22] Latimer, p. 9.

given for organic and inorganic substances in most chemistry and physics handbooks.

Since the hydrogen gas-hydrogen ion couple has been arbitrarily designated as zero it is necessary that it be used as one half cell in thermal calculations of other couples in determining their potentials as the potential of any couple by itself cannot be determined.

An example of the use of thermal data for the calculation of the oxidation potential for the half reaction,

$$AgCl + e = Ag(s) + Cl^-, \text{ or}$$

$$Ag(s) + Cl^- = AgCl + e,$$

is as follows.

		E^o
$AgCl(s) + e = Ag(s) + Cl^-$		?
$\frac{1}{2} H_2(g) = H^+ + e$		0.0000 volts

$$\frac{1}{2} H_2(g) + AgCl(s) = H^+ + Cl^- + Ag(s) \quad ?$$

The heat of reaction (DH^o) is calculated by the following method.

$$\frac{1}{2} H_2(g) + AgCl(s) = H^+ + Cl^- + Ag(s)$$

DH^o = 0   -30,360   0   -40,032   0

= -40,032 - (-30,360) = -9672 calories/mole.

$DS^o = S^o(H^+) + S^o(Cl^-) + S^o(Ag) - \frac{1}{2}S^o(H_2) - S^o(AgCl)$

= 0 + 13.17 + 10.2 - ($\frac{1}{2}$ 31.2 + 23)

= -15.2 calories/mole degree

$$DF^o = DH^o - TDS^o$$

DF^o = -9672 - 298° x (-15.2) = -5140 calories/mole.

$$DF^o = -n \underline{F} E^o, \text{ in this case } n = 1$$

$$E^o = - \frac{DF^o}{\underline{F}}$$

$$E^{O} = - \frac{-5140}{23,060} = 0.222 \text{ volts}$$

$$E^{O}$$

Thus $AgCl(s) + e = Ag(s) + Cl^-$ 0.222 volts

$Ag(s) + Cl^- = AgCl + e$ -0.222 volts[23]
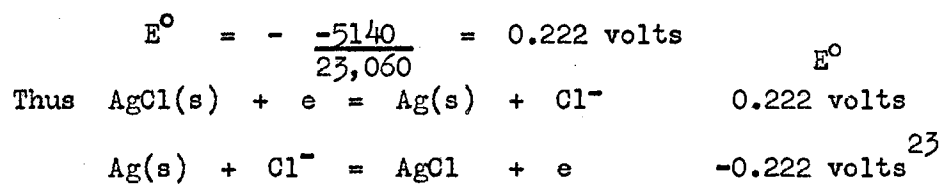
An understanding of these relationships can be an invaluable tool in predicting chemical reactions and explaining the phenomenon of oxidation-reduction reactions to Chemistry students.
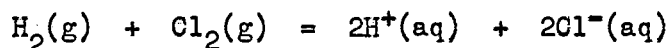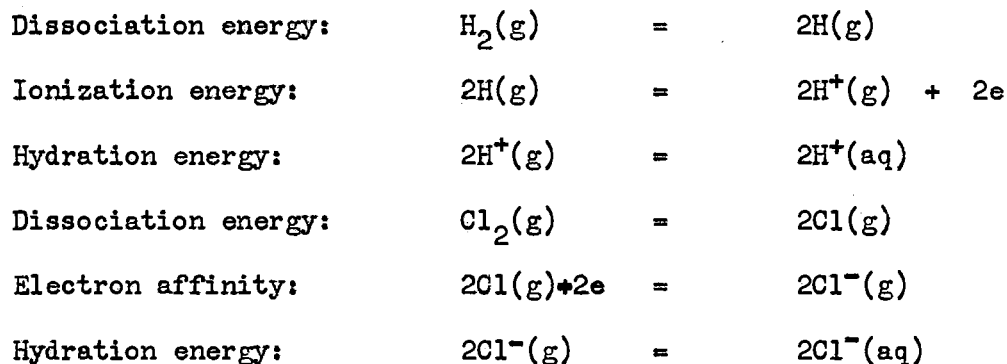
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[23]Ibid, p. 12.

CHAPTER V

DISCUSSION AND ILLUSTRATIONS

1. <u>Problems involved in energy measurements</u>. One of the problems
involved in studying the energy changes in chemical reactions is that
the elements and their ions do not exist at room temperature as monatomic
gases. When attempts are made to calculate reaction potentials under
ordinary conditions using data for gaseous monatomic states of the
elements there is usually at least one step which is very difficult to
evaluate accurately.

The energy of the reaction between hydrogen and chlorine to form
hydrochloric acid in solution,

$$H_2(g) + Cl_2(g) = 2H^+(aq) + 2Cl^-(aq)$$

could be calculated as the sum of the following steps:

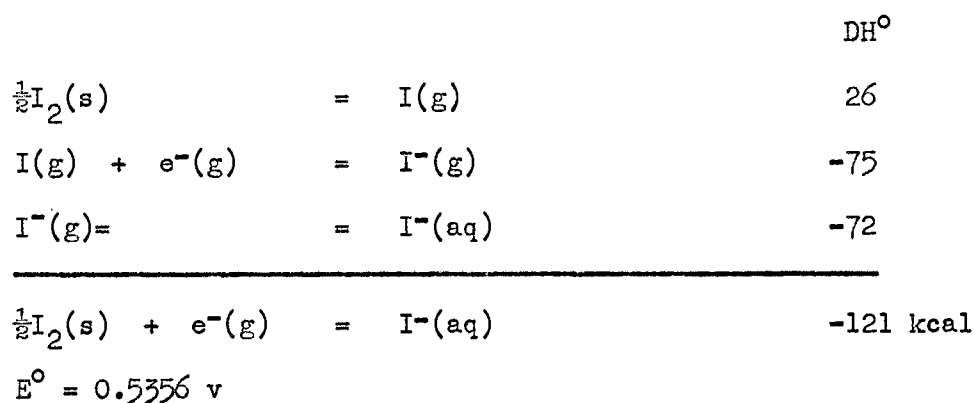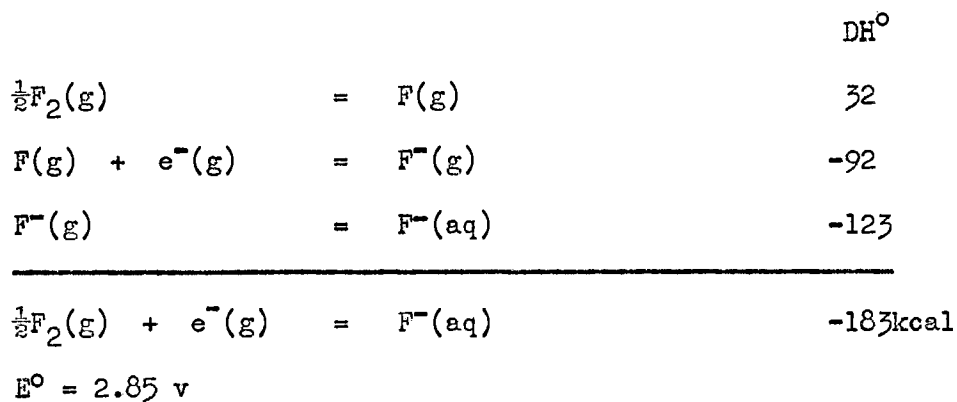|			
Dissociation energy:	$H_2(g)$	$=$	$2H(g)$
Ionization energy:	$2H(g)$	$=$	$2H^+(g) + 2e$
Hydration energy:	$2H^+(g)$	$=$	$2H^+(aq)$
Dissociation energy:	$Cl_2(g)$	$=$	$2Cl(g)$
Electron affinity:	$2Cl(g)+2e$	$=$	$2Cl^-(g)$
Hydration energy:	$2Cl^-(g)$	$=$	$2Cl^-(aq)$

The two hydration energies cannot be obtained experimentally; hence
the process is not a feasible method of determining the potential of the
chlorine-hydrogen reaction.

If the total energy of the reaction is known, however, the sum of

the hydration energies of the hydrogen and chlorine ions can be calcul-
ated.[24]

2. <u>What affects the magnitude of oxidation potentials.</u> Comparing
the relative oxidizing powers of fluorine and iodine by their heats of
reaction for the various steps that must be considered in a reaction
where they are involved. The energy or heat of reaction as the element
goes from its standard state to the gaseous monatomic state to the
gaseous ion and finally to the aqueous ion is divided into the following
steps.

			DH^o
$\frac{1}{2}F_2(g)$	=	$F(g)$	32
$F(g) + e^-(g)$	=	$F^-(g)$	-92
$F^-(g)$	=	$F^-(aq)$	-123
$\frac{1}{2}F_2(g) + e^-(g)$	=	$F^-(aq)$	-183 kcal

$E^o = 2.85$ v

|			DH^o
$\frac{1}{2}I_2(s)$	=	$I(g)$	26
$I(g) + e^-(g)$	=	$I^-(g)$	-75
$I^-(g)=$	=	$I^-(aq)$	-72
$\frac{1}{2}I_2(s) + e^-(g)$	=	$I^-(aq)$	-121 kcal

$E^o = 0.5356$ v

These equations show that fluorine is the better oxidizing agent,
in part because of the higher electron affinity, but principally because
of the greater energy of hydration of the smaller fluoride ion.

In general, a large electron affinity, large energy of hydration,

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[24]Ibid, p. 19.

and small energy of formation of the monatomic gas atom from the stand-
ard state will favor a high oxidation potential for elements forming
negative ions.

An analysis of the factors which determine the oxidizing power of
the oxygen acids and their compounds is more difficult. A half reaction,
such as that for permanganate,

$$E^o$$

$$MnO_4^- + 8H^+ + 5e = Mn^{++} + 4H_2O \quad 1.50 \text{ v}$$
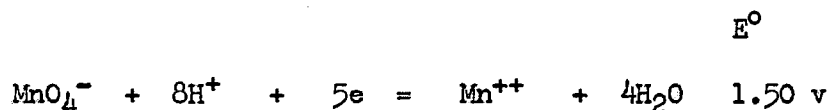
can be broken up into a number of hypothetical steps:

1. Energy of dehydration of MnO_4^-.

2. Dissociation of MnO_4^- into Mn^{+7} and $4O^{--}$.

3. Energy of hydration of Mn^{++}.

4. Energy of union of H^+ and O^{--} to form water.

5. Ionization of Mn^{++} to Mn^{+7}.

It is obvious that low values for 1 and 2 and high values for the
others will favor high oxidizing power but at present it is impossible
to evaluate several of these steps accurately.[25]

3. _Biochemical oxidation_. The biochemical reactions concerned
with oxidation and reduction deserve a separate study but, due to their
importance, mention will be made here of the basic principles involved.

In living organisms a major portion of the metabolic process
consists of oxidation and reduction reactions. The end result of these
processes is the combination of oxygen with carbon and hydrogen from
organic molecules to produce carbon dioxide and water. This over-all
oxidation process does not take place in one step, but occurs through

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[25]Ibid, p. 24.

one of several series of intermediate steps. In order that the energy be utilized to the fullest, each of the steps must be a reversible step, and the function of a number of enzymes is to ensure the reversibility of oxidation processes.

The order in which the biological oxidation processes occur depends upon the oxidation potentials of the systems involved. Electrons are transferred from systems of higher potential to systems of lower potential. That is, the reduced form of a system of more positive oxidation potential reduces the oxidized form of a system of more negative potential, and is itself oxidized. Oxygen has the most negative oxidation potential of any of the materials involved, and it can oxidize most substrates but only through carriers. These carriers, intermediate in oxidation potential between oxygen and the substrate, usually accompany oxidative enzymes. They are referred to as prosthetic groups if they are only loosely bound. In some instances, the enzyme as a whole acts as the carrier. In many cases the cofactor is simply a metallic ion.[26]

Dehydrogenases are enzymes which result in a removal of hydrogen atoms from an organic molecule. The initial stage of a chain of oxidations. An example is the transfer of hydrogen atoms from a substrate to a substance known as coenzyme I. Thus the substrate is oxidized and coenzyme I is reduced. The hydrogen ion + the electron removed combine with oxygen to form water and the coenzyme which was reduced becomes re-oxidized in a subsequent reaction and then is ready for the first reaction again.[27]

The basic mechanism of all oxidation-reduction reactions involves

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[26]Brey, p. 219.

[27]W. H. Peterson and F. M. Strong, General Biochemistry, (New York, 1953), p. 282.

the transfer of electrons. It should be realized, furthermore, that a certain increment of energy becomes available at each of the steps of the oxidation-reduction chain and that this energy can be transferred to functions useful to the organism by appropriate stepwise mechanism.[28]

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[28]Ibid, p. 283.

CHAPTER VI

SUMMARY AND CONCLUSIONS

The summary may be made in two parts.

Part I:

(a) All chemical reactions result in a transfer of electrons from one atom to another or sharing of electrons by atoms,[29] but not all of these are considered oxidation and reduction reactions. It should be recalled from chapter III that electron-transfer reactions involve oxidation-reduction couples, or pairs of species which differ by the presence of one or more electrons.

(b) Each couple has an oxidation potential which is a relative measure of the tendency for it to donate or to accept electrons in the process of the reaction. This measurement is made on a comparative basis with the hydrogen gas-hydrogen ion couple which is arbitrarily taken as zero and is expressed in volts.

(c) The potential of the reaction which is measured is the result- ant of the potentials of both couples. Only the algebraic sum or differ- ence of the potentials of both couples is experimentally obtainable. This may be illustrated by the fact that electrons will not be given up if there is not an acceptor to take them. Thus oxidation (loss of elect- rons) is impossible without reduction (gain of electrons).

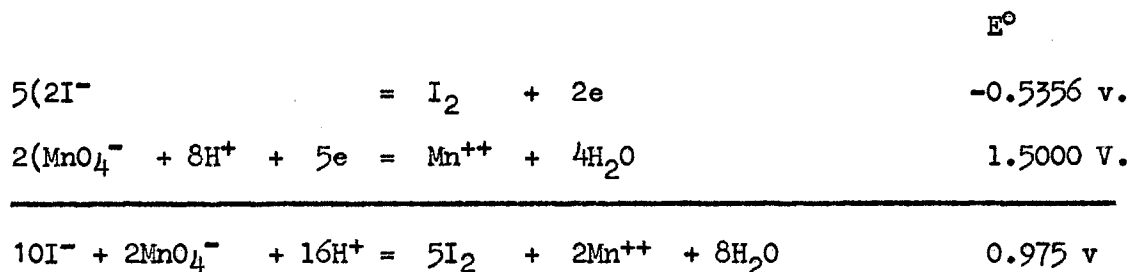(d) The sum of the potentials must be positive for a reaction to

[29]B. Smith Hopkins & John C. Bailor, Jr., General Chemistry for Colleges, (Boston, 1956), p. 223.

be spontaneous. The movement of an electron, even if it is only from
one atom to another with which it collides constitutes the flow of a
minute electrical current.[30] For this transfer to take place the diff-
erence of the electron donating tendency and the electron accepting
tendency must be positive.

(e) Analysis of a situation involving a chemical reaction illus-
trating the components of the summation stated above.

> The situation: On dissolving a soluble crystalline solid
> which is known to contain iodide ion in water, a colorless
> solution is obtained. Adding to this solution a small amount
> of sulfuric acid as a source of hydrogen ion and some pot-
> assium permanganate (violet color) as a source of permanganate
> ion the violet color vanishes almost immediately.

From a standard oxidation potential table the potential of the
couple $2I^- = I_2 + 2e$ is found to be -0.5356 volts based on its reaction
with the hydrogen ion-hydrogen gas couple which is zero. Likewise the
permanganate ion in the presence of hydrogen ion-manganese ion plus
water has the potential 1.50 volts. The algebraic sum of the two couples
is calculated as follows.

			E^O
$5(2I^-$	$= I_2$	$+ 2e$	-0.5356 v.
$2(MnO_4^- + 8H^+ + 5e$	$= Mn^{++}$	$+ 4H_2O$	1.5000 V.
$10I^- + 2MnO_4^- + 16H^+ =$	$5I_2$	$+ 2Mn^{++} + 8H_2O$	0.975 v

With a working knowledge of the four components of the illustration
as stated it is possible to analyze various chemical reactions and to
determine the chemical changes that are involved. It is possible also to

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[30]Ibid, p. 223.

make calculation beforehand so that the results of the experiment may be predicted.

Part II:

Thermodynamics expresses the driving force of a reaction in terms of change in free energy. The free energy of a chemical reaction is a measure of the maximum available work which can be obtained in going from the initial to the final state; and is related to the oxidation potential of the reaction by the equation,

$$DF \ (cal) \ = \ -E \ n \ 23,060.$$

The free energy of a reaction may be calculated if the free energies of formation are known for all the reactants and products. The free energy of formation of the products less the free energy of formation of the reactants yields the free energy change for the reaction.

The free energy is related to the equilibrium constant for the reaction and is represented by the following equation.

$$DF^o \ = \ -2.303 \ R \ T \ log \ K.$$

The free energy may also be calculated from its relation to the heat of reaction, the temperature at which the reaction takes place and the entropy change of the reaction.

$$DF \ = \ DH \ - \ TDS$$

The heat of reaction may be determined experimentally or if the heat of formation of all the products and reactants are given, the heat of reaction is equal to the heat of formation of the products less the heat of formation of the reactants.

The entropy change may also be calculated on the same basis as the heat of reaction.

Since the hydrogen gas-hydrogen ion couple has been arbitrarily set as zero, it must be used in the thermal calculations of the DH and DS for the specific couple in question. An example of the calculation is cited

in chapter IV.

Once again it may be stated that an understanding of these relationships can be invaluable in explaining potentials of chemical reactions.

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