Chapter 19 – **The Determination of a Solubility Product Constant by an Electrochemical Method**	**NAME:**	
	Lab Section:	
	Date:	**Sign-Off:**

Chapter 19 –
The Determination of a Solubility Product Constant by an Electrochemical Method

Introduction

The solubility product constant of a solid may be used to determine if a compound is soluble or not (qualitatively) under aqueous conditions or may be used to compare the relative solubilities of individual compounds in an aqueous mixture, suspension or solution of the compounds. The lesser the solubility product constant (K_{sp}), the more insoluble the compound in aqueous conditions; conversely, the greater the K_{sp}, the more soluble the compound in aqueous conditions. There are many methods by which to determine the K_{sp} of a compound. These methods include precipitometric methods, by which an indicator is used to mark the point of precipitation of a solid in a titrimetric application. This method is fraught with difficulties and is very time consuming.

Another method in which K_{sp}'s are determined is through the application of electrochemistry: the use of a "battery" which provides the data for application in the Nernst equation. If we had a battery as follows,

$$\mathrm{Ca}\,|\,\mathrm{Ca}^{2+}\ (\text{sat'd }\mathrm{CaSO_4})\,\|\,\mathrm{Ca}^{2+}\ (0.1\ \mathrm{M})\,|\,\mathrm{Ca}$$

it would be rather simple to determine the K_{sp} by measuring the potential of this battery. But, how does one accomplish this operation?

The first step is to set up the appropriate half-reactions and set up the Nernst equation for manipulation after measuring the potential of the cell (E_{cell} = +0.04499 V in this case):

RXN TYPE	HALF-RXN	E^o_{cell}
OXIDATION	$Ca \rightarrow Ca^{2+}$ (sat'd) + $2e^-$	+2.84 V
REDUCTION	Ca^{2+} (0.1 M) + $2e^- \rightarrow Ca$	-2.84 V
SUM	Ca^{2+} (0.1 M) $\rightarrow Ca^{2+}$ (sat'd $CaSO_4$)	0.00 V

$$E_{cell} = E^o_{cell} - \frac{(0.0592)}{n} \log \frac{[Ca^{2+}](sat'd)}{[Ca^{2+}](0.1M)}$$

Another way of looking at this form of the Nernst equation is as follows:

$$E_{cell} = E^o_{cell} - \frac{(0.0592)}{n} \log \frac{[\text{ions at anode}]}{[\text{ions at cathode}]}$$

This reduces to:

$$E_{cell} = -\frac{(0.0592)}{n} \log \frac{[\text{ions at anode}]}{[\text{ions at cathode}]}$$

Since n = 2, the equation reduces to:

$$E_{cell} = -0.0296 \log \frac{[\text{ions at anode}]}{[\text{ions at cathode}]}$$

We know the E_{cell} and the [ions at cathode]: +0.04499 V and 0.1M, respectively. Therefore, the only variable we do not know is the $[Ca^{2+}]$ at the anode, i.e., in the saturated solution. This variable is solvable -- one unknown, one equation, it is solvable. By manipulating the equation, the $[Ca^{2+}]$ at the anode is equal to 3.021×10^{-3}M.

What do we do with this information? Let's look at the dissociation of $CaSO_4$:

$$CaSO_4 \rightarrow Ca^{2+} + SO_4^{2-}$$

$$K_{sp} = [Ca^{2+}][SO_4^{2-}]$$

If we set the solubility of $CaSO_4$ as being dependent on the solubility of Ca^{2+} (S), then the K_{sp} is equivalent to the following:

$$K_{sp} = [S][S] = S^2$$

We know the solubility of Ca^{2+} in the saturated solution, for we just solved for it. Therefore, the K_{sp} must, in this case, be equal to the square of the $[Ca^{2+}]$ in solution at the anode, i.e., in the saturated solution:

$$K_{sp} = (3.021 \times 10^{-3})^2 = 9.12 \times 10^{-6}$$

Experimental

Group 1		Group 2	
Chemicals	Supplies	Chemicals	Supplies
FeS	2: 100-150 mL beakers	Cu wire $CuSO_4 \cdot 5H_2O$	2: 100-150 mL beakers
$FeSO_4$	1: "U"-tube	con HNO_3	1: "U"-tube
Distilled H_2O	2: Cotton plugs	3M KOH	2: Cotton plugs
1M KNO_3	1: Voltmeter with electrodes	Distilled H_2O	1: Voltmeter with electrodes
	2: Nails	1M KNO_3	2: Cu wires

Group 3		Group 4	
Chemicals	Supplies	Chemicals	Supplies
Zn metal $ZnCl_2$	2: 100-150 mL beakers	Mg ribbon $MgCl_2$	2: 100-150 mL beakers
con HCl	1: "U"-tube	con HCl	1: "U"-tube
3M KOH	2: Cotton plugs	3M KOH	2: Cotton plugs
Distilled H_2O	1: Voltmeter with electrodes	Distilled H_2O	1: Voltmeter with electrodes
1M KNO_3	2: Zn ribbons	1M KNO_3	2: Mg ribbons

Additional supplies include graduated cylinders, electronic pan balances, hoods and hot plates as necessary.

Individual Group Instructions

Group 1

Fill one of your beakers roughly two-thirds full with distilled water. To this water, add enough FeS to make a saturated solution (this won't take much). In the other beaker, add enough $FeSO_4$ to 75 mL of distilled water to make a 0.1M solution of the Fe^{2+}. Fill the "U"-tube with the KNO_3 solution and plug each end with cotton. It is important that there are no air bubbles in your tube, and that the cotton plugs are moist throughout the plug.

Insert each end of the "U"-tube into each beaker. Clamp the negative electrode from the voltmeter to a nail and insert it into the saturated solution of FeS. Clamp the positive electrode to the other nail and insert it into the 0.1M solution of Fe^{2+}. Turn on the voltmeter as per the general instructions from the pre-lab lecture, read and record the voltage. Perform this experiment in triplicate and complete the data/calculation form below. You will be determining the K_{sp} for FeS.

Group 2

Coil about 10 cm of Cu wire in a beaker in the hood and add 4 mL of con HNO_3 to it. Allow the reaction to progress to completion, then add about 30 mL distilled water to the solution. Add, to this solution while stirring, 30 mL of 3M KOH. This will be your saturated solution for Cu^{2+}. In the other beaker, add enough $CuSO_4 \cdot 5H_2O$ to 75 mL of distilled water to make a 0.1M solution of Cu^{2+}. Fill the "U"-tube with the KNO_3 solution and plug each end with cotton. It is important that there are no air bubbles in your tube, and that the cotton plugs are moist throughout the plug. Insert each end of the "U"-tube into each beaker. Clamp the negative electrode from the voltmeter to a piece of Cu wire and insert it into the saturated solution of $Cu(OH)_2$. Clamp the positive electrode to the other piece of Cu wire and insert it into the 0.1M solution of Cu^{2+}. Turn on the voltmeter as per the general instructions from the pre-lab lecture, read and record the voltage. Perform this experiment in triplicate and complete the data/calculation form below. You will be determining the K_{sp} for $Cu(OH)_2$.

Group 3

Place about 0.5 grams of Zn metal in a beaker in the hood and slowly add 8 mL of con HCl to it. Allow the reaction to progress to completion, then add about 30 mL distilled H_2O, followed by 40 mL of 3 M KOH, while stirring, to this solution. This will be your saturated solution for Zn^{2+}. In the other beaker, add enough $ZnCl_2$ to 75 mL of distilled water to make a 0.1M solution of Zn^{2+}. Fill the "U"-tube with the KNO_3 solution and plug each end with cotton. It is important that there are no air bubbles in your tube, and that the cotton plugs are moist throughout the plug. Insert each end of the "U"-tube into each beaker. Clamp the negative electrode from the voltmeter to a piece of Zn ribbon and insert it into the saturated solution of $Zn(OH)_2$. Clamp the positive electrode to the other piece of Zn ribbon and insert it into the 0.1M solution of Zn^{2+}. Turn on the voltmeter as per the general instructions from the pre-lab lecture, read and record the voltage. Perform this experiment in triplicate and complete the data/calculation form below. You will be determining the K_{sp} for $Zn(OH)_2$.

Group 4

Place about 1.5 inches of Mg ribbon in a beaker in the hood and slowly add 8 mL con HCl followed with about 30 mL distilled H_2O, then by 40 mL of 3M KOH, while stirring, to this solution. This will be your saturated solution for Mg^{2+}. In the other beaker, add enough $MgCl_2$ to 75 mL of distilled water to make a 0.1M solution of Mg^{2+}. Fill the "U"-tube with the KNO_3 solution and plug each end with cotton. It is important that there are no air bubbles in your tube, and that the cotton plugs are moist throughout the plug. Insert each end of the "U"-tube into each beaker. Clamp the negative electrode from the voltmeter to a piece of Mg ribbon and insert it into the saturated solution of $Mg(OH)_2$. Clamp the positive electrode to the other piece of Mg ribbon and insert it into the 0.1M solution of Mg^{2+}. Turn on the voltmeter as per the general instructions from the pre-lab lecture, read and record the voltage. Perform this experiment in triplicate and complete the data/calculation form below. You will be determining the K_{sp} for $Mg(OH)_2$.

ALL GROUPS

When you have accomplished the third trial, remove the metal electrodes from the solutions (the electrodes which correspond to your salts) and then determine the potential of the cell by dipping the electrodes directly into the solutions **one** time. Wipe off the electrodes from the voltmeter carefully, afterwards. Determine the K_{sp} from this one determination of the cell potential and compare it against your other results.

Clean up your work area, dispose of the reagents as instructed and perform your calculations and complete the problem set following before next week’s lab.

Data and Calculations

Data	Calculations	Trial 1	Trial 2	Trial 3	Trial 4
Name of Salt for 0.1M Solution					
Mass of Salt for 0.1M Solution					
Actual Molarity of Salt for 0.1M Solution					
E_{cell}					
Name of Salt for K_{sp} Determination					
Molar Concentration of Ion Actually in Solution at the Anode					
K_{sp} Expression for Your Salt					
K_{sp} Expression in Terms of Solubility for Your Salt					
K_{sp} for Your Salt					
Average K_{sp} for Your Salt					
Theoretical K_{sp} (Use CRC)					
% Error					

Problem Set – Electrochemistry, Thermodynamics and K_{sp} Determinations

Given that oxidation in a battery occurs at the anode (**an** ox ia is a helpful mnemonic to remember this -- **an** for "anode"; ox for "oxidation"), that reduction occurs at the cathode and that the reaction occurs spontaneously when the voltage of the cell (potential; E^o_{cell}) is positive, determine the following for each half-reaction pair listed below:

a) what is the E^o_{cell}?
b) which is the cathode?
c) which is the anode?
d) write the combined, complete and balanced reaction.

The following example may be helpful for you:

$Zn^{2+} + e^- \rightarrow Zn$ $E^o = -0.763$ V
$Cr^{3+} + 3e^- \rightarrow Cr$ $E^o = -0.74$ V

a) $E_{cathode} - E_{anode} = E^o_{cell}$

$\therefore -0.74 - (-0.763) = 0.023$ V

b) Cr is the cathode

c) Zn is the anode

d)

$$\begin{array}{c} 3(Zn \rightarrow Zn^{2+} + 2e^-) \\ \underline{2(Cr^{3+} + 3e^- \rightarrow Cr)} \\ 2Cr^{3+} + 3Zn \rightarrow 2Cr + 3Zn^{2+} \end{array}$$

1. $Mg^{2+} + 2e^- \rightarrow Mg$ $E^o = -2.37$ V
$Co^{2+} + 2e^- \rightarrow Co$ $E^o = -0.277$ V

2. $Pb^{2+} + 2e^- \rightarrow Pb$ $E^o = -0.126$ V
$Cu^{2+} + 2e^- \rightarrow Cu$ $E^o = 0.337$ V

3. $Ag^+ + e^- \rightarrow Ag$ $E^o = 0.7991$ V
$Hg^{2+} + 2e^- \rightarrow Hg$ $E^o = 0.854$ V

4. $Br_2 + 2e^- \rightarrow 2Br^-$ $E^o = 1.065$ V
$Cl_2 + 2e^- \rightarrow 2Cl^-$ $E^o = 1.3595$ V

5. $MnO_2 + 4H^+ + 2e^- \rightarrow Mn^{2+} + 2H_2O$ $E^o = 1.23$ V
$Al^{3+} + 3e^- \rightarrow Al$ $E^o = -1.66$ V

The conditions from above are not always perfectly met in the laboratory. It is therefore necessary to consider these non-perfect conditions for a reaction of the type:

$$eE + fF \rightarrow gG + hH$$

at non-standard conditions (activity of pure solids and liquids → 1; partial pressures are used for the activities of gases; and molarities are used for the activities of solution components). Without going through the derivation of the Nernst equation (you will probably do this in lecture), it may be arranged to read:

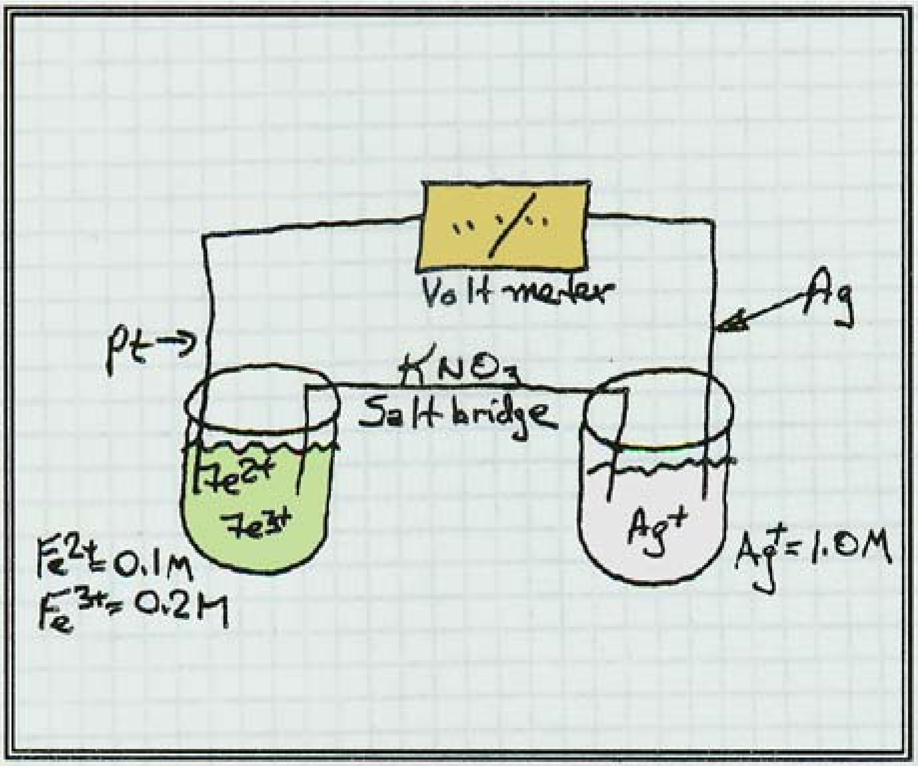
$$E_{cell} = E^{o}_{cell} - (0.0592/n)\log\frac{[G]^{g}[H]^{h}}{[E]^{e}[F]^{f}}$$

OR, it may be written in the following form:

$$E_{cell} = E^{o}_{cell} - (0.0592/n)\log\frac{[\text{Products}]}{[\text{Reactants}]}$$

Where E_{cell} is the measured potential of a battery; E^{o}_{cell} is the potential at standard conditions; "n" is the number of electrons in the reaction; [Products] is the molar concentration of the products; [Reactants] is the molar concentration of the reactants.

To understand what this means, let's look at an example of a battery:



There are two reactions that we are concerned with which are occurring:

$$\mathrm{Fe^{3+} + e^- \rightarrow Fe^{2+}} \qquad E^o = +0.771\ \mathrm{V}$$
$$\mathrm{Ag^+ + e^- \rightarrow Ag} \qquad E^o = 0.800\ \mathrm{V}$$

Note that we start with the half-reactions written in standard reduction form, i.e., electrons are written on the left side of each half-reaction.

We know that the anode contains the iron solutions and the cathode the silver ions. $\therefore$ the reactions must be running as written:

OXIDATION	$\mathrm{Fe^{2+} \rightarrow Fe^{3+} + e^-}$	$E^o = -0.771$ V
REDUCTION	$\mathrm{Ag^+ + e^- \rightarrow Ag}$	$E^o = 0.800$ V

$$E^o_{cell} = 0.029\ \mathrm{V}$$

$\therefore$ our Nernst expression is as follows (remember the $\mathrm{Fe^{2+}}$ is 0.1M, $\mathrm{Fe^{3+}}$ is 0.2M and the $\mathrm{Ag^+}$ is 1.0M):

$$E_{cell} = 0.029 - (0.0592/1e^-) \log \frac{([\underline{0.2}])}{([0.1][1.0])}$$

$$E_{cell} = 0.029 - 0.0592 \log 2$$

$$E_{cell} = 0.0112\ \mathrm{V}$$

Hence, given that the E_{cell} is positive, this battery will work.

There is, however, one detail with which one must become familiar in chemistry: how chemists "write" a battery (using the same example as we just calculated):

$$\mathrm{Pt}\,|\,\mathrm{Fe^{2+}}\ (0.1\mathrm{M}),\ \mathrm{Fe^{3+}}\ (0.2\mathrm{M})\,\|\,\mathrm{Ag^+}\ (1.0\mathrm{M})\,|\,\mathrm{Ag}$$

This means that the electrode at the anode is made of Pt; the salts in the solution at the anode are in the concentrations in the parentheses; the "|" separates the solid from the ions (Pt/$\mathrm{Fe^{2+}}$, $\mathrm{Fe^{3+}}$; Ag/$\mathrm{Ag^+}$) the "‖" represents the salt bridge to complete the circuit ($\mathrm{KNO_3}$ in this case). By convention, the anode is written on the left and the cathode on the right of this "short-hand" notation. Also keep in mind that Tables of Standard Reduction Potentials are a necessary evil in these computations.

For the next 5 questions, calculate the E_{cell} for the listed batteries and determine if they will work.

6. $Pt \mid Sn^{4+}$ (0.05M), Sn^{2+} (0.15M) $\|$ Pb^{2+} (0.2M) $\mid Pb$

7. $Cu \mid Cu^{2+}$ (0.25M) $\|$ Cu^{+} (0.4M) $\mid Cu$

8. $Cr \mid Cr^{2+}$ (0.3M) $\|$ S, H^{+} (0.05M), H_2S (0.1M) $\mid Pt$

9. $Pb \mid Pb^{2+}$ (0.3M) $\|$ $Mg(OH)_2$, OH^{-} (0.005M) $\mid Mg$

10. $Ag \mid Ag^{+}$ (0.03M) $\|$ Au^{3+} (0.025M) $\mid Au$

This next section has to do with the application of the E^o_{cell} to the calculation of the free energy of this reaction and then to the calculation of the equilibrium constant for the reaction. This assumes standard conditions exist and that 1J/C = 1V, or 1CV = 1J (C = coulomb; J = Joule; V = Volt). The following is an example of this application:

Determine the free energy and the equilibrium constant from the oxidation of SO_2 by $Cr_2O_7^{2-}$.

$$\begin{array}{ll} SO_4^{2-} + 4H^+ + 2e^- \rightarrow 2H_2O + SO_2 & E^o = 0.17\text{ V} \\ Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O & E^o = 1.33\text{ V} \end{array}$$

are the basic half-reactions.

Write and balance the half-reactions in the appropriate order:

$$\begin{array}{rl} Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O & E^o = 1.33\text{ V} \\ \underline{-3(SO_2 + 2H_2O \rightarrow SO_4^{2-} + 4H^+ + 2e^-)} & \underline{E^o = -0.17\text{V}} \\ Cr_2O_7^{2-} + 2H^+ + 3SO_2 \rightarrow 3SO_4^{2-} + H_2O + 2Cr^{3+} & E^o = 1.16\text{ V} \end{array}$$

Now, calculate the ΔG° (the free energy change):

$$\Delta G^\circ = -n\Im E^o$$

where "n" = number of electrons in the reaction; $\Im$ = the Faraday constant (96,487 Coulombs/mol e^-) and E^o = potential of the cell at standard conditions.

Plugging in the appropriate numbers:

$$\Delta G^\circ = (-6\ e^-)\left(\frac{96{,}487\text{ C}}{e^-}\right)(1.16\text{ V})\left(\frac{1\text{ kJ}}{1000\text{ J}}\right)$$

$$\Delta G^\circ = -671.55 \text{ kJ}$$

At room temperature, determine the equilibrium constant, K, for the reaction:

$$\Delta G^\circ = -2.303 \text{ R T log K}$$

R = 0.001987 kcal/mol·K @ 25°C and 4.184 kJ = 1 kcal

$$-671.55\text{kJ} = -2.303 \left(\frac{0.001987 \text{ kcal}}{\text{mol·K}}\right)\left(\frac{4.184 \text{ kJ}}{1 \text{ kcal}}\right)(298 \text{ K}) \log K$$

$$\log K = 117.7$$

$$\text{antilog } 117.7 = K = 5.012\text{X}10^{117}$$

For the next 5 problems, determine the free energy change for the reaction and the equilibrium constant for the reaction, as well. Additionally, determine if the reaction is favored as written or not.

11. The oxidation of Cr^{2+} by Sn^{4+}.

12. The oxidation of MnO_2 by BrO_3^-.

13. The oxidation of Cl^- by Fe^{2+}.

14. The oxidation of O_2 by BrO_3^-.

15. The oxidation of Cu by Cu^{1+}.

The last section of this problem set has to do with the application of the Nernst equation towards determining the K_{sp} of various chemicals. If, for example, we had the following battery:

$$\text{Ag}\,|\,\text{Ag}^+ \text{ (sat'd AgCl)}\,\|\,\text{Ag}^+ \text{ (0.1M)}\,|\,\text{Ag}$$

and you had determined the E_{cell} to be +0.229 V, how would you go about determining the K_{sp} for AgCl?

First, set up the appropriate half-reactions:

OXIDATION	$Ag \rightarrow Ag^+ \text{ (sat'd)} + e^-$
REDUCTION	$Ag^+ \text{ (0.1M)} + e^- \rightarrow Ag$
SUM	$Ag^+ \text{ (0.1M)} \rightarrow Ag^+ \text{ (sat'd AgCl)}$

$$\text{The } E^o_{cell} = 0.$$

$$E_{cell} = 0 - (0.0592/1)\log\frac{[Ag^+]}{[0.1]}$$

$$E_{cell} = +0.229 \text{ V}, \therefore$$

$$0.229 = -(0.0592)\ (\log[Ag^+] - \log[0.1])$$

$$-3.868 = \log[Ag^+] + 1$$

$$-4.868 = \log[Ag^+]$$

$$[Ag^+] = \text{antilog } -4.868 = 1.355X10^{-5}$$

$$\text{Since } K_{sp} = [Ag^+][Cl^-],$$

$$K_{sp} = (1.355X10^{-5})^2$$

$$\therefore K_{sp} = 1.84X10^{-10}$$

For the next 5 problems, calculate the K_{sp} for the solid given the battery and the E_{cell}.

16. $Al|Al^{3+}$ (sat'd $Al(OH)_3$)$\|Al^{3+}$ (0.1M)$|Al$ $E_{cell} = +0.1497$ V

17. $Cr|Cr^{3+}$ (sat'd $Cr(OH)_3$)$\|Cr^{3+}$ (0.1M)$|Cr$ $E_{cell} = +0.1363$ V

18. $Ca|Ca^{2+}$ (sat'd $CaSO_4$)$\|Ca^{2+}$ (0.1M)$|Ca$ $E_{cell} = +0.04499$ V

19. $Fe|Fe^{2+}$ (sat'd $Fe(OH)_2\|Fe^{2+}$ (0.1M)$|Fe$ $E_{cell} = +0.125$ V

20. $Cd|Cd^{2+}$ (sat'd CdS)$\|Cd^{2+}$ (0.1M)$|Cd$ $E_{cell} = +0.371$ V

About The Author

Dr. Carman, 20 September 2004, 10:55 a.m., Mt Rose, Nevada, 10,774 feet.

Dr. Carman graduated from Otis Junior-Senior High School in Otis, CO, in 1976, with his High School Diploma. Following a brief hiatus from higher education, he attended the United States Army Academy of Health Sciences, in Ft. Sam Houston, TX, in 1978, and was trained as a Medical Laboratory Technician. Following this training, he received gainful employment at the Logan County Hospital in Oakley, KS, and was cross-trained in Respiratory Therapy and X-ray Technology.

Following these training (and employment through mid-1985) periods in the clinical realm, he attended Colby Community College in Colby, KS, and received his Associate of Arts Degree **(A.A.)** in Chemistry in 1981. Concurrently, Dr. Carman attended the University of Kansas Medical Center, Outreach Program in Oakley, KS, in 1981, for EMT Training. Following receipt of his A.A., Dr. Carman attended Fort Hays State University in Hays, KS, following a family tradition (his paternal grandfather was on the first football team at FHSU; Dr. Carman is a third generation graduate of FHSU) and in 1984 received his Bachelor of Arts Degree **(B.A.)** in Chemistry with teaching minors in

Biology and Physics. Upon completion of a year of post-graduate education at FHSU, Dr. Carman was accepted into the University of Nevada [School of Medicine, Division of Biochemistry] Reno, Biochemistry Graduate Program in Reno, NV, and, in 1990, was awarded the degree of Doctor of Philosophy **(Ph.D.)** in Endocrine Biochemistry.

Since 1990, Dr. Carman has been a member of the faculty at Western Nevada Community College beginning from Teaching Assistant (1990-1991) to instructor (1991-1994) to professor (1994 to present) and including a brief period as Lead Instructor (2001-2002) and as the Division Chair (2002-2004) for the Science and Allied Health Division.

Dr. Carman's hobbies include hiking, snow-shoeing, woodworking, writing, riflery and pistolry and perpetually re-building, remodeling and re-structuring his course content – albeit slowly and painfully most days – and his website (http://tooldoc.wncc.edu).