A LOGICAL SEQUENCE OF TOPICS IN TEACHING CHEMICAL THERMODYNAMICS, WITH SPECIAL EMPHASIS ON THE FUNDAMENTAL PRINCIPLES AND THEIR DEVELOPMENT

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A LOGICAL SEQUENCE OF TOPICS IN TEACHING CHEMICAL THERMODYNAMICS, WITH SPECIAL EMPHASIS ON THE FUNDAMENTAL PRINCIPLES AND THEIR DEVELOPMENT†

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Over the years, I have been involved, more or less regularly, in teaching chemical thermodynamics to students of various disciplines. In particular, my primary aim has been to reach, not those students who are going to specialize in thermodynamics for its own sake, but those students who need to develop a firm grasp of the fundamental principles and the methods of application of thermodynamics as one of the necessary and important tools of their work.

We know that thermodynamics is basically important to all fields of science and engineering: Physical Sciences; Chemical Sciences; Life Sciences; and all branches of Engineering, particularly Chemical, Metallurgical, Nuclear, and Mechanical. In my opinion, chemical thermodynamics is the most important discipline that can be learned by any chemist, whether he be in physical, organic, inorganic, analytical, polymer, electro, biological, or any other kind of chemistry.

I think we can all agree that thermodynamics is one of the most interesting, most elegant, and most powerful subjects that can be studied by anyone. Thermodynamics can be very fascinating for the pure theorist as well as intensely interesting for the experimental scientist and the engineer. Because thermodynamics deals with all forms of energy and their interconversion and with all forms of matter and their interconversion, every process that occurs can be subjected to the powerful scrutiny of thermodynamics.

It is well known that the technological advancement of a country goes hand in hand with its production and consumption of energy, including energy from coal, petroleum, natural gas, water power, and atomic fuels. Since thermodynamics is the science of energy, and since the production and control of energy are so important to man, it is clear that the more expert we become in thermodynamics the more it is possible for us to develop increasingly greater control over the forces and the matter of the world in which we live.

In detail, there are almost as many different ways of teaching Chemical Thermodynamics as there are teachers of the subject. What I want to do

† The material is based largely on the author's book on "Chemical Thermodynamics" published by Wiley, New York (1950)
here is to share with you my experiences in teaching thermodynamics, with the hope that you may derive some benefit therefrom.

In former years, many schools had separate courses labelled "Chemical Thermodynamics". In one or two schools, the course was given in the Junior Year of the College or University curriculum in Chemistry. In some schools, the course was given in the Senior or last Baccalaureate Year, but in most of these schools, the course was given in the First Year of Graduate Studies.

In recent years, however, "Chemical Thermodynamics" is tending to disappear as a separate course. Increasingly, different parts of the subject of Chemical Thermodynamics are being taught in various other courses, a part here and another part there. When this is done, the student is presumed to have had enough Chemical Thermodynamics from these several parts and the separate integrated course is dropped from the curriculum. Under such a system, the student acquires part of his knowledge of Chemical Thermodynamics in the course in General Chemistry, another part in the course in Analytical Chemistry, and another and perhaps major part in the course in Physical Chemistry. But the student will normally not have the integrated course that will bring to him a realization and understanding of the beauty, elegance, and power of Chemical Thermodynamics. Since there is an increasing tendency to present the subject in different parts in different courses, little sense of relation among the various parts is made evident, much to the disadvantage of the student. I can picture a situation wherein a student, having completed his first year of chemistry and having learned some part of thermodynamics in it, comes to his second year and is informed: "Now just forget the thermodynamics you learned last year, this is the way we are going to do it." And then again, as he enters the third year, he receives the same advice: "Discard the thermodynamics you learned last year. We will do it this way."

The purpose of my report to you today is to urge a firm reestablishment of an integrated course in Chemical Thermodynamics in the curriculum for the degree of Bachelor of Science in Chemistry, and to present for the broad spectrum of students in such a course what is in my opinion a logical sequence of topics in Chemical Thermodynamics, with emphasis on the fundamental principles. In the teaching of thermodynamics, it is important not to make the subject more complicated and complex than it really is.

For most undergraduate students majoring in chemistry or chemical engineering, I believe that the subject of "Chemical Thermodynamics" can best be presented as an integrated whole, proceeding topic by topic in logical sequence, with a substantially rigorous development, with concrete examples, and with the important applications being clearly delineated in every direction. For such students, one can present the fundamental principles as the trunk of the tree of learning of this discipline, and then as the subject develops one can add branches to the tree at appropriate places in proper directions. In this manner, the student can continue to build on his tree of thermodynamics throughout his entire lifetime.

First, let me present the list of topics which I identify in the course, together with what I consider to be the logical sequence for best learning.

In this course, the number of lectures may be varied from 45 to 60, depending upon local circumstances, the special interests of the Instructor,
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the maturity of the students, and the depth to which the given topics are to be covered. Also, it is possible to abbreviate considerably one or more of the given topics. I wish now to present the topics in proper sequence, making appropriate comments as we go along.

Table 1 gives the names of the topics in order of presentation, together with the number of one-hour (50-minute) lectures devoted to each topic. As previously mentioned, the number of lectures can be varied to accommodate the special interest of the Instructor and his students. We now proceed to discuss these topics in certain groups.

The first five topics constitute the background material. The first lecture

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Total number of lectures: 60
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is devoted to the following: Appropriate introductory statements, giving some idea of the beauty, elegance, and power of the subject; clear definition of terms, emphasizing the need for good communication and understanding; some discussion of the thermodynamic concepts, including the idea of a thermodynamic system, the fact that we deal with only five fundamental properties, and that all other thermodynamic properties and functions are defined in terms of these.

The second lecture gives a rigorous description and definition of the present unified scale of atomic masses, with its development from the previously separate chemists' and physicists' scales which it replaced. The third lecture presents a discussion of temperature, explaining how the zero-pressure gas scale of temperature can be realized experimentally in the laboratory, how our former international scale of temperature was based on two experimentally realizable defining points with their difference in temperature being defined so that the value of the absolute zero of temperature was variable, and how the present scale utilizes the absolute zero together with one experimentally realizable defining point, the triple-point of water, with the value of this point being fixed by definition. The practical or working scale of temperature and the thermodynamic scale of temperature are discussed.

The fourth lecture presents first the story of the present day fundamental units of measurement, length, mass, and time, and then the story of the fundamental constants, distinguishing, for clarity of understanding, the defined constants, the values of which are fixed entirely by definition, the five or six basic constants, the values of which are determined by experimental measurements, and the derived constants, the values of which are derived from the defined and the basic constants with appropriate physical relations. The matter of conversion factors concludes this lecture. The fifth lecture discusses the present day actual unit of energy, the erg or joule, and describes the various "wet" calories and the development of the modern defined "dry" calorie. Here we point out that eventually the calorie will disappear as a unit of energy in favour of the joule.

With the material in these five lectures, the student is equipped with the peripheral information he will need to proceed directly into the subject of thermodynamics proper without having to backtrack at any point for background information. I may at this point say that the subject of thermodynamics itself is developed without the burden of its complex historical development. The thought here is that the student can absorb the material more easily and rapidly in this fashion, and, that later, he can learn the historical development with much greater appreciation of what the pioneers in the subject accomplished.

I should mention here that in the very first lecture, the student is introduced to the five fundamental thermodynamic properties, namely: $P$, Pressure; $V$, Volume; $T$, Temperature; $E$, Energy; and $S$, Entropy. At the same time, we show a number of the other thermodynamic properties and functions that can be defined in terms of the five fundamental properties, as follows:

Enthalpy (or Heat Content): $H = E + PV$

Gibbs Energy or Free Energy: $G = E + PV - TS = H - TS$
Fugacity: \( f_i = P_i \exp \left( \frac{1}{RT} \right) \int_0^P (Vi - RT/P) dP \)

Activity: \( a_i = f_i/f_0 \)

Activity coefficient: \( \gamma_i = a_i/N_i; \gamma_i = a_i/m_i; \gamma_i = a_i/P_i \)

Heat Capacity (at constant \( P \)): \( C_p = (\partial (E + PV)/\partial T)_p = (\partial H/\partial T)_p \)

Joule–Thomson Coefficient: \( \mu = (\partial T/\partial P)_{E+PV} = (\partial T/\partial P)_H \).

The next five topics deal with energy. The sixth topic deals with the First Law and is presented in the simple concept that, anytime anything ever happens, the change in energy of a given system is equal to the energy which it takes in minus the energy which it gives off. That is to say, for every kind of energy, the sign is taken as plus going into the system and minus coming out. Included in this lecture is a tabulation of the magnitudes of changes of energy associated with various processes.

The seventh topic gives a discussion of the Einstein relation between mass and energy, and gives thermodynamic applications to some nuclear reactions.

In the eighth topic, we introduce, by definition in terms of the fundamental properties, two new thermodynamic properties, the enthalpy or heat content, and the heat capacity, at constant pressure and at constant volume.

Next comes a discussion of gases, ideal and real, and their behaviour under the First Law. The ideal gas is defined here. Included here also is a discussion of isothermal and adiabatic processes, reversible and irreversible processes, and the work of compression and expansion of a gas, both isothermally and adiabatically.

Finally, in this group of topics, we present the energy of a substance as a function of temperature and its physical state. Here we simply show what happens to a substance as it is taken from the absolute zero of temperature successively from the solid to the gaseous state, through its temperatures of transition, fusion, and vaporization.

The next several topics deal with entropy and the properties that involve change of entropy with pressure, volume, or temperature. Under “entropy and the second law” are discussed spontaneous change, concept of entropy, reversible process, statement of the second law, and the relation between entropy and probability. Entropy is introduced here without reference to the Carnot cycle. Under “entropy and thermodynamic engines” are derived the quantitative relations, involving the temperatures of the hot and cold reservoirs, covering the work engine, refrigerating engine, and heating engine. This is done simply by using the first and second laws, without reference to the Carnot cycle. The next topic covers the “entropy of substances in relation to temperature, pressure, volume, and physical state”, and includes the change of entropy with change in phase and the entropy of mixing ideal gases. The next topic covers the change of energy, and of enthalpy or heat content, with pressure and with volume. Included here is a discussion of the Joule experiment, the adiabatic and the isothermal Joule–Thomson experiment, and the Washburn experiment. Under the “heat capacity of substances”, we discuss heat capacity in relation to temperature and physical state, equations for heat capacity as a function of temperature, the difference between heat capacity at constant pressure and that at constant volume, and the variation of heat capacity with pressure and with volume.

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Then we come to the point where we bring together the first and second laws. In the topic on “useful energy and free energy”, we discuss useful energy, free energy, spontaneous change, and useful energy, general criterion of equilibrium, and criteria of equilibrium for special cases. The topic of criteria of equilibrium is summarized as follows:

**General criterion:** \[ dE + PdV - TdS = 0. \]

At constant \( V \) and \( S \): \[ dE = 0. \]

At constant \( V \) and \( E \): \[ dS = 0. \]

At constant \( V \) and \( T \): \[ d(E - TS) = 0. \]

At constant \( P \) and \( T \): \[ d(E + PV - TS) = 0. \]

**Definition:** \[ G = E + PV - TS = \text{Gibbs Energy or Free Energy} \]

**Criterion for equilibrium at constant \( P \) and \( T \):** \[ dG = 0 \text{ or } \Delta G = 0. \]

The next topic deals with the relations among thermodynamic properties and functions and covers the five fundamental properties and the defined functions. Also here is demonstrated the identity of the scales of temperature provided by the ideal gas and by the second law.

Under the topic of “heats and energies of reactions and processes”, we discuss the specifications of the process and of the property measured, the variation of the heat of reaction with temperature, the principle of the modern thermochemical method, the calorimetric part and the chemical part of a thermochemical investigation, corrections to reference states, the assignment of the temperature for the reaction or process, and the assembly of a table of heats of formation.

Under the topic of “thermodynamic functions from statistical calculations”, we present the simple general method for such calculations, to give, as a function of temperature, for a given atom or molecule, its energy, enthalpy function, free energy function, entropy, and heat capacity. Discussed are the entropy at the absolute zero of temperature, the contributions arising from translational, rotational, and vibrational degrees of freedom, from electronic states of energy, from restricted internal rotation, from nuclear spin, and from the mixing of isotopes.

Under the topic of “entropy and the third law of thermodynamics”, we introduce the concept of the so-called Third Law of Thermodynamics or Nernst Heat Theorem, and discuss cases of conformity and non-conformity with the requirements for applying the Third Law. Then follows a discussion of entropy of nuclear spin, entropy of mixing isotopes, entropy associated with randomness in the structure of crystals, entropy associated with non-equilibrium distribution of molecules among rotational states of energy, entropy of solutions and of gases at the absolute zero of temperature, and the entropy of different crystalline forms of the same pure substance at the absolute zero of temperature.

Under the topic of the “equilibrium constant and the change in free energy for reactions of ideal gases”, we discuss the free energy of an ideal gas as a function of pressure at constant temperature, the free energy of mixing ideal gases, the definition of the proper quotient of pressures, the definition of the equilibrium constant, the relation between the change in free energy and the equilibrium constant, the relation between the equilibrium constant and the change in enthalpy and the change in entropy, the
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significance of the change in energy for a chemical reaction, and the significance of the change in entropy for a chemical reaction. We conclude this topic with a general statement regarding the behaviour of atoms in a chemical reaction.

Because of its special importance, and the need to have the student understand the overall relationships, the foregoing points are developed along the following lines:

We have

\[ G = E + PV - TS = H - TS \]

For any given process,

\[ \Delta G = \Delta H - \Delta(TS). \]

For constant temperature and standard states,

\[ \Delta G^\circ = \Delta H^\circ - T\Delta S^\circ. \]

But

\[ \Delta G^\circ = -RT \log_e K. \]

Hence

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

and

\[ \log_e K = - \Delta H^\circ/RT + \Delta S^\circ/R. \]

For any given chemical reaction, we are normally interested in maximizing the quantity of products or \( K \). Hence, we ask what makes \( K \) large.

For a given temperature, \( \log_e K \), and hence \( K \), increases with increase in \( \Delta S^\circ \) and increases with decrease in \( \Delta H^\circ \). But increase in \( \Delta S^\circ \) comes with increase in the number of states of existence, which corresponds to greater freedom. And decrease in \( \Delta H^\circ \) comes with decrease in the enthalpy and energy of the system, which comes with increase in the binding forces of the system, which corresponds to greater security.

The final state of equilibrium for the atoms involved in a given reaction, with the possibility of forming either reactant or product molecules, is a compromise between these two more or less opposing factors: greater freedom or greater entropy, as measured by \( \Delta S^\circ \) and greater security or lesser energy, as measured by \(-\Delta H^\circ/T\).

Looking again at the equation

\[ \log_e K = - \Delta H^\circ/RT + \Delta S^\circ/R, \]

we note that temperature appears in the first term on the right but not the second. For very, very low temperatures, the first term on the right will become quite large while the second term will change relatively little, and hence, at very, very low temperatures, the value of the equilibrium constant \( K \) will be determined largely by \( \Delta H^\circ \). On the other hand, for very, very high temperatures, the first term on the right will approach zero in value, relative to \( \Delta S^\circ/R \), and the value of \( K \) will be determined largely by \( \Delta S^\circ \).

Under the topic of "equilibrium between different phases of one pure substance", we discuss the escaping tendency of molecules from their given state, free energy as a measure of escaping tendency, the phase rule, and change of pressure with temperature for the equilibrium between two phases of one substance. We conclude this topic with the development of the
quantitative relations governing the equilibrium between two phases of one pure substance: liquid and gaseous, solid and liquid, solid and gaseous, and two solid phases.

Under the topic of "fugacity and standard states", we discuss fugacity as a measure of escaping tendency, the definition of fugacity (showing how it is defined for convenience in calculation), the fugacity of gases, the thermodynamic standard reference state for gases, the difference in properties between the real and the ideal conditions, the fugacity of liquids and of solids, the thermodynamic standard reference states for liquids and for solids, the variation of fugacity with pressure at constant temperature and with temperature at constant pressure, the evaluation of the fugacity of gases, equations of state for gases, and the compressibility factor for gases.

The thermodynamic standard reference state for liquids and solids is straightforward since this is taken as the real state of the liquid or solid at a pressure of one atmosphere at the given temperature. But the thermodynamic standard reference state for a gas is more complicated and is explained as shown in Figure 1. Here the solid line is for the real gas and the dashed line for the ideal state. A given real gas at $A$ may be taken to the same pressure in the ideal state by going along the real line to zero pressure and then by simple calculation along the ideal line to $H$. At $F$, the given real gas has a fugacity of 1 and a pressure greater than 1. At $B$, the given real gas has a pressure of 1 and a fugacity of less than 1. Though the pressure and fugacity are equal at $E$ for the real state and at $G$ for the ideal state, they are quite different as may be determined from measurement of the enthalpy in the two states. To go from any given real state $A$ to the standard state $S$,
one simply takes the given gas along the real line to zero pressure and then along the ideal line to $S$ by simple calculation for an ideal gas.

Under the topic of "solutions and partial molal and apparent molal properties", we discuss the problem of specifying the composition of solutions and then define the partial molal property and the apparent molal property. Then we discuss the basic partial molal equations, the relations holding for binary solutions, the relations between the apparent and partial molal quantities, thermodynamic equations involving partial molal properties (showing how these equations are the same as for the straight molal properties), and the evaluation of partial molal properties. We close this topic with a discussion of apparent and partial molal properties of volume, heat capacity, and heat content, with a final word about partial molal free energy and entropy of substances in solution.

Under the topic of the "ideal solution", we define the ideal solution by a simple thermodynamic equation, and then show how from this equation and the first and second laws of thermodynamics we can derive the values of the partial molal properties of the components of the ideal solution. This is followed by a discussion of the entropy of mixing components to form an ideal solution, the equilibrium between a pure solid substance and an ideal liquid solution, the equilibrium between an ideal liquid solution and an ideal solid solution of the same components, the equilibrium between a pure gaseous substance and an ideal liquid solution, and the equilibrium between an ideal liquid solution and a gaseous solution of the same components.

Under the topic of the "dilute real solution", we define the dilute real solution, and then show how, over the range of concentration satisfied by the simple definition of the dilute real solution, the solution has the properties of an ideal solution made up of the actual major component and a hypothetical solute with definable properties. Following this discussion of the fugacity of the solute and solvent of the dilute real solution, comes discussion of the change in freezing point of the solution with pressure and composition, the elevation of the boiling point, the distribution of a solute between two solvents, and osmotic pressure.

Under the topic of "real solutions and activity and activity coefficient", we discuss partial molal free energy and entropy and their variation with pressure and temperature, the definition of activity, thermodynamic standard reference states for the components of solutions, the variation of activity with pressure and temperature, activity in different phases at equilibrium, evaluation of a partial molal property for one component in a binary solution from the values for the other component, and evaluation of activity from vapour pressures, from the distribution of a solute between two solvents, from the lowering of the freezing point, and from the elevation of the boiling point. Also discussed are activities of strong electrolytes in aqueous solution, definition of activity coefficient, and the activity coefficient of strong electrolytes in aqueous solution.

The thermodynamic standard reference state for the solvent in any liquid solution is normally taken as the pure solvent at the given temperature and a pressure of one atmosphere. Presentation of the thermodynamic standard reference state for the solute in a non-aqueous solution is accomplished by
means of the diagram shown in Figure 2. Here, the solid line gives the fugacity of the solute as a function of its mole fraction in the given non-aqueous liquid solution. The point, $f_2^o$, at $N_2 = 1$, gives the hypothetical standard state for the solute, as determined by its behaviour in the dilute range, and $f_2^*$ is the fugacity of the actual pure solute, in the same physical state, liquid, as in the solution.

For the solute in an aqueous liquid solution, the thermodynamic standard state is as shown in Figure 3, where the solid line gives the fugacity of the solute in the aqueous liquid solution as a function of the molality. The point, $f_2^o$, at $m = 1$, gives the hypothetical standard state for the solute, as determined by its behaviour in the dilute range.

Under the topic of “equilibrium constant and the standard change in free energy”, we discuss the standard change in free energy, the definition of the proper quotient of activities, the definition of the equilibrium constant, the relation between the standard change in free energy and the equilibrium constant, the variation with temperature of the standard change in free energy and of the equilibrium constant, why the equilibrium constant is

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**Figure 2.** Thermodynamic standard reference state for the solute in a non-aqueous solution

**Figure 3.** Thermodynamic standard state for the solute in an aqueous liquid solution
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independent of pressure at a given temperature, the effect of pressure on the concentrations of the components of a chemical reaction at equilibrium, and equilibrium in a chemical reaction at constant volume.

Given any chemical reaction, as

\[ bB + cC = mM + nN. \]

The Proper Quotient of Activities is defined as

\[ Q_a = \frac{(a_M)^m (a_N)^n}{(a_B)^b (a_C)^c}. \]

The Equilibrium Constant, \( K \), is defined as the Proper Quotient of Activities at equilibrium:

\[ K = Q_a^e = \frac{(a_{M^e})^m (a_{N^e})^n}{(a_{B^e})^b (a_{C^e})^c}. \]

\[ \Delta F^o = -RT \log K. \]

\[ (\partial K/\partial P) = 0. \]

For equilibria in various states, as gaseous, non-aqueous liquid, and aqueous liquid, the equilibrium constant \( K \), which is invariable at a given temperature, is related to the proper quotient of other concentration variables as follows (\( m = \) molality, \( N = \) mole fraction, \( C = \) concentration, in moles per litre):

For an aqueous solution: \( K = Q_{a^e} = Q_{\gamma^e} Q_{m^e}. \)

For a non-aqueous solution: \( K = Q_{a^e} = Q_{\gamma^e} Q_{N^e}. \)

For gases at constant total pressure: \( K = Q_{a^e} = Q_{\gamma^e} Q_{N^e} P^{(m+n-b-c)}. \)

For gases at constant total volume: \( K = Q_{a^e} = Q_{\gamma^e} Q_{C^e} (RT)^{(m+n-b-c)}. \)

Under the topic of "electromotive force and free energy and galvanic cells and standard electrode potentials", we discuss the galvanic cell, the relation between electromotive force and free energy, the variation of electromotive force with pressure and temperature, the relation between electromotive force and activity and the equilibrium constant, and standard single electrode potentials.

Under the topic of "thermodynamic properties of aqueous ions of strong electrolytes", we discuss the conventions as to reference states, the standard heat of formation, the standard free energy of formation, and the standard entropy.

Under the topic of "thermodynamic application of the Debye–Hückel theory of strong electrolytes in dilute solution", we present a simple picture of the theory, and derive the thermodynamic relations for free energy, activity, activity coefficient, and relative partial molal enthalpy, heat capacity, volume, compressibility, and expansibility. This topic is included because of its usefulness in extrapolating to infinite dilution to obtain properties for the standard state.

Under the topic of "equilibrium between different phases of two or more components", we discuss the free energy of components in different phases,
the phase rule, binary systems with liquid and gaseous phases, binary systems of liquid and solid phases, and systems of more than two components.

Under the topic of "special applications of thermodynamics", we show how the normally constant variables can be introduced into the regular thermodynamic equations, covering gravitational field, centrifugal force, magnetic field, electrical field, surfaces and surface tension, and elasticity.

Under the topic of the "data of chemical thermodynamics" we review the modern sources of thermodynamic data, including journals and the output of our continuing data-compiling projects. Some discussion of the standard order of arrangement of the chemical compounds is given.

And, finally, under "thermodynamic calculations", we carry the student through a number of representative thermodynamic calculations, including equilibrium constants for chemical reactions, evaluation of thermodynamic properties for real conditions at high pressures, equations for vapour pressures, evaluation of heats of vaporization from data on vapour pressures and compressibilities, equilibria in reactions at constant volume, equilibria in reactions of isomerization, etc.

In conclusion, I may say that I have tried this method of presentation quite a number of times, most recently a year ago to a class of about 110 University students, a mixture of second and third year students in chemistry and chemical engineering. I realize that the method I have suggested will not appeal to all students nor to all Instructors. I do believe, however, that this kind of presentation, appropriately modified to fit local situations and interests, will serve admirably for the majority of students of chemistry and chemical engineering.

What I am stressing is the logical sequence of topics to maximize learning for those first taking the subject. This sequence provides great flexibility for the Instructor. As he proceeds along this path of learning with his students, the Instructor has total freedom to use his best personal methods to explain given topics and to spend more or less time at each stop on the way according to his own special interests and the nature of his students.