Thermodynamic Properties and Energy Functions of Solutions.

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ABSTRACT

The thermodynamic properties of a system are important in the analyses and calculations of chemical processes. Relationships derived thermodynamically start from a rigorous basis, and as a consequence, may represent an actual situation more closely. Among the more important thermodynamic properties are those of solutions. A convenient method of obtaining useful information about solutions is to analyze the experimental data obtained from calorimetric, volumetric, and vapor pressure measurements.

A unique calorimeter based on the principle of thermogrammetry was developed. The calorimeter interior was free from unnecessary devices which cause heat effects which are not readily observed. It had a fifty-three junction thermopile which served as an extremely sensitive temperature detector. Vapor space was eliminated to eliminate vaporization - condensation error. Heats-of-mixing were obtained for binary systems including ethanol-water, acetone-water, ethanol-acetone at 30°C; and methanol-water, methanol benzene at various temperatures between 25° and 60°C covering the entire concentration range. The effect of temperature on activity coefficients was then calculated.

The heats-of-mixing for systems ethanol-water and acetone-water were combined with existing vapor pressure
data to obtain partial molar quantities. Also the entropy changes upon mixing were calculated.

A rigorous method was developed to obtain the absolute values of various energy functions of pure components. The results for water are $G^\circ_{H_2O, 20^\circ C} = 1318 \text{ cal/g-mole},$

$\Delta H^\circ_{H_2O, 20^\circ C} = 1316 \text{ cal/g-mole},$ $H^\circ_{H_2O, 20^\circ C} = 4865 \text{ cal/g-mole},$

$E^\circ_{H_2O, 20^\circ C} = 4863 \text{ cal/g-mole}.$ Also $G^\circ_{CH_3OH, 20^\circ C} = 522 \text{ cal/g-mole},$

and $G^\circ_{CH_3COCH_3, 30^\circ C} = 260 \text{ cal/g-mole}.$ The numerical values are regarded as thermal energies and do not include atomic or nuclear energies.
INTRODUCTION

The successful application of various equilibrium stages in chemical processes depend upon the knowledge of vapor liquid equilibria of the mixture encountered. Most investigations on vapor-liquid equilibria are made at environmental conditions. Ordinarily activity coefficients are measured and reported at laboratory conditions. Often it is desired to use these data at other temperatures and a method of correcting for temperature is needed. Thermodynamic equations relating the rate of change in the activity coefficient with temperature to heats of solution and density of solution are well known. Unfortunately data on heats of solution which are good enough for this purpose are very scarce. Therefore, the development of a simple calorimeter for the rapid and precise measurement of heat-of-mixing is very essential.

This research is part of a project involving the prediction of thermodynamic and transport properties of mixtures. A calorimeter was developed and operated with various binary liquid systems. The data collected showed reasonable agreement with literature values and were used in graphical integration to predict the temperature effect on activity coefficients.
In Chapter I, some thermodynamic relations are reviewed briefly. Specifically the concept of partial molar quantities is important in interpreting phenomena in non-ideal solutions. In Chapter II, classification of non-ideal solutions is introduced. The intermolecular forces play an important role in causing the departure from ideality in actual solutions. Chapter III reviews the measurements and applications of heats of mixing. Chapter IV describes a new calorimeter and the procedure of experiment, and also shows experimental results. Chapter V develops a method to calculate the absolute values of four energy properties. The equations used are rigorous without any assumptions. Possible errors are from experimental measurements. Chapter VI discusses some possible extension of present project.
CHAPTER I

REVIEW ON PROPERTIES OF SOLUTIONS

Partial Molar Properties. A solution is a system consisting of more than one component in a single homogeneous phase. In this sense, gaseous mixtures are solutions, whereas liquid or solid mixtures must be in a complete homogeneity to be described as solutions. Although solutions exhibit wide variety of behavior, rigorous thermodynamic principles developed for pure substances may also apply to solutions which may contain several species provided the functional relations are modified to account for the variations in composition. Usually the properties of a solution are not additive properties of the pure components. The actual contribution is represented in terms of partial molar properties.

For any component $i$ in a solution, the partial molar quantity of an extensive property $E$ is defined by

$$
\bar{E}_i = (\frac{\partial E}{\partial n_i})_{T, P, n_j}, \quad (1-1)
$$

where $j$ designates all components other than $i$, and the superscript bar indicates partial molar quantity. For example, in the case of the partial molar volume and the partial molar enthalpy,
\[ V_i = \left( \frac{\partial V}{\partial n_i} \right)_{T, P, n_j} \quad , \quad (1-2) \]

\[ H_i = \left( \frac{\partial H}{\partial n_i} \right)_{T, P, n_j} \quad . \quad (1-3) \]

Since the partial molar quantities represent the true contribution to any extensive property of a solution, it follows that

\[ E = \sum n_i \bar{E}_i \quad . \quad (1-4) \]

This implies that

\[ U = \sum n_i \bar{U}_i \quad , \quad (1-5) \]

\[ H = \sum n_i \bar{H}_i \quad , \quad (1-6) \]

\[ V = \sum n_i \bar{V}_i \quad , \quad (1-7) \]

\[ S = \sum n_i \bar{S}_i \quad , \quad (1-8) \]

\[ A = \sum n_i \bar{A}_i \quad , \quad (1-9) \]

\[ G = \sum n_i \bar{G}_i \quad . \quad (1-10) \]

Analogous to the functional relations of pure substances, the partial molar energy functions are defined as:

\[ \bar{H}_i = \bar{U}_i + \bar{PV}_i \quad , \quad (1-11) \]
Chemical Potentials. The chemical potential is regarded as a chemical driving tendency useful to describe equilibrium phenomena. Just as a difference in voltages causes electricity to flow, a difference of chemical potential may provide a driving force to cause a chemical reaction to occur or a mass transfer to proceed. Equilibrium condition exists only when there is no difference in chemical potentials. It is an intensive property introduced by Willard Gibbs and may be expressed as:

\[ \mu_i = \bar{G}_i = \left( \frac{\partial G}{\partial n_i} \right)_T,P,n_j = \left( \frac{\partial U}{\partial n_i} \right)_V,S,n_j \]

\[ \left( \frac{\partial H}{\partial n_i} \right)_S,P,n_j \quad \left( \frac{\partial A}{\partial n_i} \right)_T,V,n_j \]

Although the chemical potential of a component is equal to the partial molar free energy, the other partial derivatives in equation 1-14 are not partial molar quantities, since they are not restricted to constant temperature and pressure.

With the aid of the concept of chemical potential, the total derivatives of four important energy functions
for a solution with variable compositions may now be expressed in a set of equations as:

\[ dU = TdS - PdV + \sum \mu_i n_i \quad , \quad (1-15) \]
\[ dG = -SdT + VdP + \sum \mu_i n_i \quad , \quad (1-16) \]
\[ dH = TdS + VdP + \sum \mu_i n_i \quad , \quad (1-17) \]
\[ dA = -SdT - PdV + \sum \mu_i n_i \quad . \quad (1-18) \]

**Fugacities.** The term "fugacity" was introduced by Lewis and Randall\(^1\), originally to define the free energy of a non-ideal gas as

\[ G_T = RT \ln f + C \quad , \quad (1-19) \]

where \( C \) is a constant dependent only on the temperature. By this definition the fugacity is related to the pressure by

\[ f = \phi P \quad , \quad (1-20) \]

where \( \phi \) is known as fugacity coefficient and for a perfect gas, \( \phi = 1.0 \). In this sense one may consider the fugacity as having a generalized characteristic of pressure. However,

A more complete definition of fugacity with regard to a gas is

\[ \mu = RT \ln f + \mu^\circ(T) \]  \hspace{2cm} (1-21)

\[ \lim_{P \to 0} \frac{f}{P} = 1.0 \]  \hspace{2cm} (1-22)

The quantity \( \mu^\circ(T) \) is called the standard chemical potential of a pure component and is a function of temperature only. For any component \( i \) of a solution, the definition of fugacity becomes

\[ \mu_i = \left( \frac{\partial G}{\partial n_i} \right)_{T,P,n_j} \]

\[ = RT \ln f_i + \mu_i^*(T,P) \]  \hspace{2cm} (1-23)

\[ \lim_{P \to 0} \frac{f_i}{(N_i P)} = 1.0 \]  \hspace{2cm} (1-24)

and \( \mu_i^*(T,P) \) is a function both of temperature and pressure\(^2\).

---

\(^2\) Both \( \mu_i \) and \( \mu_i^* \) are standard chemical potentials. The former depends on the temperature only whereas the latter depends on both temperature and pressure. The choice of the superscript \( \circ \) or \( * \) depends on the choice of standard system. \( \circ \) refers to a pure component at temperature \( T \) and 1 atm pressure. \( * \) refers to a pure component at the temperature and the pressure of the system.
When the liquid and the vapor of a solution are in equilibrium at constant temperature and pressure, equation 1-16 implies that the chemical potentials of each component in both phases are equal and

\[ \overline{\mu}_i^L = \overline{\mu}_i^V , \]  

and therefore,

\[ f_i^L = f_i^V . \]  

Thermodynamic Classification of Solutions.

Solutions are in general classified into ideal solutions and non-ideal solutions. This is merely based on empirical observations and the convenience of setting up their pertinent mathematical models. Actually the characteristics of solutions do not belong to any particular classification due to the interactions of molecular forces. Nevertheless, by means of this broad classification, experimental data are more easily analyzed and applied for design calculations. Non-ideal liquid solutions are further subdivided into athermal, regular, associated, and solvated solutions.

Ideal Solutions. An ideal solution is in general defined by

\[ \mu_i = \mu_i^*(T,P) + RT \ln x_i , \]  

(1-27)
for all components of the mixture. At this point it is interesting to use equation 1-27 as a starting point to derive a few thermodynamic properties of mixing. First rearranging equation 1-16 holding temperature and composition constant, we find that

\[
\left( \frac{\partial G}{\partial T} \right)_{P,n_i} = -S \quad (1-28)
\]

Differentiating equation 1-28 with respect to \( n_i \) at constant temperature, pressure, and \( n_j \) yields

\[
\left( \frac{\partial^2 G}{\partial T \partial n_i} \right)_{T,P,n_j} = \left( \frac{\partial \mu_i}{\partial T} \right)_{P,n_j} = \left( \frac{\partial S}{\partial n_i} \right)_{T,P,n_j}
\]

\[
= -S_i \quad (1-29)
\]

Now in general,

\[
\left( \frac{\partial \mu_i}{\partial T} \right)_{P,n} = \frac{1}{T} \left( \frac{\partial \mu_i}{\partial T} \right)_{P,n} - \frac{\mu_i}{T^2} \quad (1-30)
\]

According to the definition of chemical potential and Gibbs free energy,

\[
\mu_i = G_i = H_i - TS_i \quad (1-31)
\]

Substitute equations 1-29 and 1-31 into equation 1-30, we obtain
Similarly, for a pure component, it is found that
\[
\left( \frac{\delta (\frac{\mu_i}{T})}{\delta T} \right)_{P,n} = -\frac{S_i}{T} - \frac{\mu_i}{T^2} = -\frac{H_i^0}{T^2}.
\] (1-32)

Now divide equation 1-27 by the temperature, and differentiate with respect to temperature at constant pressure and composition yields
\[
\left( \frac{\delta (\frac{G_i^0}{T})}{\delta T} \right)_{P,n} = -\frac{H_i^0}{T^2}.
\] (1-33)

Comparing equations 1-32 and 1-33 with equation 1-34, we obtain the identity
\[
\bar{H}_i = H_i^0.
\] (1-35)

Thus, for any component \(i\) in an ideal solution, the partial molar enthalpy and the specific enthalpy in the pure state at the same temperature and pressure are equal. This is equivalent to say that the heats of mixing for an ideal solution are zero for the entire range of composition.
\[ \Delta H = 0 \quad . \quad (1-36) \]

In an analogous procedure, it is easily seen that

\[ \bar{V}_i = V_i^0 \quad , \quad (1-37) \]
\[ \Delta V = 0 \quad , \quad (1-38) \]

and

\[ \bar{S}_i = S_i^0 - R \ln x_i \quad . \quad (1-39) \]

Since

\[ \Delta U = \Delta H - P\Delta V \quad , \]

and \( \Delta H = 0, \Delta V = 0 \), it follows that

\[ \Delta U = 0 \quad . \quad (1-40) \]

From equation 1-39 the entropy of mixing per mole is found as

\[ \Delta S = - R \sum x_i \ln x_i \quad . \quad (1-41) \]

Consequently,

\[ \Delta G = \Delta H - T \Delta S \]
\[ = RT \sum x_i \ln x_i \quad , \quad (1-42) \]

and

\[ \Delta A = \Delta U - T \Delta S \]
\[ = RT \sum x_i \ln x_i \quad . \quad (1-43) \]
Phase Equilibrium of Ideal Solutions. For vapor-liquid equilibrium at constant temperature and pressure,

\[ \mu_i^L = \mu_i^G \]  

(1-25)

For an ideal gas in a mixture of gases, it may be shown that \^3

\[ \mu_i = G_i^0 + RT \ln p_i \]  

(1-44)

where \( G_i^0 \) is the chemical potential of the pure gas at the existing temperature and 1 atm. pressure, and \( p_i \) is the partial pressure of \( i \) in the gaseous mixture. Equating equations 1-27 and 1-44, we obtain

\[ \mu_i^* + RT \ln x_i = G_i^0 + RT \ln p_i \]  

(1-45)

noting that \( \mu_i^* \) is the chemical potential of pure liquid \( i \) at the temperature and pressure of the solution. Upon rearrangement, equation 1-45 becomes

\[ \frac{p_i}{x_i} = \exp \left( \frac{\mu_i^* - G_i^0}{RT} \right) \]  

(1-46)

In this expression, \( G_i^0 \) is a function of temperature only and \( \mu_i^* \) is a function both of temperature and pressure.

However, under ordinary conditions it may be proved that the effect of pressure on $\mu_i^*$ is negligible and $\mu_i^*$ may be approximated as a function of temperature only. Consequently the right hand side of equation 1-46 is a function only of temperature and we may write

$$p_i/x_i = C_i(T). \quad (1-47)$$

When $x_i$ approaches unity, $p_i$ approaches $P_i^0$ which is the vapor pressure of pure $i$ at $T,P$. Therefore $C_i$ equals to $P_i^0$. Thus equation 1-47 becomes

$$p_i = x_i P_i^0. \quad (1-48)$$

Equation 1-48 is the Raoult's law. It may be applied to ideal solutions at ordinary conditions$^4$. When $x_i$ approaches zero, for a non-ideal solution, $p_i$ approaches an empirical constant $k_i$ and we may write

$$p_i = x_i k_i \quad \text{as } x_i \to 0. \quad (1-49)$$

Equation 1-49 is known as the Henry's law, and valid only at infinite dilutions.

Now according to the Dalton's law, the partial

---

4. At very high pressures, equation 1-48 may not apply. However, according to Lewis and Randall, we may write $f_i = y_i f_i^o$. Any mixture which obeys this equation is referred to as a "perfect solution".
pressure of a gas in a mixture is the pressure that it would exert if it alone occupied the whole volume of the mixture at the same temperature; and the total pressure of the mixture is the sum of the partial pressure of the constituents. Thus

\[ p_i = y_i^P \]  \hspace{1cm} (1-50)

Equating equations 1-48 and 1-50, we obtain

\[ x_i P_i^0 = y_i^P \]

or

\[ y_i / x_i = P_i^0 / P = K_i \]  \hspace{1cm} (1-51)

where \( K_i \) is called the phase equilibrium constant for ideal solution at low pressures.

**Non-Ideal Solutions.** A non-ideal solution may be expressed by

\[ \mu_i = \mu_i^* + RT \ln \gamma_i x_i \]

\[ \gamma_i \rightarrow 1.0 \hspace{0.5cm} \text{as} \hspace{0.5cm} x_i \rightarrow 1.0 \]  \hspace{1cm} (1-52)

for each component of the mixture. \( \gamma_i \) is termed the activity coefficient first introduced by G. N. Lewis. It is usually a function of temperature, pressure, and composition.
Bjerrum and Guggenheim\textsuperscript{5} defined the non-ideality of a solution in a little different manner as

\[ \mu_i = \mu_i^* + \Phi_i RT \ln x_i , \]
\[ \Phi_i \rightarrow 1 \quad \text{as} \quad x_i \rightarrow 1.0 \quad , \quad (1-53) \]

where \( \Phi \) is called the osmotic coefficient. Comparing equations 1-52 and 1-53, we see that

\[ \Phi = 1 + \frac{\ln \gamma_i}{\ln x_i} \quad . \quad (1-54) \]

In fact \( \Phi \) is much more sensitive to deviations from ideality than \( \gamma \) and is used especially in connection with dilute electrolyte solutions where \( \gamma \) differs from unity very slightly.

Equating equations 1-44 and 1-52 and after rearrangement, we see that

\[ \frac{p_i}{\gamma_i x_i} = c_i = \exp \left( \frac{\mu_i^* - \mu_i^c}{RT} \right) \quad . \quad (1-55) \]

Since \( \mu_i^* \) and \( \mu_i^c \) are characteristics of pure components,

\textsuperscript{5} Guggenheim, E. A. \textit{Thermodynamics}. Amsterdam, 1949.
$C_j$ is independent of composition.

Now for equilibrium between vapor and liquid phases under constant $T$ and $P$, equation 1-26 tells us

$$f_i^L = f_i^V .$$ (1-26)

For liquid phase, by the definitions of fugacity (equations 1-23, 1-24) and non-ideality (equation 1-52),

$$f_i^L = \gamma_i x_i f_i^o .$$ (1-56)

At low pressures, it may be assumed that gases obey the ideal gas law; and vapor phase forms ideal solution. Then

$$f_i^o = p_i^o ,$$ (1-57)

and

$$f_i^V = p_i = y_i p .$$ (1-58)

By a simple algebraic manipulation it follows that

$$\gamma_i = \frac{y_i p}{x_i P_i} .$$ (1-59)

Equation 1-59 is often used to determine numerical $\gamma$'s at low pressures by vapor pressure measurements using equilibrium apparatus.

The Effect of Temperature and Pressure on Activity Coefficients. If the technique of cross differentiation is applied to equation 1-16, two important Maxwell-type
relations are obtained. Rewriting equation 1-16,

\[ dG = - SdT + VdP + \sum \mu_i \, dn_i \quad . \quad (1-16) \]

From this equation, two important reciprocity relations may be derived as

\[
\begin{align*}
\left( \frac{\delta \mu_i}{\delta T} \right)_{P, n_i, n_j} &= -\left( \frac{\delta S}{\delta n_i} \right)_{T, P, n_j} = - \bar{S}_i, \quad (1-60) \\
\left( \frac{\delta \mu_i}{\delta P} \right)_{T, n_i, n_j} &= \left( \frac{\delta V}{\delta n_i} \right)_{T, P, n_j} = \bar{V}_i. \quad (1-61)
\end{align*}
\]

Substituting equation 1-60 into equation 1-12 yields

\[ \mu_i = \bar{G}_i = \bar{H}_i + T \left( \frac{\delta \mu_i}{\delta T} \right)_{P, n_i, n_j}, \]

or by rearrangement

\[ \left( \frac{\delta \mu_i}{\delta T} \right)_{P, n_i, n_j} = - \frac{\bar{H}_i}{T^2}. \quad (1-62) \]

Now equation 1-52 may be written as

\[ \ln \gamma_i + \ln x_i = \frac{1}{RT} \left( \mu_i - \mu_i^* \right). \quad (1-63) \]

By partial differentiation of equation 1-63 with respect to temperature at constant pressure and composition and with respect to pressure at constant temperature and composition, we obtain

\[ \left( \frac{\delta \ln \gamma_i}{\delta T} \right)_{P, n_i, n_j} = \frac{1}{R} \left( \frac{\delta \left( \frac{\mu_i}{T} \right)}{\delta T} - \frac{\delta \left( \frac{\mu_i^*}{T} \right)}{\delta T} \right)_{P, n_i, n_j}. \]
At the limiting concentration, $\gamma_i$ approaches unity when the solution concentration approaches that of pure component $i$. Thus, observing equations 1-64 and 1-65, we see that

$$\left( \frac{\partial \ln \gamma_i}{\partial T} \right)_{p,n_{i,n_j}} = \frac{1}{R} \left[ \frac{H_i}{T^2} - \frac{\partial \left( \frac{\mu_i^*}{T} \right)}{\partial T} \right]_{p,n_{i,n_j}} \tag{1-64}$$

and

$$\left( \frac{\partial \ln \gamma_i}{\partial p} \right)_{T,n_{i,n_j}} = \frac{1}{RT} \left( \frac{\partial \mu_i}{\partial p} - \frac{\partial \mu_i^*}{\partial p} \right)_{T,n_{i,n_j}} \tag{1-65}$$

At the limiting concentration, $\gamma_i$ approaches unity when the solution concentration approaches that of pure component $i$. Thus, observing equations 1-64 and 1-65, we see that

$$\frac{\partial \left( \frac{\mu_i^*}{T} \right)}{\partial T} = - \frac{H_i^o}{T^2} \tag{1-66}$$

and

$$\frac{\partial \mu_i^*}{\partial p} = V_i^o \tag{1-67}$$

Therefore

$$\left( \frac{\partial \ln \gamma_i}{\partial T} \right)_{p,n} = \left( \frac{H_i^o - \bar{H}_i}{R T^2} \right)_{p,n} \tag{1-68}$$

and

$$\left( \frac{\partial \ln \gamma_i}{\partial p} \right)_{T,n} = \left( \frac{\bar{V}_i - V_i^o}{R T} \right)_{T,n} \tag{1-69}$$

Equations 1-68 and 1-69 show the dependence of the activity...
coefficient on temperature and pressure respectively. For liquid solutions at low pressures, the effect of pressure on activity coefficient is negligible. The dependence on temperature is much more significant. However, for practical purposes it too is often neglected. To obtain a quantitative idea of this temperature effect, it may be said that a variation of 30°C, might cause 5% change in the activity coefficient (see Figures 11 and 12 in Chapter IV).

The Gibbs-Duhem Equation. There are various forms of the Gibbs-Duhem equation which are of particular value in testing the consistency of experimental measurements as well as minimizing the number and smoothing the experimental data required to evaluate the properties of a system. In general the famous Gibbs-Duhem equation is

\[ SdT - VdP + \sum_i n_i d\mu_i = 0 \]  \hspace{1cm} (1-70)

For a special condition of constant temperature and pressure

\[ \sum_i n_i d\mu_i = 0 \] \hspace{1cm} (1-71)

Equation 1-71 may be expressed in various forms. For a binary solution

\[ n_1 \left( \frac{\partial \mu_1}{\partial n_1} \right)_{T,P} = n_2 \left( \frac{\partial \mu_2}{\partial n_2} \right)_{T,P} \] \hspace{1cm} (1-72)
The Thermodynamic Excess Functions. In the study of actual solutions the deviation from ideality is measured in terms of such excess properties of mixing as free energy, enthalpy, and volume, etc. This provides a useful basis for treatment of non-ideal solutions. The thermodynamic excess function is the difference between the thermodynamic function of mixing for an actual system and a hypothetical ideal system at the same temperature, pressure, and composition. Mathematically, for any property $E$ of mixing,

$$
\Delta E^E = \Delta E_{\text{actual}}^M - \Delta E_{\text{ideal}}^M
$$

The following is a summarized list of the excess properties of a binary solution.

1. Excess Gibbs free energy:

$$
\Delta G^E = \Delta G_{\text{ad}}^M - \Delta G_{\text{id}}^M
\quad = RT \left( x_1 \ln \gamma_1 + x_2 \ln \gamma_2 \right)
$$
(2) Excess enthalpy:

\[ \Delta H^E = \Delta H^M_{\text{act}} - \Delta H^M_{\text{id}} \]

\[ = \Delta H^M - 0 \]

\[ = \Delta H^M \] \hspace{1cm} (1-78)

\[ \Delta H^E = -T^2 \frac{\partial (\Delta G^E / T)}{\partial T} \]

\[ = -RT^2 \left( x_1 \frac{\partial \ln \gamma_1}{\partial T} + x_2 \frac{\partial \ln \gamma_2}{\partial T} \right) \] \hspace{1cm} (1-79)

(3) Excess entropy:

\[ \Delta S^E = -\frac{\partial (\Delta G^E)}{\partial T} \]

\[ = -RT \left( x_1 \frac{\partial \ln \gamma_1}{\partial T} + x_2 \frac{\partial \ln \gamma_2}{\partial T} \right) \]

\[ - R \left( x_1 \ln \gamma_1 + x_2 \ln \gamma_2 \right) \] \hspace{1cm} (1-80)

(4) Excess volume:

\[ \Delta V^E = \Delta V^M_{\text{act}} - \Delta V^M_{\text{id}} \]

\[ = \Delta V^M - 0 \]

\[ = \Delta V^M \] \hspace{1cm} (1-81)

\[ \Delta V^E = \frac{\partial (\Delta G^E)}{\partial p} \]

\[ = RT \left( x_1 \frac{\partial \ln \gamma_1}{\partial p} + x_2 \frac{\partial \ln \gamma_2}{\partial p} \right) \] \hspace{1cm} (1-82)
(5) Excess internal energy:
\[ \Delta U^E = \Delta U^M \nabla T_{\text{ex}} - \Delta U^M \nabla T_{\text{ad}} \]
\[ = \Delta U^M - 0 \]
\[ = \Delta U^M \]  
(1-83)

\[ \Delta U^E = \Delta H^E - P^E V^E \]
\[ = -RT\left[ x_1 \frac{\partial \ln \gamma_1}{\partial T} + x_2 \frac{\partial \ln \gamma_2}{\partial T} \right] \]
\[ + \rho \left( x_1 \frac{\partial \ln \gamma_1}{\partial \rho} + x_2 \frac{\partial \ln \gamma_2}{\partial \rho} \right) \]  
(1-84)

(6) Excess heat capacity:
\[ \Delta C_p^E = \frac{\partial (\Delta H^E)}{\partial T} \]
\[ = -2RT \left( x_1 \frac{\partial \ln \gamma_1}{\partial T} \right) + x_2 \frac{\partial \ln \gamma_2}{\partial T} \]  
\[ - RT^2 \left( x_1 \frac{\partial^2 \ln \gamma_1}{\partial T^2} + x_2 \frac{\partial^2 \ln \gamma_2}{\partial T^2} \right) . \]  
(1-85)

From the above list it would be possible to study all the excess functions in terms of the activity coefficients. However, it would become more difficult to measure precisely those derivatives of the second order and higher orders. Therefore, except the entropy of mixing, most excess functions of mixing are obtained directly from the experimental measurements.
Intermolecular Forces. An insight into the non-ideal behavior of real solutions is not a simple matter. There are interactions of molecular forces, overlapping of electronic clouds, changes in molecular shapes, statistical probability of molecular orientations, breaking or forming of bond energies, and so forth. Studies along the line of intermolecular forces has been successful in interpreting observed macroscopic measurements. Reasonably correct calculations are obtained for the case of completely disordered molecules of dilute gas or completely ordered crystal near the absolute zero of temperature. Between these extremities exist various possibilities and the mathematical formulation will often involve parameters which can not be calculated. In order to handle a more realistic situation than the simple hard sphere case, several models of potential function has been suggested such that each applies to a special system under consideration. These functions of potential energy are based on a postulation that there are intermolecular forces of attraction and repulsion in nature. The former varies with distance fairly slowly whereas the latter changes
rapidly with distance.

There are three kinds of long-range intermolecular forces, mainly,

(1) Dipole-dipole interaction: This force is electrostatic in nature and is the strongest among all. There is unsymmetrical distribution of charges in an unsymmetrical molecule that a permanent dipole moment exists. The unlike charges of molecules attract each other and the effect depends on their relative orientation. However, the thermal agitation interferes with the molecular orientation such that the attraction decreases with increase in temperature.

(2) Induced dipole interaction: When a non-polar molecule is near a polar molecule, induced polarization takes place. The resulting attractive forces are weaker and depend upon the polarizabilities of molecules. (1) and (2) are sometimes called Van der Waals forces.

(3) London dispersion interaction: This force is the weakest of all. It arises as a result of the distortion of electronic orbits in the molecules. It is related to the electromagnetic phenomena of induced absorption and emission of light by the molecules.

The short range interaction is a repulsive interaction. It arises from the overlapping of the electron clouds when the molecules are close enough. The force is
highly directional and falls off rapidly with distance.

The quantitative study of molecular interactions is brought with many difficulties. Since many approximate formulations are valid only when molecules are separated at a great distance, as in a gas with distance of about ten times the molecular diameter, the liquid solutions having molecular distances of about the dimensions of the molecules themselves present complications in accounting for the geometrical factor, mainly the averaging of r's in the potential functions. For this reason any suggested potential function at the present time is semiempirical in origin; the theory gives the interaction functional form, and the experimental data determines the adjustable parameters.

When molecules are idealized as rigid spheres and non-polar, the force of interaction $F$ is written as

$$ F(r) = -\frac{d\phi}{dr} $$

$$ \phi(r) = \int_0^\infty F(r) \, dr \quad . \quad (2-1) $$

The potential energy of interaction $\phi(r)$ includes repulsive and combined attractive forces. The exact functional form of $\phi(r)$ is not known; however, many forms have been suggested among which are the rigid sphere type, point centers of repulsion, square well potential, Sutherland
model, Lennard–Jones potential, Buckingham potential, rigid ellipsoids of revolution, Kihara potential, Keesom potential, Stockmayer potential. Among these the Lennard–Jones potential is one of the simplest and used most widely. It is simple yet explains qualitatively the picture of intermolecular forces and quantitatively reproduces the experimental results under some conditions. When the Lennard–Jones form is found to be inadequate then improvement or modification or even the suggestion of a new form may be made with by study of experimental data. The Lennard–Jones potential has been used to calculate the bulk properties of gases and liquids with better results obtained for spherical non-polar molecules. It may be written as

$$
\phi (r) = 4 \varepsilon \left[ \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^{6} \right],
$$

(2-2)
in which \( \sigma \) is termed the collision diameter and \( \varepsilon \) is a characteristic energy of interaction between the molecules. We see that the equation shows weak attraction at large separations varying with \( r^{-6} \) and strong repulsion at small separations varying with \( r^{-12} \). The choice of the exponents

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6 and 12 is optional; the choice of 12 appears to be as good as any in the range 10-14, and 12 just happened to be twice 6. The parameters $\sigma$ and $\epsilon$ are estimated from experimental viscosity and thermal-conductivity data, or from empirical relationships and even from approximations. When mixtures are involved, various forms of the mixture rule may be suggested. For the simplest case of binary non-polar mixtures

$$\sigma_{12} = \frac{\sigma_1 + \sigma_2}{2} \quad (2-3)$$

$$\epsilon_{12} = \sqrt{\epsilon_1 \epsilon_2} \quad (2-4)$$

**Classification of Non-Ideal Solutions.** To relate the molecular interactions to the observed properties of mixing is one of many important goals of recent research. Success in this not only depends on the correct formulation for intermolecular energy but also on the establishment of suitable expression for liquid structure. There are many kinds of model for liquids which are developed by the theory of statistical mechanics. However, just as in the studies of turbulent flow in fluid mechanics, the

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mathematics involved is very complicated so that after simplifying assumptions have been made the results are often not realistic. Further a general theory of liquid structure is still in the process of development. Thermodynamic properties such as free energy of mixing, heat of mixing, entropy of mixing, and volume of mixing are often used to test the suggested model of liquid. Therefore it is helpful to classify liquid mixtures according to the departures of macroscopic mixing properties from ideality. Following Hildebrand's\textsuperscript{3} classification, we may have regular, athermal, associated and solvated solutions.

**Regular Solutions.** These are those showing non-zero heat of mixing but the excess entropy of mixing is zero. Thus

\[ \Delta G^E = \Delta H^E \quad , \quad (2-5) \]

\[ \Delta S^E = 0 \quad , \]

\[ \Delta S^M = - R \sum_i x_i \ln x_i \quad . \quad (2-6) \]

The departure from ideality arises from enthalpy of mixing alone and the ideal entropy of mixing implies that the

solutions are in complete randomness. This system is represented by benzene-carbon tetrachloride binary solution showing identical $\Delta G^E$ and $\Delta H^E$.

Athermal Solutions. Here the deviation from ideality originates in entropy effects and the heat of mixing is zero or negligible. Thus

$$\Delta G^E = -T \Delta S^E,$$  \hspace{1cm} (2-7)

$$\Delta H^E = 0.$$

(2-8)

It may be shown from a statistical mechanics that the excess entropy of mixing is closely related to the excess volume and to the change of the free volume of the solution with composition. An example of this type system is butyl valerianate-benzene binary where $T \Delta S^E > \Delta H^E$. The excess entropy of mixing may be affected by the size or the shape of the molecules or both. Solutions of chain molecules with different chain lengths such as the n-heptane--n-hexadecane mixture have the excess entropy due to the difference in molecular sizes. On the other hand in the case of the benzene-diphenyl system, the entropy effect comes from the difference in molecular shape. The latter is said to have a lesser effect than the former and is related to the very different symmetries of the two molecules so that the rotational and vibrational motion...
is probably altered by mixing.

Associated Solutions. In the regular solution the heat of mixing is in the order of thermal energy of 600 calories per gram mole solution. In the associated solution the molecules are associated and the energy of association is much greater than the thermal energy. For example, two acetic acid molecules may be associated in the relative configuration of

\[
\text{CH}_3 - \text{C} \equiv \text{O} \cdots \text{H} \equiv \text{O} \equiv \text{C} \equiv \text{CH}_3
\]

through hydrogen bonding. The interaction energy is relatively high and has a magnitude of 8,000 calories per gram mole solution. This will imply that the association configuration is very stable. Furthermore this interaction causes the rotational and vibrational states of each molecule to change into a rather restricted degree of freedom. Thus association complexes are only possible with molecules having considerable electric charges near the surface, such as nitriles, ketones, alcohols, amines, and water. Experimentally associated solutions exhibit large deviations from ideal behavior, and it may be assumed that the major part of these deviations are due to the formation of associated complexes. If we neglect the deviations from ideality from the effect of sizes and shapes of complexes and monomers,
a hypothetical system termed the "ideal associated solution" is formed. For this model the observed heat of mixing includes the heat of reaction of association or dissociation and the intermolecular energy of the resulting monomer-complex mixture. Moreover it may be shown that the activity coefficients are independent of the complexity of the mode of association or dissociation.
CHAPTER III
A LITERATURE REVIEW ON HEATS OF MIXING
AND THEIR MEASUREMENTS

Heats of Mixing. Data from the measurements of heat-of-mixing are not only useful in the design calculations of industrial processes but also important in providing basic information for the analysis of thermodynamic systems. Usually the calorimetric measurements are performed under ordinary conditions of 1 atm. and a room temperature of 25°C. Only recently, due to the improvement in the design of calorimeters, measurements are possible to cover a range of temperature. This enables one to extend the original analysis into a broader sense with a better understanding of the insight of liquid structure. However, in addition to the fact that there are available only limited reliable data, the reported data were often obtained by different methods of measurement using different types of calorimeter. For this reason, it is important to make a greater effort in developing the theories, experimental methods, design of equipment, and collection of data related to the measurements and applications of heat-of-mixing.

In principle, from the determination of Gibbs free energy of mixing over a range of temperatures, the heat-of-
mixing may be calculated by
\[ \Delta H^m = \frac{\partial \left( \frac{\Delta G^m}{T} \right)}{\partial \left( \frac{1}{T} \right)} \]  
(3-1)

However, the numerical differentiation on data of vapor pressure measurements are often inaccurate such that the quantities obtained are seldom, if ever, of comparable accuracy to those which have been measured directly by a calorimeter.

In the absence of a correct expression of the intermolecular energy, heats of mixing are usually fitted with empirical relation in the form of a power series as
\[ \Delta H^m = x(1-x) \left[ A + B(1-2x) + C(1-2x)^2 + \cdots \right] \]  
(3-2)

Relative partial molar heats, \( \Delta \bar{H}_i \) ( \( \Delta \bar{H}_i = \bar{H}_i - H_i^0 \)), are obtained by numerical differentiation of \( \Delta H^m/x \), as a function of \( x_1/x_2 \) data\(^9\). In fact a plot of \( \Delta H^m/x_1 \) as a function of \( x_2/x_1 \) is very nearly linear over the composition range while \( \Delta H^m/x_2 \) vs. \( x_1/x_2 \) undergoes a rapid change of slope; and conversely, a plot of \( \Delta H^m/x_2 \) is very nearly linear over the range in which \( \Delta H^m/x_1 \) vs.

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$x_2/x_1$ goes through a maximum. Accordingly, the values of $\Delta \tilde{H}_i$ are obtained from these nearly linear portions. The results of differentiation is check by

$$\Delta \tilde{H}^N = x_1 \Delta \tilde{H}_1 + x_2 \Delta \tilde{H}_2 \quad . \quad (3-3)$$

Alternately the $\Delta \tilde{H}_i$'s are calculated from the change of $\ln \gamma_i$ with temperature at a fixed composition using

$$\Delta \tilde{H}_i = \frac{R \Delta \ln \gamma_i}{\Delta \frac{1}{T}} \quad . \quad (3-4)$$

The temperature intervals should reflect the proper rate of change of $\ln \gamma_i$ vs. $1/T$ in the non-linear regions.

If the heat of mixing increases as the temperature increases, it probably reaches a maximum at a certain temperature, and at a still higher temperature level, it will probably decreases as the temperature is increased. This is to be expected if the temperature coefficient of interassociation between unlike molecules is greater than the temperature coefficient of intra-association of like molecules. In addition to the ordinary heat effects resulting from regular molecular interactions, association gives rise to endothermic heats of mixing, and dissociation results in exothermic heats of mixing.

Effect of Temperature on Activity Coefficients.

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A knowledge of the molar Gibbs function \( G(T, P, x) \) as a function of absolute temperature \( T \), pressure \( P \), and mole fraction \( x \) is required for a complete thermodynamic description of a binary mixture. The Gibbs function \( G(T, P^*, x) \) can be obtained at a standard low pressure \( P^* \), usually at 1 atm., and at various temperature, from vapor pressure measurements. However, it requires the differentiation of experimental results leading to a greater possibility of incurring errors in calculation. It is therefore desirable to obtain the effect of temperature on the Gibbs function \( G \) by combining vapor pressure measurements with calorimetric measurements of heat of mixing.

The dependence of the activity coefficients on temperature is related to the heat of mixing by

\[
d \ln \gamma_i = - \frac{\Delta H^M - \chi_2 \frac{\partial (\Delta H^M)}{\partial \chi_2}}{R \cdot T^2} \, dT \quad . \tag{3-5}
\]

In addition, \( \gamma_i \) is related to the excess Gibbs function \( G^E(T, P^*, x) \) at temperature \( T \), a standard low pressure \( P^* \), and mole fraction \( x \) by

\[
R \cdot T \ln \gamma_i = \Delta G^E - \chi_2 \frac{\partial (\Delta G^E)}{\partial \chi_2} \quad . \tag{3-6}
\]

This \( \gamma_i \) also has an empirical relation with measured partial

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pressure $p_i$ and vapor pressure $P_i^o$ as

$$
\ln \gamma_i = \ln \frac{p_i}{P_i^o (1-x_i)} + \left( \frac{B_{ii} - V_i^o}{R T} \right) - \frac{2}{(R T)^2} \left( B_{ii}^2 (P - P_i^o)^2 \right) (3-7)
$$

where $p_i$ is the partial pressure of component $l$, $P_i^o$ is its vapor pressure in the pure state. $V_i^o$ is the molar volume of pure liquid $l$, and $B_{ii}$ is the second virial coefficient of gaseous component $l$. Integration of equation 3-5 yields an integration constant $\phi(x)$, independent of temperature, but rather a function of only $x$. $\phi(x)$ is evaluated by solving equations 3-5 and 3-7. The $\ln \gamma_i$ thus obtained is substituted into equation 3-6, which by integration gives temperature-concentration dependence of $\Delta G^F$.

Incidently, if equation 3-5 is integrated between the temperatures $T_1$ and $T_2$, then

$$
\ln \frac{\gamma_i, T_2}{\gamma_i, T_1} = - \int_{T_1}^{T_2} \frac{\Delta H^m - x_i \frac{\partial (\Delta H^m)}{\partial x_i}}{R T^2} \ d T (3-8)
$$

By graphical integration of the right hand side of equation 3-8, the ratio of activity coefficients of component $l$ at two temperatures at a fixed composition is obtained. It is convenient to set one of the

temperature at the temperature of room, and \( T \), at the other temperature is calculated using data from calorimetric measurements.

**Correlations of Data.** Experimental data are very often fragmentary. They require interpretation, interpolation and extrapolation, statistical treatment, presentation, storage and so forth. Here in the case of heats of mixing as well as liquid mixture enthalpies, we may consider three types of correlation.

(1) **Intermolecular Theory:** This purely theoretical method is well presented by Prigogine\(^\text{14}\), Hirschfelder and et. al., and Pierotti\(^\text{15}\). It explains qualitatively the non-ideal phenomena of liquid mixtures, but there is little success in obtaining quantitative predictions.

(2) **Correlating Equations:** Useful correlations are mostly obtained in a manner partly empirical but based on some theoretical concept. Relations in the

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form of power series were used by Guggenheim\textsuperscript{16}, Scatchard\textsuperscript{17}, Redlich\textsuperscript{18} and so on. This has an advantage that the experimental data can always be fitted into an equation with sufficient number of exponential terms. Useful concepts and assumptions are helpful in setting up empirical equations. For instance, in analogous to "Group Contribution", Wilson and Deal\textsuperscript{19} assumed that with regard to a system of amine-water binary, the interaction between molecules is equal to the sum of group interactions which are not influenced by other atoms or groups within the molecule. Moreover, high heats of solution are assumed to be due to hydrogen bonds formed by the water hydrogen and amino nitrogen. With these assumptions the empirical equation below was derived.

$$
\Delta H^E = 9235 - 3415 \xi^* + 639.6 \xi E^C_b
$$

\textsuperscript{17} Scatchard, G. Trans. Farad. Soc., 33, 160 (1937).
\textsuperscript{18} Redlich, O., Ch. Eng. Prog. Symposium Ser. No. 2, 48, 49 (1952).
This equation is only valid at infinite dilution, and \( c^* \) and \( B^c_0 \) are structural parameters.

Data may also be correlated graphically. For example, Canjar and Peterka\(^{20}\) plotted enthalpies of liquid mixtures vs. molal average boiling point. They define the molal average boiling point as

\[
B = \varepsilon x_i B_i
\]

where \( B_i \) is normal boiling point of pure component \( i \). The correlation included both temperature and pressure effects.

(3) Equations of State: Equations of state are analytical formulations of the relationships among \( P \), \( V \), and \( T \). Their suitable application in thermodynamic calculations of mixture properties depends on the formulation of a correct mixture rules.

Korvezee\(^{21}\) suggested in 1953 that graphs presenting the excess properties divided by the product of the mole fraction might be preferable to the common excess function plots.

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Using this idea a plot of the type $\Delta H^E/x_1, x_2$ vs. $x_1$ has been used increasingly in recent years for the simple presentation of data. In some cases $x_1 x_2/\Delta H^E$ vs. $x_1$ is more nearly linear, and for this reason it is especially useful for smoothing data particularly in the region where the heat of mixing changes very rapidly with concentration. On the other hand the function $\Delta H^E/x_1, x_2$ vs. $x_1$ is more convenient to use and appears to be in a more formal form. It may be noted that excess function rather than mixing function is used (though $\Delta H^E = \Delta H^\prime, \Delta G^E = \Delta G^\prime$). This is because $\Delta G^\prime/x_1, x_2$ approaches infinity at both $x_1 = 0$ and $x_1 = 1.0$, but $\Delta G^E/x_1, x_2$ remains finite at both $x_1 = 0$ and $x_1 = 1.0$.

**Calorimeters.** In order to determine accurately the heats of mixing, the calorimeter used should provide precise and accurate measurements despite the presence of various thermal effects. In addition, it must be capable of covering a complete range of composition over a broad temperature scale. Usually a calorimeter consists of:

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(1) A vessel with a stirring device where liquids are mixed.

(2) A sensor to detect temperature changes.

(3) A measurable heat source.

(4) An isothermal environment.

Unlike the measurements of heating values where standard apparatus, such as flow calorimeter, Parr oxygen bomb calorimeter are available, there is no ready-made calorimeter suitable for the measurement of heats of mixing. Therefore the design and setting up of apparatus varies from laboratory to laboratory.

Recent investigations show that the presence of excess vapor space in a mixing compartment is a major contribution to the overall error. This is due to condensation of vapor when the vapor space is reduced by expansion of the liquid upon mixing; or evaporation when the vapor space is enlarged by contraction of the liquid after mixing. Therefore when designing a mixing vessel the effect of a vapor space should be considered carefully. On the other hand if no air space were provided, then for liquids which expand on mixing, the final pressure might be several tens of atmospheres. It is obvious that the ideal design is one in which there is no air space and no pressure effect due to a volume change on mixing. Methods of accounting for volume changes include a flexible metal
diaphragm, insertion in the top of a calorimeter a capillary tube provided with an end bulb, confining the liquids before and after mixing under mercury, etc. The use of mercury as a separating medium is sometimes undesirable because of the possible catalytic effect on mixtures in addition to its appreciable heat capacity. Other thermal effects include heat flow effects between the calorimeter and its surroundings, stirring, heat capacitance of the compartment and internal parts.

For a good calorimeter, it appears desirable to consider the following features:

(1) Use vessel with large enough volume (say 100 ml.) such that errors in weighing is negligible.
(2) Efficient stirring.
(3) No vapor space.
(4) Minimization of heat losses due to conduction, convection, and radiation.
(5) Avoid bulky internal parts.
(6) High sensitivity in temperature measurement.
(7) Rapid attainment of original temperature after mixing.
(8) The interior of the calorimeter must be inert to the systems under study.
Skinner$^{24}$ discussed various types of calorimeters; and derived mathematically the thermodynamic effect of the presence of a vapor space. Mrazek and van Ness$^{25}$ built a continuous calorimeter capable of taking data over an entire concentration range with a single experimental run. This was an important experimental time saving breakthrough.


The absolute values of many thermodynamic properties of pure components are not known. Although volumes are always expressed in absolute quantities, and by consequence of the third law of thermodynamics, the absolute values of entropies are calculable, other important thermodynamic functions such as Gibbs free energy, enthalpy, internal energy, Helmholtz free energy do not have a pertinent method available for the calculation of their absolute values. There were brilliant works to present enthalpy data, \( H^\circ_T - H^\circ_0 \), above absolute zero temperature, however, there has not yet any thermodynamic law to state that \( H^\circ_0 \) is zero at absolute zero. Therefore \( H^\circ_T - H^\circ_0 \) is still a relative quantity rather than an absolute term. In this work, we will try to develop a method, whereby absolute values of free energy are calculable from experimental measurements. Once these are obtained, other properties may be calculated using exact thermodynamic relations.

At this point it may be noted that there are several choices of presentation of data such as tabular, graphical, and mathematical. For the purpose of explaining the method and calculational procedure,
sequences of tabular and graphical presentation is adopted in the following sections and Chapter V to give the best understanding with a minimum of wording. As mentioned earlier, a complete thermodynamic study of solutions require a combination of vapor pressure measurements and calorimetric measurements. The vapor pressure data were obtained from the literature since this is already well developed. In the present studies, a unique method of calorimetry was developed with which data on heats of mixing were collected. It is hoped that this type of calorimetry will become widely used and facilitate more extended researches in the field of solution thermodynamics.

**Systems Studied.** Heats of mixing were measured for the systems methanol-benzene and methanol-water at several temperatures between 30° and 60°C. The results were used to study the effect of temperature on activity coefficients. In addition, the effect of concentration was included.

Isothermal heats of mixing at 30°C were also obtained for systems ethanol-water, water-acetone, acetone-ethanol. These were combined with vapor pressure measurements (obtained from the literature) to calculate molar Gibbs free energy and enthalpy of pure water, ethanol, and acetone.

**Reagents.** The reagents used were methanol, ethanol, benzene, acetone, and water. The methanol, benzene, and
acetone were products of Mallinckrodt Chemical Works and of analytical reagent grade. The ethanol was a product of U.S. Industrial Chemicals Co., Division of National Distillers and Chemical Corporation and of analytical reagent grade. Distilled water was obtained from the Unit Operations Laboratory in the Department of Chemical Engineering at Louisiana State University.

**Experimental Procedure.** The apparatus is shown in Figures 1a, 1b, and 2. The calorimeter body, G, was a 150 ml vessel made from 51 mm. O.D. pyrex glass tube. It was fitted with

1. a very tiny stirrer, S.
2. heater coil H made from 28 gage chromel, type A, wire having a resistance of 4.10 ohms per foot.
3. thermopile T having 53 junctions of 32 gage copper-constantan thermocouples.
4. a neoprene plug D with a glass tubing attached to a second vessel E. This vessel E was also made from 51 mm. O.D. pyrex glass tube.

The calorimeter G, vessel E, and reference junctions of thermopile T were immersed in an isothermal water bath W. The water bath was made of polypropylene with a thick plate glass at one front side. Any mixing action inside the calorimeter was clearly visible. The water bath was connected to a circulator C equipped with: (1) an on-off
Fig. 1-a. Schematic Diagram of Experimental Set Up for the Measurement of Heats of Mixing
**Fig. 1-b. Calorimeter Cell Dimensions**

*(Actual Size)*

- Made of 2 mm thick Pyrex tubing.
- I.D. 3 mm Neoprene plug.
- 47 mm diameter.
- 45 mm height.
- Bead to be fastened tightly.
- 3 mm thick Neoprene O-ring.

*Calorimeter Cell*

*Scale: Full*

*Drawn by: C.Y. Liu*

*Date: July 10, 1968*
Fig. 2. Experimental Apparatus for Measurements of Heats of Mixing
mercury temperature controller, (2) a refrigerator, (3) a heater, (4) a circulating pump. This thermo-electric circulator is a product of Scientific Apparatus Inc. A thermometer F measured the bath temperature. The leads from heater H were connected through (1) a 30,000 ohms per volt multitester V (Radio Shack Corporation) for measuring the voltages, (2) an ammeter A (W.H. Welch Scientific Co.), and finally to (3) a filtered D.C. power supply P (model D 612 T, Electro Products Laboratories). The leads from thermopile T were connected to a potentiometer-recorder R (Minneapolis-Honeywell Regulator Corporation, Brown Instruments Division). This thermopile-recorder combination gave a reading of 4.643 scale per one degree centigrade out of possible 100 which was equivalent to a length of 27.95 cm. Usually a mixing operation gave rise to a temperature change of 5°C or so resulting in a recorder reading of about 23.

At the beginning of an experiment, vessel G contained a measured amount (weighed to an accuracy of 0.0001 g using a 160 g capacity type H 6 balance made by Mettler Instrument Corporation) of one of the pure components, and vessel E contained a weighed amount of the second component. The water bath was at a constant temperature throughout the entire operation. At least two hours was required between introduction of the reagents
and beginning of the mixing to insure that the reagents had reached an isothermal temperature of the water bath. Then clamp X of vessel E was opened to introduce the second component, until the liquid completely filled vessel G. This introduction of the second component was within a short period of 3 to 5 seconds that the temporary presence of a vapor space before vessel G was filled would not allow enough time for a vaporization or condensation to take place. Thus vaporization-condensation error was eliminated. The temperature change due to heat of mixing was detected by the thermopile and recorded on the potentiometer. The value of heat of mixing was measured by input of a known quantity of electrical energy. The introduction of electricity should be in such a manner to produce a nearly identical temperature-time history curve obtained from actual heat of mixing. A stop watch was used to measure the duration of current flow. Four to five introductions of electricity for each mixing were made, then the one equivalent to heat of mixing was obtained by interpolation. The last step involved:

(1) cut off the area under temperature-time curve and weigh,

(2) plot electrical energy (as ordinate) vs. weight (as abscissa) of paper,

(3) by the weight of paper cut from temperature-
time curve due to heat of mixing, the corresponding energy scale may be read from the ordinate.

The above calorimetry was different from the conventional Dewar flask type method. The major difference was that instead of minimizing the heat transfer loss due to conduction and convection using adiabatic condition, the present calorimeter allowed both types of heat transfer to take place (heat transfer due to radiation was negligible). The amount of heat was taken into account by the temperature-time curve termed a thermogram. Another difference was that usually the second component was separated by a thin metal foil in a flask or contained in a glass bulb. Mixing was caused by piercing the metal foil or crushing the glass bulb. In the present method, the second component had a container of its own, the amount of discharge was controlled simply by manipulating a clamp. The construction of a fifty-three junction thermopile was very unusual. It gave an extremely sensitive temperature measurements. Other calorimeters used one to four junctions or at the most ten junctions of thermocouples or a single probe resistance type thermister for temperature measurements. To make the interior of calorimeter visible was as important as any other features. This ensured

(1) the stirrer was turning properly to give a
sufficient mixing,

(2) liquid level was controlled such that no vapor space was allowed,

(3) the heater was at a proper position that no short circuit existed.

**Experimental Results.** The heats of mixing were measured for a complete range of concentrations for the binary systems ethanol-water, ethanol-acetone, and acetone-water at 30°C, for the system methanol-water at 25°, 30°, 35°, 40°, 45°, and 50°C, for the system methanol-benzene at 30°, 35°, 40°, 45°, 50°, 55°, and 60°C. The results are listed in Table 1, 2, and 3, and are plotted as Figures 3, 4, 5, 6, and 7. Literature values of heats of mixing for methanol-benzene system are available at 25°, 35°, and 45°C. They are also plotted in Figure 3 and show good agreement with the present experimental results. The maximum deviation of the experimental results from literature values is 4.33% for methanol-benzene binary at 45°C. Figures 8 and 9 show the effect of temperature on heat-of-mixing.

---

<table>
<thead>
<tr>
<th>$x_{\text{CH}_3\text{OH}}$</th>
<th>Temp. °C</th>
<th>$\Delta H$</th>
<th>$x_{\text{CH}_3\text{OH}}$</th>
<th>Temp. °C</th>
<th>$\Delta H$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.314</td>
<td>30</td>
<td>300</td>
<td>0.678</td>
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<td>270</td>
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<tr>
<td>0.278</td>
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## Heats of Mixing, Btu/lb. mole of solution
### Methanol-water

<table>
<thead>
<tr>
<th>$x_{\text{CH}_3\text{OH}}$</th>
<th>Temp. °C</th>
<th>$\Delta H$</th>
<th>$x_{\text{CH}_3\text{OH}}$</th>
<th>Temp. °C</th>
<th>$\Delta H$</th>
</tr>
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<tbody>
<tr>
<td>0.10</td>
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<td>-245.5</td>
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<td>-140</td>
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<td>0.49</td>
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<td>-352</td>
<td>0.671</td>
<td>50</td>
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<td>0.714</td>
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<td>-239</td>
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<td>-112</td>
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</table>
### Table III. Heats of Mixing, Cal/g-mole of solution

**Systems:** Ethanol-Water; Acetone-Water; Ethanol-Acetone at 30°C

<table>
<thead>
<tr>
<th>Ethanol-Water</th>
<th>Acetone-Water</th>
<th>Ethanol-Acetone</th>
</tr>
</thead>
<tbody>
<tr>
<td>$x_{\text{ethanol}} \Delta H$</td>
<td>$x_{\text{acetone}} \Delta H$</td>
<td>$x_{\text{ethanol}} \Delta H$</td>
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<tr>
<td>0.058</td>
<td>-99.4</td>
<td>0.058</td>
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<tr>
<td>0.128</td>
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<td>0.128</td>
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<tr>
<td>0.151</td>
<td>-179</td>
<td>0.151</td>
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<tr>
<td>0.163</td>
<td>-180</td>
<td>0.163</td>
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<td>0.216</td>
<td>-168</td>
<td>0.216</td>
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<td>0.348</td>
<td>-133</td>
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<td>0.595</td>
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<td>0.737</td>
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<td>0.832</td>
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<td>0.847</td>
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<td>33</td>
<td>0.62</td>
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<td>0.768</td>
<td>82.1</td>
<td>0.816</td>
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<tr>
<td>0.858</td>
<td>92.6</td>
<td></td>
</tr>
<tr>
<td>0.928</td>
<td>64</td>
<td></td>
</tr>
</tbody>
</table>
Fig. 3. Heats of Mixing
Methanol-benzene

\[ \Delta H, \text{ Btu/lb, mole of solution} \]

\[ x_{\text{CH}_3\text{OH}} \]
Fig. 4. Heats of Mixing

Methanol-water

\[ \Delta H, \text{ Btu/lb, mole of solution} \]

\[ x_{\text{CH}_3\text{OH}} \]

\( 25^\circ \text{C} \)
Fig. 5. Heat of Mixing

Ethanol–water binary at 30°C
Fig. 6.
Ethanol-Water Binary at 30°C

Heat of Mixing

$\Delta H$, cal/g-mole solution

Mole fraction ethanol

0.0
0.2
0.4
0.6
0.8
1.0

0
100
200
300
Fig. 7. Heat of Mixing
Acetone-Water Binary at 30°C
Fig. 8. Effect of Temperature on Heats of Mixing

Methanol-benzene

\[ \Delta H, \text{ Btu/lb mole of solution} \]

\[ \text{Temperature, } ^\circ\text{C} \]
Fig. 9. Effect of Temperature on Heats of Mixing

Methanol-water
(1) Sample Calculation of $\Delta H$. $\Delta H$'s were calculated by the procedure as shown in the following example.

System: acetone-water binary mixture at 30\(^\circ\)C and 1 atm.

Weight of water = 6.1270 g
Weight of acetone = 119.3877 g

g-mole of water = 6.1270/18 = 0.341

g-mole of acetone = 119.3877/58.08 = 2.06

Total number of g-mole = 0.341 + 2.06 = 2.401

Mole fraction of water = 0.341/2.401 = 0.142
Mole fraction of acetone = 2.06/2.401 = 0.858

The mixing of acetone and water caused the temperature of the system to decrease (endothermic in this case). This was detected by the thermopile and recorded on the potentiometer as a temperature-time curve corresponding to M in Figure 10. The quantity of heat was measured by introducing electrical energy. Several different introductions of electricity resulted in curves A, B, and C, etc. The energy was calculated by

\[ \text{joules} = (\sec)(\text{volts})(\amp) \]

Then curves M, A, B, and C, etc. were cut off and weighed to an accuracy of ± 0.0001 g. Interpolation among A, B, and C, etc. were made using a plot of energy vs. weight of paper and the quantity of heat corresponding to M was
Fig. 10. A Typical Thermogram for Heats of Mixing Effects
read off from this plot. The following table lists some of the numbers used for the above procedure.

<table>
<thead>
<tr>
<th>Curve</th>
<th>Time (sec)</th>
<th>Amp</th>
<th>Volts</th>
<th>Joules</th>
<th>Wt. of paper (mg.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>M</td>
<td>47.5</td>
<td>1.68</td>
<td>7.4</td>
<td>930</td>
<td>18.8</td>
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<td>A</td>
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<td>2.34</td>
<td>10.75</td>
<td>590</td>
<td>13.4</td>
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<td>B</td>
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<td>2.34</td>
<td>10.75</td>
<td>805</td>
<td>18.8</td>
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<td>25.3</td>
<td>2.45</td>
<td>11.25</td>
<td>497</td>
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<td>D</td>
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<td>2.44</td>
<td>11.25</td>
<td>472.5</td>
<td>9.7</td>
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<tr>
<td>E</td>
<td>14.2</td>
<td>2.44</td>
<td>11.25</td>
<td>384.5</td>
<td>8.0</td>
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</tbody>
</table>

The heat of mixing was

\[ \Delta H = \frac{930}{2.401} = 387 \text{ joules/g-mole} \]

\[ = 92.5 \text{ cal/g-mole} \]

\[ = 167 \text{ Btu/lb mole} \]

(2) Partial Molar Heats of Mixing. The quantity \( \Delta H^m \) is usually termed the "integral heat of mixing" per mole of solution. It may be written as

\[ \Delta H^m = H - x_1 H_1^0 - x_2 H_2^0 \]

\[ = x_1 (\bar{H}_1 - H_1^0) + x_2 (\bar{H}_2 - H_2^0) \]

where \( H \) is the total enthalpy of the final mixture, \( H_1^0 \)

and \( H_2^0 \) are the molar enthalpies of pure substances 1 and 2, \( \bar{H}_1 \)

and \( \bar{H}_2 \) are partial molar enthalpies of 1 and 2 in the mixture. The quantities \( \bar{H}_1 - H_1^0 \)

and \( \bar{H}_2 - H_2^0 \) are called the "differential heat of mixing" or "partial molar heat of mixing" per mole of component 1 and 2 respectively.
Furthermore,
\[ \bar{H}_1 - H_1 = -RT \frac{\partial \ln \gamma_i}{\partial T} \]
\[ \bar{H}_2 - H_2 = -RT \frac{\partial \ln \gamma_i}{\partial T} \]  \hspace{1cm} (4-2)

Equation 4-2 shows that the differential heat of mixing can be calculated from the temperature variation of the activity coefficients.

The partial molar heats of mixing for acetone-water, ethanol-water binaries at 30°C are listed in Tables 4 and 5. The method of calculation is discussed in Chapter 6.

(3) Effect of Temperature on Activity Coefficients. The heat-of-mixing data obtained in the experiments were used to calculate the temperature dependence of the activity coefficients. This was done by graphically integrating the right hand side of the equation

\[ \ln \frac{\gamma_{i, T_2}}{\gamma_{i, T_1}} = -\int_{T_1}^{T_2} \left( \Delta H - x_i \frac{\partial (\Delta H)}{\partial x_i} \right) \frac{1}{RT^2} \, dT \] \hspace{1cm} (4-3)

The results are plotted as Figures 11, 12, 13, and 14. The results show that for endothermic systems the activity coefficients decrease with an increase in temperature and for exothermic systems the activity coefficients increase with increasing temperature.
Table IV.
Partial Molar Heats of Mixing, Cal/g-mole
System of Acetone-Water Binary at 30°C
1 = Acetone, 2 = Water

<table>
<thead>
<tr>
<th>$x_1$</th>
<th>$\bar{H}_1 - H_1^0$</th>
<th>$\bar{H}_2 - H_2^0$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1</td>
<td>-780</td>
<td>-60</td>
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<tr>
<td>0.2</td>
<td>-105</td>
<td>-165</td>
</tr>
<tr>
<td>0.3</td>
<td>120</td>
<td>-235</td>
</tr>
<tr>
<td>0.4</td>
<td>225</td>
<td>-280</td>
</tr>
<tr>
<td>0.5</td>
<td>235</td>
<td>-290</td>
</tr>
<tr>
<td>0.6</td>
<td>215</td>
<td>-265</td>
</tr>
<tr>
<td>0.7</td>
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<td>-225</td>
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<td>0.8</td>
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<td>-175</td>
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<tr>
<td>0.9</td>
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</table>
Table V.
Partial Molar Heats of Mixing, Cal/g-mole
System of Ethanol-Water Binary at 30°C
1 = Ethanol, 2 = Water

<table>
<thead>
<tr>
<th>$x_1$</th>
<th>$\bar{H}_1 - H_1^o$</th>
<th>$\bar{H}_2 - H_2^o$</th>
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</thead>
<tbody>
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<td>0.1</td>
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<td>-245</td>
</tr>
<tr>
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<td>-245</td>
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<tr>
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</tr>
<tr>
<td>0.7</td>
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</tr>
<tr>
<td>0.8</td>
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<td>-165</td>
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<tr>
<td>0.9</td>
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</table>
Fig. 11. Effect of Temperature on Activity Coefficients

Methanol-benzene

Temperature, °C

\[ \frac{\chi_{CH_3OH} - T_x}{\chi_{CH_3OH} - CT_x} \]
Fig. 12. Effect of Temperature on Activity Coefficients

Methanol-water
Fig. 13. Effect of Concentration on Activity Coefficients

Methanol-benzene
Fig. 14. Effect of Concentration on Activity Coefficients

Methanol-water

\[ \frac{y_{\text{CH}_3\text{OH}}}{y_{\text{CH}_3\text{OH}}, 30^\circ C} \]

\[ \begin{array}{cccc}
0.1 & 0.2 & 0.3 & 0.4 \\
0.98 & 0.99 & 1.01 & 1.04 \\
\end{array} \]
(4) The Gibbs free energies of mixing and entropies of mixing for ethanol-water, acetone-water binaries at 30°C are listed in Tables 6, 7, 8, and 9 and Figures 15, 16, 17, and 18. The calculations of $\Delta G$'s and $(\bar{G}_i - G_i^\circ)$'s are discussed in Chapter 5. $T^\circ S$ is calculated by $T^\circ S = \Delta H - \Delta G$. The calculation of $(\bar{S}_i - S_i^\circ)$'s is discussed in Chapter 6.
### Table VI.
Partial Molar Free Energies of Mixing, Cal/g-mole  
System of Ethanol-Water Binary at 30°C  
1 = Ethanol, 2 = Water

<table>
<thead>
<tr>
<th>$x_1$</th>
<th>$\bar{G}_1 - G_1^\circ$</th>
<th>$\bar{G}_2 - G_2^\circ$</th>
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</thead>
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<td>0.3</td>
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</tr>
<tr>
<td>0.4</td>
<td>-305</td>
<td>-145</td>
</tr>
<tr>
<td>0.5</td>
<td>-305</td>
<td>-145</td>
</tr>
<tr>
<td>0.6</td>
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<td>-235</td>
</tr>
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<td>0.7</td>
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</tr>
<tr>
<td>0.8</td>
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<td>-530</td>
</tr>
<tr>
<td>0.9</td>
<td>-30</td>
<td>-1170</td>
</tr>
</tbody>
</table>
Table VII.
Partial Molar Free Energies of Mixing, Cal/g-mole
System of Acetone-Water Binary at 30°C

1 = Acetone, 2 = Water

<table>
<thead>
<tr>
<th>$x_1$</th>
<th>$\bar{G}_1 - G_1^\circ$</th>
<th>$\bar{G}_2 - G_2^\circ$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1</td>
<td>-390</td>
<td>-20</td>
</tr>
<tr>
<td>0.2</td>
<td>-225</td>
<td>-45</td>
</tr>
<tr>
<td>0.3</td>
<td>-190</td>
<td>-55</td>
</tr>
<tr>
<td>0.4</td>
<td>-170</td>
<td>-60</td>
</tr>
<tr>
<td>0.5</td>
<td>-235</td>
<td>-5</td>
</tr>
<tr>
<td>0.6</td>
<td>-220</td>
<td>-45</td>
</tr>
<tr>
<td>0.7</td>
<td>-140</td>
<td>-190</td>
</tr>
<tr>
<td>0.8</td>
<td>-70</td>
<td>-410</td>
</tr>
<tr>
<td>0.9</td>
<td>-20</td>
<td>-685</td>
</tr>
</tbody>
</table>
Table VIII.
Partial Molar Entropies of Mixing, Cal/(g-mole)(°K)
System of Ethanol-Water Binary at 30°C
l = Ethanol, 2 = Water

<table>
<thead>
<tr>
<th>x₁</th>
<th>T(\bar{S}_1 - S^o₁)</th>
<th>T(\bar{S}_2 - S^o₂)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.09</td>
<td>-25</td>
<td>-25</td>
</tr>
<tr>
<td>0.2</td>
<td>310</td>
<td>-80</td>
</tr>
<tr>
<td>0.3</td>
<td>380</td>
<td>-100</td>
</tr>
<tr>
<td>0.4</td>
<td>380</td>
<td>-100</td>
</tr>
<tr>
<td>0.5</td>
<td>330</td>
<td>-55</td>
</tr>
<tr>
<td>0.6</td>
<td>285</td>
<td>0</td>
</tr>
<tr>
<td>0.74</td>
<td>190</td>
<td>190</td>
</tr>
<tr>
<td>0.8</td>
<td>135</td>
<td>365</td>
</tr>
<tr>
<td>0.9</td>
<td>50</td>
<td>720</td>
</tr>
</tbody>
</table>
Table IX.

Partial Molar Entropies of Mixing, Cal/(g-mole)(°K)

System of Acetone-Water Binary at 30°C

1 = Acetone, 2 = Water

<table>
<thead>
<tr>
<th>$x_1$</th>
<th>$T(\bar{S}_1 - S^*_1)$</th>
<th>$T(\bar{S}_2 - S^*_2)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1</td>
<td>-390</td>
<td>-40</td>
</tr>
<tr>
<td>0.2</td>
<td>120</td>
<td>-120</td>
</tr>
<tr>
<td>0.3</td>
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<td>-180</td>
</tr>
<tr>
<td>0.4</td>
<td>395</td>
<td>-220</td>
</tr>
<tr>
<td>0.5</td>
<td>470</td>
<td>-285</td>
</tr>
<tr>
<td>0.6</td>
<td>435</td>
<td>-220</td>
</tr>
<tr>
<td>0.7</td>
<td>330</td>
<td>-35</td>
</tr>
<tr>
<td>0.78</td>
<td>235</td>
<td>235</td>
</tr>
<tr>
<td>0.9</td>
<td>40</td>
<td>1300</td>
</tr>
</tbody>
</table>
Fig. 15. Gibbs Free Energy of Mixing
Ethanol-Water Binary at 30°C
Fig. 16. Gibbs Free Energy of Mixing
Acetone-Water Binary at 30°C
Fig. 17. Entropy of Mixing
Ethanol-Water Binary at 30° C
Fig. 18. Entropy of Mixing
Acetone-Water Binary at 30°C
CHAPTER V
PREDICTION OF MOLAR GIBBS FREE ENERGY

It has long been an existing fact that the absolute values of energy properties, \( G \) (Gibbs free energy), \( H \) (enthalpy), \( A \) (Helmholtz free energy), \( U \) (internal energy) are never known. Fortunately the difference in these properties are sufficient for various thermodynamic manipulations either in science or in engineering. However, the lack of knowledge concerning the intrinsic characteristics of these properties causes difficulties in theoretical studies of molecular behavior. In the following, an attempt is made to calculate the absolute quantity of molar Gibbs free energy. Then the other properties, mainly \( A, H, U \), may be obtained from corresponding thermodynamic relations. It is hoped that in the future this will aid in the formulation of partition function of molecular energies, correlation of thermodynamic properties, studies in intermolecular forces and so forth.

**Gibbs Duhem Equation.** The Gibbs function is a natural function of the variables \( T, P, x_1, x_2, \ldots, x_n \) and is particularly convenient in the analysis of problems involving constant temperature and pressure, especially when dealing with thermodynamic problems which concern phase or chemical equilibrium.
By definition, for a binary mixture

\[ G = G(T, P, x_1, x_2) \]  \hspace{1cm} (5-1)

Total differentiation yields

\[
dG = \left( \frac{\partial G}{\partial x_1} \right)_T \rho_1 x_2 \, dx_1 + \left( \frac{\partial G}{\partial x_2} \right)_T \rho_1 x_1 \, dx_2 \\
+ \left( \frac{\partial G}{\partial T} \right)_P \rho_1 x_1 x_2 \, dT + \left( \frac{\partial G}{\partial \rho} \right)_T \rho_1 x_1 x_2 \, d\rho
\]

\[ = \bar{G}_1 \, dx_1 + \bar{G}_2 \, dx_2 - S \, dT + \nu \, d\rho \]  \hspace{1cm} (5-2)

For the condition of constant \( T, P \), equation 5-2 becomes

\[ dG = \bar{G}_1 \, dx_1 + \bar{G}_2 \, dx_2 \]  \hspace{1cm} (5-3)

From Euler's theorem\(^{26}\)

\[ G = x_1 \bar{G}_1 + x_2 \bar{G}_2 \]  \hspace{1cm} (5-4)

Upon total differentiation we find that

\[ dG = \bar{G}_1 \, dx_1 + \bar{G}_2 \, dx_2 + x_1 \, d\bar{G}_1 + x_2 \, d\bar{G}_2 \]  \hspace{1cm} (5-5)

Combining equations 5-3 and 5-5 we obtain an important

relation known as Gibbs Duhem equation

\[ x_1 d\bar{G}_1 + x_2 d\bar{G}_2 = 0 \]  \hspace{1cm} (5-6)

**Partial Molar Gibbs Free Energy.** The Gibbs free energy of mixing may be written as

\[ \Delta G = G - x_1 G_1^o - x_2 G_2^o \]

\[ = x_1 (\bar{G}_1 - G_1^o) + x_2 (\bar{G}_2 - G_2^o) \]  \hspace{1cm} (5-7)

where \( G \) is the total Gibbs free energy of the mixture, \( \bar{G}_1 \) and \( \bar{G}_2 \) are the partial Gibbs free energy of component 1 and 2 respectively, and \( G_1^o \) and \( G_2^o \) are molar Gibbs free energy of pure 1 and pure 2 respectively. \( \bar{G}_1 - G_1^o \) and \( \bar{G}_2 - G_2^o \) are termed the partial molar Gibbs free energy of mixing per mole of 1 and 2 respectively.

By differentiating equation 5-7 with respect to \( x_1 \) noting \( x_2 = 1 - x_1 \), we find that

\[ \frac{\partial (\Delta G)}{\partial x_1} = (\bar{G}_1 - G_1^o) - (\bar{G}_2 - G_2^o) + x_1 \frac{\partial \bar{G}_1}{\partial x_1} + x_2 \frac{\partial \bar{G}_2}{\partial x_1} \]  \hspace{1cm} (5-8)

Combining equations 5-6 and 5-8 we obtain

\[ \frac{\partial (\Delta G)}{\partial x_1} = (\bar{G}_1 - G_1^o) - (\bar{G}_2 - G_2^o) \]  \hspace{1cm} (5-9)

Now with reference to Figure 19, AFC is a curve of \( \Delta G \) vs. \( x_1 \), and DG is a tangent line at F. Eliminating \( (\bar{G}_1 - G_1^o) \) between equations 5-7 and 5-9, we see that
Fig. 19. Graphical Interpretation of Partial Molar Gibbs Free Energies
\[ x_1 (\bar{G}_2 - G^o_1) + x_2 (\bar{G}_2 - G^o_2) = \Delta G = x_1 \frac{\partial (\Delta G)}{\partial x_1} \]

or
\[
\bar{G}_2 - G^o_1 = \Delta G - x_1 \frac{\partial (\Delta G)}{\partial x_1} = FB - AB \frac{FE}{ED} = FB - FE = DA . \tag{5-10}
\]

Similarly
\[
\bar{G}_1 - G^o_1 = GC . \tag{5-11}
\]

Thus, the values of the partial molar Gibbs free energy relative to the molar Gibbs free energy are given by the intercepts of a tangent line at \( x_1 = 0 \) and \( x_1 = 1.0 \) from a curve of \( \Delta G \) vs. \( x_1 \).

**Prediction of Molar Gibbs Free Energy.** The procedure for obtaining the absolute molar Gibbs free energy is best explained with actual numerical calculations on ethanol-water binary mixture at 20°C. The useful equations are equations 5-3, 5-4, 5-6, 5-10, and 5-11.

(1) \( \Delta G \). Table 10 lists the vapor pressure data on ethanol-water mixture at 20°C obtained from the literature. These are converted into activity coefficients using

---

Table X.
Partial Pressures and Activity Coefficients of
Ethanol-Water Binary System at 20°C

<table>
<thead>
<tr>
<th>x(ethanol)</th>
<th>x(water)</th>
<th>p(ethanol)</th>
<th>p(water)</th>
<th>γ_\text{ethanol}</th>
<th>γ_\text{water}</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>1.0</td>
<td>0.0</td>
<td>17.5</td>
<td>1.0</td>
<td>1.0</td>
</tr>
<tr>
<td>0.0416</td>
<td>0.9584</td>
<td>6.7</td>
<td>16.8</td>
<td>3.7</td>
<td>1.0</td>
</tr>
<tr>
<td>0.089</td>
<td>0.911</td>
<td>12.6</td>
<td>15.9</td>
<td>3.25</td>
<td>1.0</td>
</tr>
<tr>
<td>0.143</td>
<td>0.857</td>
<td>17.1</td>
<td>15.1</td>
<td>2.74</td>
<td>1.008</td>
</tr>
<tr>
<td>0.207</td>
<td>0.793</td>
<td>20.7</td>
<td>14.7</td>
<td>2.295</td>
<td>1.06</td>
</tr>
<tr>
<td>0.281</td>
<td>0.719</td>
<td>23.5</td>
<td>14.5</td>
<td>1.82</td>
<td>1.15</td>
</tr>
<tr>
<td>0.37</td>
<td>0.63</td>
<td>25.6</td>
<td>14.1</td>
<td>1.59</td>
<td>1.28</td>
</tr>
<tr>
<td>0.476</td>
<td>0.524</td>
<td>28.0</td>
<td>13.1</td>
<td>1.35</td>
<td>1.43</td>
</tr>
<tr>
<td>0.61</td>
<td>0.39</td>
<td>31.2</td>
<td>11.3</td>
<td>1.173</td>
<td>1.655</td>
</tr>
<tr>
<td>0.779</td>
<td>0.221</td>
<td>35.8</td>
<td>7.5</td>
<td>1.053</td>
<td>1.84</td>
</tr>
<tr>
<td>0.9504</td>
<td>0.0496</td>
<td>42.3</td>
<td>1.9</td>
<td>1.02</td>
<td>2.19</td>
</tr>
<tr>
<td>1.0</td>
<td>0.0</td>
<td>43.6</td>
<td>0.0</td>
<td>1.0</td>
<td>1.0</td>
</tr>
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</table>
Table XI.

Partial Pressures and Activity Coefficients of Acetone-Water Binary System at 30°C

<table>
<thead>
<tr>
<th>$x_{\text{water}}$</th>
<th>$x_{\text{acetone}}$</th>
<th>$P_{\text{water}}$ mm.Hg.</th>
<th>$P_{\text{acetone}}$ mm.Hg.</th>
<th>$\gamma_{\text{water}}$</th>
<th>$\gamma_{\text{acetone}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.0</td>
<td>0.0</td>
<td>31</td>
<td>0</td>
<td>1.0</td>
<td>5.02</td>
</tr>
<tr>
<td>0.9667</td>
<td>0.0333</td>
<td>34</td>
<td>47</td>
<td>1.135</td>
<td>4.75</td>
</tr>
<tr>
<td>0.928</td>
<td>0.072</td>
<td>34</td>
<td>96</td>
<td>1.182</td>
<td>4.07</td>
</tr>
<tr>
<td>0.883</td>
<td>0.117</td>
<td>30</td>
<td>134</td>
<td>1.097</td>
<td>4.07</td>
</tr>
<tr>
<td>0.829</td>
<td>0.171</td>
<td>34</td>
<td>157</td>
<td>1.321</td>
<td>3.27</td>
</tr>
<tr>
<td>0.764</td>
<td>0.236</td>
<td>29</td>
<td>182</td>
<td>1.223</td>
<td>2.745</td>
</tr>
<tr>
<td>0.682</td>
<td>0.318</td>
<td>35</td>
<td>189</td>
<td>1.656</td>
<td>2.115</td>
</tr>
<tr>
<td>0.58</td>
<td>0.42</td>
<td>29</td>
<td>205</td>
<td>1.61</td>
<td>1.74</td>
</tr>
<tr>
<td>0.446</td>
<td>0.554</td>
<td>20</td>
<td>225</td>
<td>1.45</td>
<td>1.445</td>
</tr>
<tr>
<td>0.263</td>
<td>0.737</td>
<td>21</td>
<td>236</td>
<td>2.57</td>
<td>1.14</td>
</tr>
<tr>
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<td>1.0</td>
<td>0</td>
<td>281</td>
<td>1.0</td>
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</tr>
</tbody>
</table>
and the results are listed in the same table as well as plotted as Figures 20 and 21. $\Delta G$'s are calculated by combining equations 1-42 and 1-77,

\[
\Delta G_{\text{ideal}} = RT \left( x_1 \ln x_1 + x_2 \ln x_2 \right),
\]

\[
\Delta G = \Delta G_{\text{non-ideal}} - \Delta G_{\text{ideal}} = RT \left( x_1 \ln \gamma_1 + x_2 \ln \gamma_2 \right)
\]

\[
\Delta G_{\text{non-ideal}} = \Delta G^E + \Delta G_{\text{ideal}}
\]

\[
= RT \left( x_1 \ln \gamma_1 x_1 + x_1 \ln \gamma_1 x_2 \right).
\]

Calculated values of $\Delta G$'s are listed in Table 12. Incidentally experimental data on heats of mixing from Figure 6 are also listed in the same table, whereby $T^S = \Delta H - \Delta G$ is calculated.

(2) $(\bar{G}_1 - G_1^0)$'s and $(\bar{G}_2 - G_2^0)$'s. These are the ordinate intercepts at $x_1 = 1.0$ and $x_1 = 0$ of the tangent lines from curve $\Delta G$ vs. $x_1$ as indicated by equations 5-10 and 5-11, and Figure 19. Numerical values are listed in Table 6.

(3) $G_1^0 - G_2^0$. $G_1^0$ and $G_2^0$ are the absolute values of molar Gibbs free energy of pure component 1 and pure component 2, where 1 is ethanol and 2 is water. Prior
Fig. 20. Activity Coefficient
Ethanol-Water Binary at 20°C
Fig. 21. Activity Coefficient
Acetone-Water Binary at 30°C
Table XII.
Calculation of Gibbs Free Energy Changes, cal/g-mole sol'n
System of Ethanol-Water Binary at 30°C
1 = C₂H₅OH, 2 = H₂O

<table>
<thead>
<tr>
<th>x₁</th>
<th>γ₁</th>
<th>x₁γ₁</th>
<th>ln x₁γ₁</th>
<th>x₁ ln x₁γ₁</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1</td>
<td>3.2</td>
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<td>-1.13944</td>
<td>-0.113944</td>
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<td>0.2</td>
<td>2.3</td>
<td>0.46</td>
<td>-0.77653</td>
<td>-0.155306</td>
</tr>
<tr>
<td>0.3</td>
<td>1.8</td>
<td>0.54</td>
<td>-0.61619</td>
<td>-0.184857</td>
</tr>
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<td>0.4</td>
<td>1.5</td>
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<tr>
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<tr>
<td>0.6</td>
<td>1.2</td>
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<td>-0.32851</td>
<td>-0.197106</td>
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<td>0.7</td>
<td>1.1</td>
<td>0.77</td>
<td>-0.26137</td>
<td>-0.182959</td>
</tr>
<tr>
<td>0.8</td>
<td>1.03</td>
<td>0.824</td>
<td>-0.19359</td>
<td>-0.154872</td>
</tr>
<tr>
<td>0.9</td>
<td>1.01</td>
<td>0.909</td>
<td>-0.09542</td>
<td>-0.085878</td>
</tr>
<tr>
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<td>1.0</td>
<td>1.0</td>
<td>0.00000</td>
<td>0.00000</td>
</tr>
</tbody>
</table>
### Table XII
Calculation of Gibbs Free Energy Changes, cal/g-mole sol'n
System of Ethanol-Water Binary at 30°C

\[ l = C_2H_5OH, \quad 2 = H_2O \]

(Continued)

<table>
<thead>
<tr>
<th>( x_2 )</th>
<th>( \gamma_1 )</th>
<th>( x_1 \gamma_1 )</th>
<th>( \ln x_1 \gamma_1 )</th>
<th>( x_1 \ln x_1 \gamma_1 )</th>
<th>( x_1 \ln x_1 \gamma_1 + x_2 \ln x_2 \gamma_2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.9</td>
<td>1.0</td>
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<td>-0.206777</td>
</tr>
<tr>
<td>0.8</td>
<td>1.06</td>
<td>0.848</td>
<td>-0.16488</td>
<td>-0.131904</td>
<td>-0.287210</td>
</tr>
<tr>
<td>0.7</td>
<td>1.18</td>
<td>0.826</td>
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<td>-0.318676</td>
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<td>0.6</td>
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<td>-0.344252</td>
</tr>
<tr>
<td>0.5</td>
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<td>-0.30789</td>
<td>-0.153945</td>
<td>-0.369340</td>
</tr>
<tr>
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<td>0.64</td>
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<td>-0.375622</td>
</tr>
<tr>
<td>0.3</td>
<td>1.7</td>
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<td>-0.384964</td>
</tr>
<tr>
<td>0.2</td>
<td>1.9</td>
<td>0.38</td>
<td>-0.96759</td>
<td>-0.193518</td>
<td>-0.348390</td>
</tr>
<tr>
<td>0.1</td>
<td>2.2</td>
<td>0.22</td>
<td>-1.51413</td>
<td>-0.151413</td>
<td>-0.237291</td>
</tr>
<tr>
<td>0.0</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Table XII.
Calculation of Gibbs Free Energy Changes, cal/g-mole soln
(Continued)
System of Ethanol–Water Binary at 30°C

<table>
<thead>
<tr>
<th>( \chi_{\text{ethanol}} )</th>
<th>( \Delta G = \frac{RT \sum x_i \ln \gamma_i x_i}{4} )</th>
<th>( \Delta H )</th>
<th>( T \Delta S = \Delta H - \Delta G )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1</td>
<td>-125.8</td>
<td>-150</td>
<td>-24.2</td>
</tr>
<tr>
<td>0.2</td>
<td>-173</td>
<td>-175</td>
<td>-2</td>
</tr>
<tr>
<td>0.3</td>
<td>-192</td>
<td>-147</td>
<td>45</td>
</tr>
<tr>
<td>0.4</td>
<td>-207.5</td>
<td>-115</td>
<td>92.5</td>
</tr>
<tr>
<td>0.5</td>
<td>-222.5</td>
<td>-87</td>
<td>135.5</td>
</tr>
<tr>
<td>0.6</td>
<td>-226</td>
<td>-65</td>
<td>161</td>
</tr>
<tr>
<td>0.7</td>
<td>-232</td>
<td>-45</td>
<td>187</td>
</tr>
<tr>
<td>0.8</td>
<td>-210</td>
<td>-29</td>
<td>181</td>
</tr>
<tr>
<td>0.9</td>
<td>-143</td>
<td>-12</td>
<td>131</td>
</tr>
</tbody>
</table>
### Table XIII.

Calculation of Gibbs Free Energy Changes, cal/g-mole sol'n

System of Acetone-Water Binary at 30°C

\( l = H_2O, \ 2 = CH_3COCH_3 \)

<table>
<thead>
<tr>
<th>( x_i )</th>
<th>( \gamma_i )</th>
<th>( x_i \gamma_i )</th>
<th>( \ln x_i \gamma_i )</th>
<th>( x_i \ln x_i \gamma_i )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1</td>
<td>3.05</td>
<td>0.305</td>
<td>-1.18745</td>
<td>-0.118745</td>
</tr>
<tr>
<td>0.2</td>
<td>2.6</td>
<td>0.52</td>
<td>-0.65393</td>
<td>-0.130786</td>
</tr>
<tr>
<td>0.3</td>
<td>2.2</td>
<td>0.66</td>
<td>-0.41552</td>
<td>-0.124656</td>
</tr>
<tr>
<td>0.4</td>
<td>1.9</td>
<td>0.76</td>
<td>-0.27444</td>
<td>-0.109776</td>
</tr>
<tr>
<td>0.5</td>
<td>1.8</td>
<td>0.90</td>
<td>-0.10537</td>
<td>-0.052685</td>
</tr>
<tr>
<td>0.6</td>
<td>1.55</td>
<td>0.930</td>
<td>-0.07258</td>
<td>-0.043548</td>
</tr>
<tr>
<td>0.7</td>
<td>1.35</td>
<td>0.945</td>
<td>-0.05658</td>
<td>-0.039606</td>
</tr>
<tr>
<td>0.8</td>
<td>1.2</td>
<td>0.96</td>
<td>-0.04083</td>
<td>-0.032664</td>
</tr>
<tr>
<td>0.9</td>
<td>1.1</td>
<td>0.99</td>
<td>-0.01006</td>
<td>-0.009054</td>
</tr>
</tbody>
</table>
Table XIII.
Calculation of Gibbs Free Energy Changes, cal/g-mole sol'n
System of Acetone-Water Binary at 30°C
1 = H₂O, 2 = CH₃COCH₃
(Continued)

<table>
<thead>
<tr>
<th>x_1</th>
<th>y_1</th>
<th>x_1 y_1</th>
<th>ln x_1 y_1</th>
<th>x_1 ln x_1 y_1</th>
<th>x_1 ln x_1 y_1 + x_1 ln y_1</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.9</td>
<td>1.08</td>
<td>0.972</td>
<td>-0.02840</td>
<td>-0.025560</td>
<td>-0.144305</td>
</tr>
<tr>
<td>0.8</td>
<td>1.1</td>
<td>0.88</td>
<td>-0.12784</td>
<td>-0.102272</td>
<td>-0.233058</td>
</tr>
<tr>
<td>0.7</td>
<td>1.2</td>
<td>0.84</td>
<td>-0.17436</td>
<td>-0.121052</td>
<td>-0.245708</td>
</tr>
<tr>
<td>0.6</td>
<td>1.32</td>
<td>0.792</td>
<td>-0.23320</td>
<td>-0.139920</td>
<td>-0.249696</td>
</tr>
<tr>
<td>0.5</td>
<td>1.5</td>
<td>0.75</td>
<td>-0.28769</td>
<td>-0.143845</td>
<td>-0.196530</td>
</tr>
<tr>
<td>0.4</td>
<td>1.8</td>
<td>0.72</td>
<td>-0.32851</td>
<td>-0.131404</td>
<td>-0.174952</td>
</tr>
<tr>
<td>0.3</td>
<td>2.25</td>
<td>0.675</td>
<td>-0.39305</td>
<td>-0.117915</td>
<td>-0.157521</td>
</tr>
<tr>
<td>0.2</td>
<td>3.0</td>
<td>0.6</td>
<td>-0.51083</td>
<td>-0.102166</td>
<td>-0.134830</td>
</tr>
<tr>
<td>0.1</td>
<td>4.3</td>
<td>0.43</td>
<td>-0.84397</td>
<td>-0.084397</td>
<td>-0.093451</td>
</tr>
</tbody>
</table>
Table XIII.
Calculation of Gibbs Free Energy Changes, "a!g-mole solu"

(Continued)
System of Acetone-Water Binary at 30°C

<table>
<thead>
<tr>
<th>$x_{\text{water}}$</th>
<th>$\Delta G = kT \sum x_i \ln \gamma_i x_i$</th>
<th>$\Delta H$</th>
<th>$\frac{\Delta S}{\Delta H - \Delta G}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1</td>
<td>-87</td>
<td>84</td>
<td>171</td>
</tr>
<tr>
<td>0.2</td>
<td>-140.2</td>
<td>92</td>
<td>232.2</td>
</tr>
<tr>
<td>0.3</td>
<td>-147.8</td>
<td>65</td>
<td>212.8</td>
</tr>
<tr>
<td>0.4</td>
<td>-150.3</td>
<td>25</td>
<td>175.3</td>
</tr>
<tr>
<td>0.5</td>
<td>-118.2</td>
<td>-28</td>
<td>90.2</td>
</tr>
<tr>
<td>0.6</td>
<td>-105.3</td>
<td>-78</td>
<td>27.3</td>
</tr>
<tr>
<td>0.7</td>
<td>-94.8</td>
<td>-120</td>
<td>-25.2</td>
</tr>
<tr>
<td>0.8</td>
<td>-81.2</td>
<td>-150</td>
<td>-68.8</td>
</tr>
<tr>
<td>0.9</td>
<td>-56.3</td>
<td>-130</td>
<td>-73.7</td>
</tr>
</tbody>
</table>
to the present time they have never been known. However, by rigorous thermodynamic equations, \( G_1^o - G_2^o \) may first be calculated, then by a geometric manipulation \( G_1^o \) and \( G_2^o \) are calculated.

From equation 5-6

\[
\frac{d G_1}{d x_1} = -\frac{x_2}{x_1} d G_2 \quad , \quad (5-6)
\]

or

\[
\frac{d \bar{G}_1}{d \bar{G}_2} = -\frac{x_1}{x_2} \quad . \quad (5-12)
\]

Rewriting equation 5-3 noting \( dx_2 = -dx_1 \),

\[
d\bar{G} = \bar{G}_1 dx_1 + \bar{G}_2 dx_2 = (\bar{G}_1 - \bar{G}_2) dx_1 \quad ,
\]

or

\[
\frac{d \bar{G}}{d x_1} = \frac{\bar{G}_1 - \bar{G}_2}{x_2} \quad . \quad (5-13)
\]

The number \(-x_2/x_1\) in equation 5-12 is the slope of a line which is tangent to the curve of \( \bar{G}_1 \) vs. \( \bar{G}_2 \). Similarly, the quantity \( \bar{G}_1 - \bar{G}_2 \) in equation 5-13 is the slope of a line which is tangent to the curve of \( \bar{G} \) vs. \( x_1 \). Both lines correspond to a particular composition of \( x_1 \). Now suppose \( x_1' = 0.4, x_1'' = 0.6, x_1''' = 0.8, x_2 = 0.2 \) are any two chosen points, then with reference to Figures 22 and 23, we proceed as follows:
(3-a) Concerning Figure 22,
slope of line \( AB = \frac{x_i'}{x_i} = -0.6/0.4 = -3/2 \)
\( AO/BO = 3/2 \)
\( AO/AB = 3/\sqrt{13} \)
from Figure 15
\( G_i' - G_i^* = -305 \)
or \( G_i' = G_i^* - 305 \)
\( G_i'' - G_i^* = -145 \)
or \( G_i'' = G_i^* - 145 \)
slope of line \( CD = \frac{x_j''}{x_j'} = -0.2/0.8 = -1/4 \)
\( CO/DO = 1/4 \)
\( CO/CD = 1/\sqrt{17} \)
from Figure 15
\( G_i'' - G_i^* = -130 \)
or \( G_i'' = G_i^* - 130 \)
\( G_i'' - G_i^* = -530 \)
or \( G_i'' = G_i^* - 530 \)
\( AG_i'/G_i'0 = 3/2 \)
or \( AG_i' = (3/2) G_i'0 \)
\( AO = AG_i' + G_i'0 = (3/2) G_i'0 + G_i' \)
\begin{align*}
&= (3/2) (G_i^* - 145) + G_i^* - 305 \\
&= (3/2) G_i^* + G_i^* - 1045/2
\end{align*}
\( CG_i''/G_i''0 = 1/4 \)
or \( CG_i'' = (1/4) G_i''0 \)
Fig. 22. Geometrical Interpretation

Used in the Calculation of $G_i^0 - G_i^1$
\[ \theta_0 = \theta_1^* + \theta_2^* \theta_0 = (1/4) \theta_3^* + \theta_2^* \]
\[ = (1/4) (G_2^o - 530) + G_1^o - 130 \]
\[ = (1/4) G_2^o + G_1^o - 1050/4 \]

line AB may be written as
\[ Y' = m'X' + b' \]
where \( m' = -3/2 \)
when \( X' = 0 \)
\[ Y' = b' = A_0 = (3/2) G_1^o + G_1^o - 1045/2 \]
thus \( Y' = (-3/2) X' + (3/2) G_1^o + G_1^o - 1045/2 \)

Similarly, for line CD
\[ Y'' = m''X'' + b'' \]
where \( m'' = -1/4 \)
when \( X'' = 0 \)
\[ Y'' = b'' = C_0 = (1/4) G_2^o + G_1^o - 1050/4 \]
thus \( Y'' = (-1/4) X'' + (1/4) G_2^o + G_1^o - 1050/4 \)

line AB intersects line CD at \( H \), therefore
at point \( H \)
\[ Y' = Y'' = Y \]
\[ X' = X'' = X \]

therefore \( (-3/2) X + (3/2) G_2^o + G_1^o - 1045/2 \)
\[ = (-1/4) X + (1/4) G_2^o + G_1^o - 1050/4 \]

after arranging and simplifying
\[ X = G_1^o - 208 \]
\[ = NO \]
substitute $X$ into $Y$

$$Y = M_0 = (-\frac{1}{4})G_1^o + 208/4 + (\frac{1}{4})G_2^o + G_i^o - 1050/4 = G_1^o - 421/2$$

(3-b) Concerning Figure 23,

$$\frac{df}{dx_i} = G_1 - G_2$$

line $G'_1x'_1$ may be written as

$$Y' = m'X' + b'$$

where $m' = \tilde{G}_1' - \tilde{G}_2'$

at $X' = 0$, $Y' = b' = G'$

$$= x'_1\tilde{G}_1' + x'_1\tilde{G}_2'$$

$$= 0.4\tilde{G}_1' + 0.6\tilde{G}_2'$$

thus $Y' = (\tilde{G}_1' - \tilde{G}_2')X' + 0.4\tilde{G}_1' + 0.6\tilde{G}_2'$

similarly, for line $G''x''$

$$Y'' = m''X'' + b''$$

where $m'' = \tilde{G}_1'' - \tilde{G}_2''$

at $X'' = 0$, $Y'' = b'' = G''$

$$= x''\tilde{G}_1'' + x''\tilde{G}_2''$$

$$= 0.8\tilde{G}_1'' + 0.2\tilde{G}_2''$$

thus $Y'' = (\tilde{G}_1'' - \tilde{G}_2'')X'' + 0.8\tilde{G}_1'' + 0.2\tilde{G}_2''$

line $G'_1x'_1$ intersects line $G''x''$ at $H$, therefore at point $H$

$$Y' = Y'' = Y$$

$$X' = X'' = X$$
Fig. 23 Geometrical Interpretation

Used in the Calculation of $G_0^*-G_1^*$
or \((G'_1 - G''_1)X + 0.4 G'_1 + 0.6 G''_1\)

\[= (G''_1 - G''_1)X + 0.8 G''_1 + 0.2 G''_1\]

or \((G^o_i - 305 - G^o_1 + 145)X\)

\[+ 0.4 (G^o_i - 305) + 0.6 (G^o_1 - 145)\]

\[= (G^o_i - 130 - G^o_1 + 530)X \]

\[+ 0.8 (G^o_i - 130) + 0.2 (G^o_1 - 530)\]

after rearranging and simplifying

\[X = -\frac{(0.4 G^o_i - 0.4 G^o_1 - 1)}{560}\]

\(X\) is equivalent to \(x''\) in Figure 23.

(3-a) Point H in Figure 22 and point H in Figure 23 are equivalent. Therefore there must be a point in Figure 22 with

\(\tilde{G}''_1 = G^o_2 - 208 = NO\)

having a slope equal to \(-x''/x''\)

From Figure 15, \(\tilde{G}''_1 = G^o_2 - 208\), or

\[\tilde{G}''_1 - G^o_2 = -208\]

corresponds to \(x'' = 0.57\).

This \(x''\) is equivalent to \(X\) in (3-b).

Therefore, \(-\frac{(0.4 G^o_i - 0.4 G^o_1 - 1)}{560}\)

\[= 0.57\]

or, \(G^o_1 - G^o_1 = 795.5\)

(4) \(G^o_i\) and \(G^o_1\). With reference to Figure 24, we rewrite information obtained in (2) and (3-a).

First take any point, say \(x_1 = 0.4, x_2 = 0.6\), we have
Fig. 24 Geometrical Interpretation
Used in the Calculation of $\gamma_1^o$ and $\gamma_2^o$
\[ G_1 - G^* = -305 \]
\[ G_2 - G^* = -145 \]
\[ G_2^* - G_1^* = 795.5 \]

the above three relations lead to
\[ \bar{G}_1 - \bar{G}_2 = -955.5 \]

Now, concerning Figure 24,

the slope of line AB = \(-x_1/x_2 = -0.4/0.6\)
\[ = -2/3 \]

\[ \frac{AG_2}{\bar{G}_1 T} = 2/3 \]
\[ \frac{AG_1}{\bar{G}_1 T} = (2/3) \bar{G}_1 T = (2/3) \bar{G}_1 = (2/3)(\bar{G}_1 - 955.5) \]

\[ \frac{AP}{PQ} = 2/3, \text{ or } PQ = (3/2)AP \]

\[ AP = G_1^* P - G_1^* \bar{G}_1 + AG_1 \]
\[ = G_1^* P - (G_1^* 0 - \bar{G}_1 0) + AG_1 \]
\[ = G_1^* P - (G_1^* - \bar{G}_1) + AG_1 \]
\[ = G_1^* P - 145 + (2/3)(\bar{G}_1 - 955.5) \]
\[ = G_1^* P + (2/3) \bar{G}_1 - 2346/2 \]

\[ TG_1 / \bar{G}_1 T = 2/3 \]
also \[ TG_1 / \bar{G}_1 T = \bar{G}_0 / (G_1^* - G_1 - BG_1^* ) \]
\[ = \bar{G}_1 / (G_1^* - \bar{G}_1 + BG_1^* ) \]
\[ = \bar{G}_1 / (305 + BG_1^* ) \]
\[ = 2/3 \]

rearranging, \[ BG_1^* = (3/2) \bar{G}_1 - 305 \]
\[ G_1^* A = G_1^* \bar{G}_1 - AG_1 \]
\[ = G_1^* 0 - \bar{G}_1 0 - AG_1 \]
\[ = G_1^* - \bar{G}_1 - (2/3)(\bar{G}_1 - 955.5) \]
\[\begin{align*}
&= 145 - \left(\frac{2}{3}\right) (\bar{G}_2 - 955.5) \\
&= - \left(\frac{2}{3}\right) \bar{G}_2 + \frac{2346}{3}
\end{align*}\]

\[SG_1^\circ/\mathcal{B}G_1^\circ = \frac{2}{3}\]

\[SG_1^\circ/\mathcal{B}G_1^\circ = SG_1^\circ/\left[\left(\frac{3}{2}\right) \bar{G}_2 - 305\right]\]

\[= \frac{2}{3}\]

after rearranging, \(SG_1^\circ = \bar{G}_2 - \frac{610}{3}\)

Now, \(\Delta QAG_2^\circ \cap \Delta QSG_1^\circ\)

therefore, \(G_1^\circ Q/G_1^\circ Q = AG_2^\circ /SG_1^\circ\)

\[= -\left(\frac{2}{3}\right) \bar{G}_2 + \frac{2346}{3}\]

\[\bar{G}_2 - \frac{610}{3}\]

also \(\Delta \bar{G}_1^\circ OG_1^\circ \cap \Delta \bar{G}_1^\circ PQ\)

therefore, \(G_1^\circ Q/G_1^\circ P = G_1^\circ G_1^\circ Q/G_1^\circ Q\)

or \(G_1^\circ Q/G_1^\circ P = (G_1^\circ Q + QG_1^\circ )/G_1^\circ Q\)

\[= 1 + G_1^\circ Q/G_1^\circ Q\]

\[= 1 + (\bar{G}_2 - \frac{610}{3}) = \left(\left(-\frac{2}{3}\right) \bar{G}_2 + \frac{2346}{3}\right)\]

\[= (\bar{G}_2 + 1736)/(\left(-\frac{2}{3}\right) \bar{G}_2 + 2346)\]

thus,

\[G_1^\circ P = (\bar{G}_2 + 145)(\left(-\frac{2}{3}\right) \bar{G}_2 + 2346)/(\bar{G}_2 + 1736)\]

now, \(G_1^\circ Q/G_1^\circ Q = G_1^\circ P/PQ\)

\[= G_1^\circ P/((3/2) \left(G_1^\circ P + (2/3) \bar{G}_2 - 2346/2\right))\]
or, \(\frac{(\tilde{G}_2 + 145)}{\tilde{G}_2 + 200} = \frac{(\tilde{G}_2 + 145)(-2\tilde{G}_2 + 2346)}{(\tilde{G}_2 + 1736)}\)

\[
(3/2) \left[ (\tilde{G}_2 + 145)(-2\tilde{G}_2 + 2346)/(\tilde{G}_2 + 1736) + (2/3) \tilde{G}_2 - 2346/3 \right]
\]

rearranging, \(\frac{(3/2)}{(3/2)} (\tilde{G}_2 + 145)(-2\tilde{G}_2 + 2346) + (2\tilde{G}_2/3 - 2346/3)(\tilde{G}_2 + 1736)(\tilde{G}_2 + 145)\)

\(- (\tilde{G}_2 + 200)(\tilde{G}_2 + 145)(-2\tilde{G}_2 + 2346) = 0\)

and finally after simplifying, \((\tilde{G}_2 + 145)(-2\tilde{G}_2 + 2346)(-1701) = 0\)

therefore, \(\tilde{G}_2 = -145\), or \(\tilde{G}_2 = 1173\)

we reject the negative \(\tilde{G}_2\),

thus \(\tilde{G}_2 = 1173\)

then \(G^*_2 = \tilde{G}_2 + 145\)

\(= 1318\)

\(G^*_1 = G^*_2 - 795.5\)

\(= 1318 - 795.5\)

\(= 552.5\)

\(\tilde{G}_1 = G^*_1 - 305\)

\(= 522.5 - 305\)

\(= 217.5\)

\(\tilde{G}_1\) and \(\tilde{G}_2\) correspond to point \(x_1 = 0.4, x_2 = 0.6\)

of the curve, \(\Delta G\) vs. \(x_1\) (see Figure 15).

In the foregoing, the condition of constant temperature and pressure is imposed to derive the Gibbs Duhem equation. This is justified since the vapor pressure
data are always obtained under constant temperature and pressure condition. The result shows at 20°C and 1 atm., the molar Gibbs free energy is 1318 cal/g-mole for water and 522.5 cal/g-mole for ethyl alcohol.

By the same procedure, from system of acetone-water binary at 30°C and 1 atm., the molar Gibbs free energy is 1031 cal/g-mole for water and 260 cal/g-mole for acetone. Comparing \((\Delta_h^0)_{20^\circ C, 1 atm} = 1318\) cal/g-mole and \((\Delta_h^0)_{30^\circ C, 1 atm} = 1031\) cal/g-mole, we immediately see the results are in good agreement. It may be noted that the molar Gibbs free energy usually decreases as the temperature increases. The vapor pressure data on acetone-water binary are not very satisfactory as we can see from Figure 21 that the points on the \(\gamma vs. \) plot are widely scattered. Despite of this, the method developed still gives very satisfactory results.

**Energy Functions.** The properties \(G\) (Gibbs free energy), \(U\) (internal energy), \(H\) (enthalpy), and \(A\) (Helmholtz free energy or total work) are often designated as energy properties. Under certain conditions of restraint, changes in these properties represent useful works. These function may also be referred to as thermodynamic potentials and are useful for describing equilibrium phenomena under different conditions. For example, at constant volume
and temperature the criterion for an equilibrium process is

\[ \Delta A = 0 \]

Similarly, for equilibrium at constant \( S, P \),

\[ \Delta H = 0 \]

For equilibrium at constant \( V, S \),

\[ \Delta U = 0 \]

And as usual, for equilibrium at constant \( T, P \),

\[ \Delta G = 0 \]

Furthermore, for nonflow processes we may write:

- At constant volume, \( \Delta U = Q - W_f \)
- At constant pressure, \( \Delta H = Q - W_f \)
- For isothermal reversible process, \( \Delta A = -W_f - W_e \)
- For isothermal reversible process \( \Delta G = -W_f \)

\( W_e \) is the work of expansion done by the system and \( W_f \) is the useful work not including \( W_e \). Comparing \( \Delta U, \Delta H, \Delta A, \) and \( \Delta G \), we immediately find that \( \Delta A \) accompanying a reversible process at constant temperature represents the maximum total work available from the system. This is often measured by operating a reversible chemical cell such as a galvanic cell where chemical energy is converted into electrical energy by means of a controlled chemical reaction.

**The Third Law of Thermodynamics.** An important thermodynamic property termed entropy is an intrinsic
property of matter so defined that an increase in entropy quantitatively measures an increase in the unavailability of the total energy of a system. The Second Law of Thermodynamics postulate the existence of an entropy function. In the Third Law the behavior of entropy is discussed. The entropy of a system may arise in several different ways and each is termed as an "aspect of the system". The following includes some example:

(1) The entropy of a substance increases with increasing temperature and volume. Since entropy is a measure of unavailability of internal energy, the amount of work is less available at a higher temperature than a lower temperature. This may be seen from the fact that at higher temperatures there is more energy to be shared; more levels are accessible to each particle causing greater complexions. Thus more energy is "bound up" internally causing decrease in the availability of useful work. Therefore temperature is an "aspect" of the system.

(2) The entropy of spin system. The atoms of paramagnetic material have magnetic moments. These moments are in a random orientation in the absence of a magnetic field. When in the presence of a field, the magnetic moments tend to align themselves despite the disordering effect of the thermal motion. The result is to produce
a greater degree of order and thus the entropy of the system is decreased.

(3) The entropy of molecular motions. The entropy may also arise from the translational, vibrational, and rotational motions of molecules, and from molecular distribution among different electronic levels.

(4) The entropy of mixing. For an ideal solution, the entropy of mixing is

\[ \Delta S = -\sum x_i R \ln x_i \]

For a non-ideal solution, the entropy of mixing must be obtained indirectly from data on activity coefficients and heats of mixing using the equation

\[ \Delta G = \Delta H - T \Delta S \]

The Third Law states that "the contribution to the entropy of a system by each aspect which is in internal thermodynamic equilibrium tends to zero at absolute zero". From this statement, a generalization can be made that the specific heats of all substances approach zero at the absolute zero of temperature. This also is a well known experimental fact. An important consequence is the use of absolute zero as a reference state for all thermodynamic calculations.
The Unattainability of Absolute Zero. Nernst first pointed out that the Third Law implies that it is impossible to cool any system down to absolute zero in a finite number of processes. A most common method of producing low temperature is the liquefaction and evaporation of gases. It is possible to reach a temperature of about 0.35°K in this way using liquid 3He which has the lowest boiling point of all liquids. A favorable system to approach closely to the absolute zero is one in which the entropy is still appreciable at very low temperatures without any tendency of "frozen-in". An important example of such system is one whose nuclei have spin and magnetic moment exhibiting a nuclear paramagnetism similar in nature to the paramagnetism arising from the electron spin. It is said that by carrying out a adiabatic demagnetization (magnetic cooling) of a nuclear paramagnetic material such as a specimen of copper, a temperature of 2x10⁻⁶°K has been obtained. At this low temperature, the forces of interaction between the nuclear moments become appreciable to cause alignment of the nuclei hence the inability of further cooling.

It is interesting to imagine that the difference between \(10^{-1}\)°K and \(10^{-6}\)°K is somewhat similar to that between \(10^{6}\)°K and \(10^{9}\)°K.

**Absolute Values of Energy Functions.** From the concept of the Third Law, we may point out two important corollaries which may be combined with the concept of molar Gibbs free energy to calculate other energy properties. First, since for most substances the entropy vanishes at absolute zero\(^{29}\), the entropy of a substance

\(^{29}\). The entropies of some materials (e.g. glycerol, ice) do not vanish near absolute zero. However, this does not violate the Third Law. Because the viscosities of these materials at their transition temperatures (the temperatures at which liquids change into solids) have become so high that they cannot change their configuration in any reasonable time. Thus the spatial configuration is "frozen-in" as may be observed by X-ray studies. Therefore the measurements made in the normal way for specific heats do not reflect the actual situation. This also implies that the aspects of entropy for these materials are not in thermodynamic equilibrium, hence the Third Law can not be applied.
at other temperatures may be calculated by integrating the right hand side of equation

\[ S_T - S_0 = S_T = \int_0^T \frac{c dT}{T} \]

Numerical values of \( S_{298}^\circ \)'s have been measured and tabulated\(^{30, 31, 32}\). Secondly, since absolute zero is unattainable, the molar Gibbs free energy calculated by the method developed in this chapter is compatible with the molar entropy listed in the literature. Therefore these two quantities may be utilized in exact thermodynamic relations to derive other energy properties. The following calculation is based on 1 g-mole of water at 20°C and 1 atm.

(1) Enthalpy.

\[ T = 273.16 + 20 = 293.16^\circ K \]

\[ G_{H_2O,20^\circ C}^\circ = 1318 \text{ cal/g-mole} \]

---


\[ S_{\text{H}_2O, 25^\circ C} = 16.716 \text{ cal/(g-mole)} (°K) \]

from Steam Table\textsuperscript{33},

\[ S_{\text{H}_2O, 25^\circ C} - S_{\text{H}_2O, 0^\circ C} = 0.0376 - 0.0708 = 0.0068 \text{ Btu/(°F)(lb)} \]

\[ = 0.068 (252) (1.8) (18) / 453.6 = 0.1224 \text{ cal/(g-mole)(°K)} \]

Therefore, \[ S_{\text{H}_2O, 0^\circ C} = 16.716 - 0.1224 = 16.5936 \text{ cal/(g-mole)(°K)} \]

Now, \[ G = H - TS \]

or, \[ H = G + TS \]

\[ H_{\text{H}_2O, 0^\circ C} = 1318 + (293.16) (16.5936) = 4865 \text{ cal/g-mole} \]

From International Critical Table\textsuperscript{34}

\[ H_{\text{H}_2O, 198.1^\circ K} - H_{\text{H}_2O, 0^\circ K} = -269,300 - (-282,600) = 13,300 \text{ joules/g-mole} \]

\[ = 3180 \text{ cal/g-mole} \]

From Steam Table\textsuperscript{33}

\[ H_{\text{H}_2O, 298.1^\circ K} - H_{\text{H}_2O, 198.1^\circ K} = 45.02 - 36.04 = 8.98 \text{ Btu/lb} = 89.8 \text{ cal/g-mole} \]


\textsuperscript{34} See footnote 27.
therefore, $\Delta H_{H_2O,20^\circ C}^0 - H_{H_2O,0^\circ K}^0$

$= 3180 - 89.8$

$= 3090.2 \text{ cal/g-mole}$

Comparing $H_{H_2O,20^\circ C}^0 = 4865 \text{ cal/g-mole}$

with $H_{H_2O,0^\circ C}^0 - H_{H_2O,0^\circ K}^0 = 3090.2 \text{ cal/g-mole}$

we see that there is a difference of

$\Delta = 4865 - 3090.2 = 1774.8 \text{ cal/g-mole}$

The above calculation shows that the molar enthalpy of

pure water at absolute zero temperature is not zero.

Furthermore, at absolute zero, $G = H = A = U$. Therefore

it may be postulated the energy properties do not vanish

at absolute zero.

(2) Internal Energy.

By definition, $H = E + PV$

or, $E = H - PV$

$V_{H_2O,20^\circ C}^0 = 0.0708 \text{ ft}^3/\text{lb}$

$E_{H_2O,20^\circ C}^0 = 4865 - (14.7 \times 144 \times 0.0708 \times 18) / (3.088)$

$= 4865 - 1.93$

$= 4863 \text{ cal/g-mole}$

(3) Total Work.

By definition, $A = E - TS$

$A_{H_2O,20^\circ C}^0 = 4863 - 3547$

$= 1316 \text{ cal/g-mole}$


The "Fourth" Law of Thermodynamics. The Zeroth, First, Second, and Third laws of thermodynamics are mathematical formulations based on past experiences either from experimental results or through observations in nature. Just as is the case with Newton's formulation of three laws in motion, these laws can never be proved mathematically. Actually other rules, theories, or equations are deduced from these laws.

The First Law is a law in conservation of energy. The Second Law explains the existence of an entropy. The Third Law discusses the behavior of entropy. At this point it seems natural to inquire a formulation of the "Fourth" Law to study the "behavior" of energy functions, where these energy functions are the basis in formulating the First Law. This Fourth Law can not be derived mathematically. It should be based on past experience. Thus far we have seen that near absolute zero, the energy functions do not vanish. It could be said that, "The energy content of a system which is in internal thermodynamic equilibrium is governed by a certain partition function and does not vanish at absolute zero".

CHAPTER VI
DISCUSSIONS, CONCLUSIONS, AND RECOMMENDATIONS

Discussion.

(1) According to Hougen, Watson, and Ragatz, there are four groups of thermodynamic properties: reference properties (temperature, pressure, volume, entropy, composition), energy properties (internal energy, Gibbs free energy, enthalpy, Helmholtz free energy), derived properties (specific heat, coefficient of expansion, coefficient of compressibility, Joule-Thompson coefficient), and path properties (work, heat). Those in the last group are properties of a process rather than a system. All the properties except energy properties have absolute values. Energy properties are usually known only relative to some arbitrary reference state. In the previous chapter we have seen that the energy properties also have absolute values. It may be that these properties can be useful in correlating transport properties.

(2) The calorimeter developed in this work which was used to measure the heat-of-mixing was unique in its design, construction, and operating principles. Unlike many other calorimeters, the present calorimeter did not require

adiabatic conditions to avoid heat losses. A moderate heat transfer rate was employed in order to record thermograms. The various sources of heat effects were included as the area under the curve of a thermogram. The only condition required for accuracy was that the thermograms corresponding to heat-of-mixing and energy introduction had to be identical. This was obtained either by adjusting the rate of introduction of the second component during mixing or by controlling the flow of current. The calorimeter internals were miniaturized thus giving a greater space for reagents; and most important of all the uncertain heat effects were reduced by avoiding bulky parts having appreciable heat capacities. The insertion of a 53 junctions thermopile in the calorimeter was an important feature of the design. This gave an extremely sensitive, fast response of the temperatures. Also the area of the thermograms were more than large enough so that they could be cut off and weighed. An alternate method to determine the areas was to use a planimeter. The entire assembly of calorimeter cell was firmly attached within a completely closed isothermal bath thus made it free from dust or any possible accidental damage. Data obtained were within 5% deviation from comparison with available literature values.

(3) The method of intercepts of tangent line was used in Chapter V to obtain the quantities $(\bar{G}_i - G_1)$'s.
However this method should be used carefully. For example it is not applicable to \( (\bar{H}_1 - \bar{H}_1^i) \)'s. We may find the reason as follow: From Fuller's theorem

\[
H = x_1 \bar{H}_1 + x_2 \bar{H}_2 \quad (6-1)
\]

By total differentiation

\[
dH = x_1 d\bar{H}_1 + x_2 d\bar{H}_2 + \bar{H}_1 dx_1 + \bar{H}_2 dx_2 \quad (6-2)
\]

From definition

\[
H = H(s, P, x_1, x_2) \quad (6-3)
\]

By total differentiation

\[
dH = \left(\frac{\partial H}{\partial x_1}\right)_s P x_1 dx_1 + \left(\frac{\partial H}{\partial x_2}\right)_s P x_2 dx_2 + \left(\frac{\partial H}{\partial s}\right)_s P x_1 ds + \left(\frac{\partial H}{\partial P}\right)_s x_1 x_2 dP \\
= \left(\frac{\partial H}{\partial x_1}\right)_s P x_1 dx_1 + \left(\frac{\partial H}{\partial x_2}\right)_s P x_2 dx_2 + T ds + V dP \\
= \bar{G}_1 d\bar{x}_1 + \bar{G}_2 d\bar{x}_2 + T ds + V dP \quad (6-4)
\]

Subtracting equation 6-4 from equation 6-2 and assuming constant temperature and pressure (this is because the heats-of-mixing were measured at constant \( T, P \) ) it yields

\[
0 = (\bar{H}_i - \bar{G}_i) d\bar{x}_1 + (\bar{H}_2 - \bar{G}_2) d\bar{x}_2 + x_1 d\bar{H}_1 + x_2 d\bar{H}_2 + T ds + V dP \\
= T (\bar{S}_1 - \bar{S}_2) d\bar{x}_1 + x_1 d\bar{H}_1 + x_2 d\bar{H}_2 - T ds \quad (6-5)
\]

clearly,

\[
x_1 d\bar{H}_1 + x_2 d\bar{H}_2 = 0 \quad (6-6)
\]

Therefore there is no Gibbs Duhem type equation for the enthalpy function. For this reason the method of tangent intercepts fails. However, this does not mean the \( (\bar{H}_1 - \bar{H}_1^i) \)'s are not calculable. Since entropy is a reference property, we may define \( S = S(T, P, x_1, x_2) \) without altering the
definition of chemical potentials. In this way the Gibbs Duhem type equation for entropy exists, thus \((\tilde{S}_i - S_i^0)\)'s may be obtained by the method of tangent intercepts. This is also true for the reference property-volume. Then \((\tilde{H}_i - H_i^0)'s\) are calculated by

\[
\tilde{H}_i - H_i^0 = \tilde{G}_i - T(\tilde{S}_i - S_i^0) - G_i^0
\]

Conclusions. For a complete study of the thermodynamic properties of a solution, it requires to combine the vapor pressure (equilibrium) measurements with calorimetric measurements. In addition, volumetric measurements are also needed. From these laboratory experiments the entire thermodynamic properties of a system may be expressed in numerical quantities. At present the quantity \(T^4S\) remain unmeasurable by direct means, it is obtained as the difference between \(\Delta H\) and \(\Delta G\). These are of significant importance in industrial applications for we know many equilibrium stages involve liquid mixtures. For example, in the gas industry, natural gas is processed in gas plants before transporting into pipelines for domestic uses. There traces of valuable chemicals are recovered and the profits involve mutimillion dollars. They utilize multistages of huge compressors where the design requires very accurate thermodynamic analysis. As we have seen in the previous chapter, the thermodynamic functions of a system are related by
rigorous mathematical equations. Therefore if a set of reasonably accurate experimental data are available, the thermodynamic analysis of a process should give valuable information for industrial design calculations.

Recommendations.

(1) The calorimeter used to measure heats of mixing may be modified to extend the temperature range. At higher temperatures the reagents must be under pressure in order to maintain the liquid phase. Therefore the calorimeter must be pressure resistant without any leakage. The data taken are useful to convert activity coefficients measured at room temperature into those at higher temperatures. The effect of pressure on activity coefficients may also be included using data from volumetric measurements (mainly $\Delta V$'s).

(2) Since all the thermodynamic properties have absolute values, they may be useful as correlation parameters in many transport properties. This probably will be important for predicting transport properties of mixtures using only the properties of pure components.
SELECTED BIBLIOGRAPHY

BOOKS


JOURNALS AND PERIODICALS


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