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ROSENBERG, Harvey Sanford, 1939-
THE SOLUBILITY OF MERCURY IN POLAR GASES.

The Ohio State University, Ph.D., 1973
Engineering, chemical

University Microfilms, A XEROX Company, Ann Arbor, Michigan

THE SOLUBILITY OF MERCURY IN POLAR GASES

DISSERTATION

Presented in Partial Fulfillment of the Requirements for
the Degree Doctor of Philosophy in the Graduate
School of The Ohio State University

By

Harvey Sanford Rosenberg, B.Ch.E., M.Sc.

* * * * *

The Ohio State University
1973

Approved by

Co-Advisers

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ACKNOWLEDGMENTS .

I want to take this opportunity to thank Professor Webster B. Kay for his helpful guidance. I am also deeply grateful to Dr. Charles W. Townley of Battelle Memorial Institute who provided me with the initiative for continuing my education. I want to thank Battelle for providing me with a staff fellowship that enabled me to perform this research.

Numerous people assisted me in various ways during the course of this work. I want to acknowledge Drs. Joseph M. Genco, Sanford G. Bloom, Gilbert E. Raines, and David L. Morrison for their help and encouragement. Dr. Sanford Reich provided me with the idea for the magnetic stirring apparatus and Don Chamberlain reduced this idea to practice by building the continuous stirrer. Gary Campbell helped with glass blowing and Phil Mohler assisted with computer programming.

Last, but not least, I want to thank my wife and children for putting up with the years of inconvenience necessitated by my graduate studies. Without their encouragement and understanding, this work would not have been possible

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"Scavengers fro Radioactive Iodine." Canadian Patent No. 907775, August 15, 1972.

FIELDS OF STUDY

Major Field: Chemical Engineering

Studies in Thermodynamics. Professor Webster B. Kay.

TABLE OF CONTENTS

	<u>Page</u>
ACKNOWLEDGMENTS	ii
VITA	iii
LIST OF TABLES	vi
LIST OF FIGURES	vii
LIST OF SYMBOLS	viii
SUMMARY	1
Chapter	
I. INTRODUCTION	4
II. THEORY	7
III. RELATED LITERATURE	26
IV. APPARATUS AND PROCEDURE	29
V. EXPERIMENTAL RESULTS	42
VI. PRECISION AND ACCURACY	53
VII. DISCUSSION OF RESULTS	65
VIII. CONCLUSIONS	87
IX. RECOMMENDATIONS	89
APPENDIX	
A. Radioactivity and Radioactive Mercury	90
B. Thermocouple Calibration	99
C. Preparation of Methanol and Acetone	102

TABLE OF CONTENTS
(Cont.)

D. Calculation of Mass of Methanol or Acetone Loaded into Sample Tubes and Gas Density	106
E. Volume Calibration	109
F. Experimental Data	113
G. Computer Program for Polynomial Regression Analysis	120
BIBLIOGRAPHY	127

LIST OF TABLES

Table	Page
1. Solubility of Mercury Vapor in Compressed Methanol and Acetone	43
2. Polynomial Regression Analysis of $\ln(c_2/c_2^0)$ vs. $1/v$. .	48
3. Polynomial and Virial Coefficients for Mercury-Methanol and Mercury-Acetone Systems	52
4. Molecular Force Constants	71
5. Pressure Correction for Methanol Isotherm in the Presence of Mercury at 260° C	83
6. Pressure Correction for Acetone Isotherm in the Presence of Mercury at 260° C	84

LIST OF FIGURES

Figure	Page
1. Constant Temperature Apparatus.	30
2. Schematic Diagram of Constant Temperature Apparatus	31
3. Schematic Diagram of Sample Tube in Vapor Bath.	34
4. Vacuum Manifold	37
5. Schematic Diagram of Vacuum Manifold.	38
6. Schematic Diagram of Apparatus for Determining Sample Tube Volume	41
7. The Concentration of Mercury in Saturated Gaseous Mixtures with Methanol	45
8. The Concentration of Mercury in Saturated Gaseous Mixtures with Acetone.	46
9. Second Virial Coefficients of Interaction for Mercury - Methanol System	67
10. Second Virial Coefficients of Interaction for Mercury - Acetone System.	68
11. Stuart Models of Methanol and Ethane.	75
12. Stuart Models of Propane, Acetone, and Isobutane.	76
13. Experimental Determinations of Interaction Second Virial Coefficients for Binary Systems with Mercury as One Component	78
14. Decay Scheme for ²⁰³ Hg.	96

LIST OF SYMBOLS

Upper Case

- A = Helmholtz free energy, cal/g-mole or quantity of radioactivity, counts/min
- B = Second virial coefficient, $\text{cm}^3/\text{g-mole}$
- C = Third virial coefficient, $\text{cm}^6/\text{g-mole}^2$
- D = Fourth virial coefficient, $\text{cm}^9/\text{g-mole}^3$
- G = Gibbs free energy, cal
- H = Heat of solution, cal/g-mole
- J = Generalized virial coefficient
- K_p = Constant reflecting the displacement of a polar dipole from the center of the molecule, dimensionless
- N = Avogadro's number, molecules/g-mole or number of atoms
- P = Total pressure exerted on a liquid, atm
- R = Gas constant, liter atm/g-mole °K
- S = Entropy, cal/°K
- T = Absolute temperature, °K
- U = Internal energy, cal
- V = Volume, liters
- Y = Young's modulus, psi

Lower Case

- a = Polynomial coefficient, $\text{cm}^3/\text{g-mole}$
- b = Polynomial coefficient, $\text{cm}^6/\text{g-mole}^2$
- b₀ = Hard-sphere volume, cm^3

c = Concentration, g-mole/liter
 f_1 = Integration constant, cal
 f_2 = Integration constant, cal
 h = Tube length, in.
 k = Boltzmann's constant, ergs/ $^{\circ}$ K or proportionality constant for detecting radioactivity, dimensionless
 l = counting index
 n = number of moles
 p = system pressure, atm or vapor pressure of a liquid, atm
 r = Intermolecular distance, Angstrom units or tube radius, in.
 s = Tensile stress, psi
 t = Decay time, days or tube wall thickness, inches
 $t_{1/2}$ = Half-life for radioactive decay, days
 v = molar volume, liters/g-mole
 v_c = critical molar volume, $\text{cm}^3/\text{g-mole}$
 x = mole fraction, dimensionless

Greek

α = Polarizability, cm^3
 ϵ = Interaction energy parameter, ergs
 θ = Angle between polar groups and some fixed molecular axis, radians
 λ = Radioactive decay constant, days^{-1}
 μ = Chemical potential, cal/g-mole or dipole moment, debyes
 ξ = Correction term for combining interaction parameters, dimensionless
 σ = Molecular distance parameter, Angstrom units

Subscripts

G = Gas

L = Liquid

a,b,c,d = Components

n = Nonpolar

m = Mixture

p = Polar

$\alpha, \beta, \gamma, \delta$ = Dummy subscripts equated to components a,b,c,d

1,2 = Components of a binary system

Superscripts

C = Condensed phase

E = Excess thermodynamic function

ℓ = Liquid phase

o = Pure saturated vapor

SUMMARY

The solubility of mercury in compressed gases may be rigorously described by thermodynamic expressions and, as such, gives a new approach to the study of intermolecular forces. The concentration of mercury in the gas phase when liquid mercury is in equilibrium with methanol or acetone was measured at pressures up to 30 atm from 220 to 300° C using a radioisotope tracer technique. Liquid mercury was tagged with ^{203}Hg , and its concentration as a vapor in the gas phase was measured with an NaI scintillation probe, both in the presence of compressed methanol or acetone and alone. The ratio of the count rates is a direct measure of the mercury solubility. The mercury concentrations in the compressed polar gases were as much as 21.6 percent greater than in pure mercury vapor at the same temperature. The mercury solubility increases with increasing pressure and decreases with increasing temperature. There is no discontinuity in mercury solubility in crossing from methanol or acetone vapor to gas when these polar compounds are not near the two-phase region.

The data were used to determine the mixed virial coefficients for mercury and the polar organic molecules. The second virial coefficient of interaction, B_{12} , for the system mercury-methanol ranges from $-126 \text{ cm}^3/\text{g-mole}$ at 220° C to $-110 \text{ cm}^3/\text{g-mole}$

at 300° C. The corresponding values for mercury-acetone at the same temperatures are -156 and -123 cm³/g-mole. The values of B_{12} are precise to within 5 percent and accurate to within 10 percent. B_{12} may be estimated by use of appropriate empirical combining rules for the molecular force constants of nonpolar mercury atoms (Lennard-Jones potential function) and polar methanol or acetone molecules (Stockmayer potential function). Better accuracy is obtained by emphasizing the nonpolar characteristics of the polar molecules and by taking account of the displacement of the dipoles from the center of the molecules.

The third virial coefficient of interaction, C_{112} , which represents the interaction of two organic molecules with one atom of mercury, could only be estimated from the data but was found to be positive for the mercury-methanol and mercury-acetone systems. The positive sign of C_{112} is indicative of the fact that when the number of methanol or acetone molecules clustering around a mercury atom increases, then their mutual interactions hinder the clustering process. The forces responsible for the mutual interactions include hydrogen bonding (methanol) and dipole formation (methanol and acetone).

The solubility of mercury in methanol or acetone can cause an error of about 1 part in 500 in the pressure of gas isotherms measured in the presence of mercury at about 35 atm, if the measured pressure is corrected by subtraction of the normal vapor pressure of mercury at the same temperature. The effect of mercury solubility on the accuracy of gas isotherms at higher pressures is still not

known. The determination of this effect requires high pressure data on mercury solubility as well as accurate values for the third virial coefficients of pure methanol and acetone.

The effect of mercury solubility on the accuracy of gas isotherms for other compounds depends upon the absolute value of B_{12} . The greater the absolute value of B_{12} , the larger the error to be expected in the gas isotherm measurements. Thus far, B_{12} has been experimentally determined for only five binary systems in which mercury is one component. The absolute value of B_{12} increases with molecular size and is greater for polar molecules than for nonpolar molecules. The largest error in gas isotherm measurements at moderate pressures attributable to mercury solubility from the available experimental values of B_{12} is about 0.2 percent.

CHAPTER I

INTRODUCTION

The earliest observations of the increase in the volatility of a condensed phase (solid or liquid) in the presence of a compressed gas were made by Hannay and Hogarth [1] who examined the solvent properties of some fluids for nonvolatile solids during the passage of the solvent through the critical point. It was shown by these workers that no precipitation of solid occurred when a solution consisting of potassium iodide dissolved in alcohol was heated in an enclosed tube to a temperature above the critical temperature of the solvent. Altshul [2] investigated the influence of temperature on the solvent power of gases; between 1903 and 1910, Centnerszwer [3, 4] made a systematic quantitative study of the critical points of solutions of different salts, and Niggli [5] pointed out the importance of critical phenomena in geological processes.

Quantitative studies of the increase in the vapor pressure of liquids and solids have been carried out by many workers. Pollitzer and Strebel [6] determined experimentally the moisture content of air, hydrogen, and carbon dioxide in equilibrium with water at 50° C and 70° C at pressures up to 200 atm. Bartlett [7], who was interested in the effect of inert gas pressure on vapor pressure in connection with the manufacture of synthetic ammonia, determined the equilibrium moisture content of hydrogen, nitrogen, and 3 to 1 mole

ratio mixtures of hydrogen and nitrogen between 25° and 50° C at pressures up to 1,000 atm. The system water-nitrogen was studied experimentally at pressures up to 300 atm by Saddington and Krase [8]. The water content of natural gas and helium under pressure has been measured by Deaton and Frost [9]. The equilibrium molar concentration of carbon dioxide in air compressed to 50 atm was measured by Gratch [10], who showed that under certain conditions the vapor pressure of carbon dioxide is increased by a factor of ten when the solid is subjected to inert gas pressure. An even more remarkable result was obtained by Diepen and Scheffer [11] in studying the solubility of naphthalene in supercritical ethylene. These workers showed that at 12° C and 100 atm, the naphthalene concentration in the ethylene gas was 25,000 times as great as it would be if the naphthalene exerted its normal vapor pressure.

The phenomenon of solubility of solids and liquids in compressed gases is of great practical interest and is important wherever compressed gases or vapors are used. In industry, the deposits of sodium chloride or silica on the blades of vapor turbines are well known; in the laboratory, it is necessary to take account of this phenomenon when purifying gases by condensation and in handling pure gases which may be contaminated by contact with liquids and solids. Of particular interest is the effect of mercury solubility on the accuracy of measurements of the volumetric behavior of compressed gases in those experiments in which mercury is used as the confining liquid. The present study on the solubility of mercury in compressed methanol and acetone vapor and

gas was, undertaken to obtain more data on the accuracy of gas isotherms measured in the presence of mercury and, more importantly, to gain an insight into the nature of intermolecular forces between unlike atoms and molecules.

CHAPTER II

THEORY

From the theoretical standpoint, it is evident that the solubility in compressed gases gives a new approach to the study of intermolecular forces. It is well known that experimental results of high pressure investigations are not in agreement with the various expressions such as Poynting's formula and Van der Waal's equation for binary systems. The theoretical aspects of the change in vapor pressure when a condensed phase is subjected to pressure by an indifferent gas have been considered by Poynting [12] who derived the following thermodynamic relation expressing the magnitude of the pressure effect:

$$\left(\frac{dp}{dP}\right)_T = \frac{v_L}{v_G} \quad (1)$$

in which

p = vapor pressure of the liquid,

P = total pressure on the liquid,

v_G = molar volume of the vapor,

v_L = molar volume of the liquid.

The increase in vapor pressure calculated by the formula is usually much less than that determined by actual experiment. This is due to the fact that the Poynting effect (enhancement of the vapor pressure caused by the hydrostatic pressure of the gas) is never obtained alone and is usually obscured by a solubility effect.

The equilibrium between a pure condensed phase and a gaseous mixture is one of very few classes of solution for which an exact treatment can be made by the methods of statistical thermodynamics. Starting with the second law of thermodynamics, the Helmholtz free energy, or work function, represented by the symbol A , is defined by [13]

$$A = U - TS \quad (2)$$

where

U = energy content of the system,

T = absolute temperature,

S = entropy.

Differentiation of equation 2 yields

$$dA = dU - TdS - SdT \quad (3)$$

and since [13]

$$TdS = dU + pdV \quad (4)$$

$$dA = -pdV - SdT \quad (5)$$

so that at constant temperature

$$A = -\int pdV \quad (6)$$

Similarly, the Gibbs free energy, represented by the symbol G , is defined by [13]

$$G = U - TS + pV \quad (7)$$

so that

$$G = A + pV \quad (8)$$

Differentiation of equation 8 yields

$$dG = dA + pdV + Vdp \quad (9)$$

so that at constant temperature

$$G = \int V dp \quad (10)$$

Also, from equations 5 and 9

$$\left(\frac{\partial A}{\partial T}\right)_V = -S = \left(\frac{\partial G}{\partial T}\right)_P \quad (11)$$

The equation of state of a perfect gas of one component may be written [14]

$$p = \frac{nRT}{V} \quad (12)$$

where n is the number of moles and V is the total volume. By integration of equation 6

$$A = nRT \ln\left(\frac{1}{V}\right) + \text{constant} \quad (13)$$

where the constant of integration is a function of n and T but not of V . Since A is an extensive property, it follows that [14]

$$A = nRT \ln\left(\frac{n}{V}\right) + nf_1(T) \quad (14)$$

whence the chemical potential is given by [14]

$$\left(\frac{\partial A}{\partial n}\right)_{V,T} = RT \ln\left(\frac{n}{V}\right) + RT + f_1(T) \quad . \quad (15)$$

Similarly, from integration of equation 10

$$G = nRT \ln p + \text{constant} \quad (16)$$

$$G = nRT \ln\left(\frac{nRT}{V}\right) + nf_2(T) \quad , \quad (17)$$

and the chemical potential is given by [14]

$$\left(\frac{\partial G}{\partial n}\right)_{p,T} = RT \ln\left(\frac{nRT}{V}\right) + f_2(T) \quad . \quad (18)$$

It follows from equation 11 that [13]

$$\left(\frac{\partial A}{\partial n}\right)_{V,T} = \left(\frac{\partial G}{\partial n}\right)_{p,T} \quad (19)$$

so by equating the two expressions for chemical potential [14],

$$f_2(T) = f_1(T) + RT - RT \ln RT \quad (20)$$

and by eliminating $f_1(T)$ and omitting the subscript from $f_2(T)$,

$$A = nf(T) + nRT \left[\ln \left(\frac{nRT}{V} \right) - 1 \right] \quad (21)$$

The function $f(T)$ is the chemical potential in the standard state of unit pressure at each temperature T .

A perfect-gas mixture is defined as one formed from perfect gases and whose Helmholtz free energy is given by the sum of the free energies of its components, when each occupies separately the total volume V at the temperature T . That is [14]

$$A = \sum_{\alpha} n_{\alpha} \mu_{\alpha}^* + RT \sum_{\alpha} n_{\alpha} \left[\ln \left(\frac{n_{\alpha} RT}{V} \right) - 1 \right] \quad (22)$$

where α is a dummy subscript which is equated successively to the components a, b, c , etc. of the mixture and μ_{α} is the chemical potential of component α defined by [14]

$$\mu_{\alpha} = \left(\frac{\partial A}{\partial n_{\alpha}} \right)_{V, T, n_b \dots} = \left(\frac{\partial G}{\partial n_{\alpha}} \right)_{p, T, n_b \dots} \quad (23)$$

The superscript $*$ denotes the pure substance in the standard state of unit pressure.

For a real gas mixture, the only equation of state that can be derived rigorously from statistical mechanics is the virial expansion [14]

$$\frac{pV}{nRT} = 1 + \sum_{\ell=2} \frac{J_{\ell} n^{\ell-1}}{V^{\ell-1}} \quad (24)$$

where J_{ℓ} is the ℓ^{th} virial coefficient of the mixture and is a function of temperature and composition only. The expanded form of equation 24 is

$$\frac{pV}{nRT} = 1 + \frac{B_m n}{V} + \frac{C_m n^2}{V^2} + \frac{D_m n^3}{V^3} + \dots \quad (25)$$

In general,

$$J_2 = B_m = \sum_{\alpha\beta} x_{\alpha} x_{\beta} B_{\alpha\beta} \quad (26)$$

$$J_3 = C_m = \sum_{\alpha\beta} \sum_{\gamma} x_{\alpha} x_{\beta} x_{\gamma} C_{\alpha\beta\gamma} \quad (27)$$

$$J_4 = D_m = \sum_{\alpha\beta\gamma\delta} x_{\alpha} x_{\beta} x_{\gamma} x_{\delta} D_{\alpha\beta\gamma\delta} \text{ etc.}, \quad (28)$$

where $\alpha, \beta, \gamma, \delta$, etc. are dummy subscripts which are replaced by all permutations of the components of the mixture, and where B, C, D, etc. are single terms in the virial coefficients which are functions only of the temperature and of the intermolecular forces between the components indicated by the subscripts, subject to the constraint that $B_{\alpha\beta}$ equal $B_{\beta\alpha}$, etc. [14]. For binary mixtures, equations 26 through 28 become

$$J_2 = B_m = x_a^2 B_{aa} + 2x_a x_b B_{ab} + x_b^2 B_{bb} \quad (29)$$

$$J_3 = C_m = x_a^3 C_{aaa} + 3x_a^2 x_b C_{aab} + 3x_a x_b^2 C_{abb} + x_b^3 C_{bbb} \quad (30)$$

$$J_4 = D_m = x_a^4 D_{aaaa} + 4x_a^3 x_b D_{aaab} + 6x_a^2 x_b^2 D_{aabb} + 4x_a x_b^3 D_{abbb} + x_b^4 D_{bbbb} \quad (31)$$

where B_{aa} , C_{aaa} , and D_{aaaa} are the virial coefficients for pure a, B_{bb} , C_{bbb} , and D_{bbbb} are the virial coefficients for pure b, and where the remaining coefficients are characteristic of the mixture and are related to the forces between molecules in the clusters indicated by the subscripts.

The thermodynamic free energy functions of real gases are conveniently tabulated by choosing as reference states the hypothetical perfect gases at the same volume or at the same pressure as the real gas.

Thus, there is a different reference state for every real state of the system. Thermodynamic functions referred to such states are called excess functions and denoted here by a superscript ^E. The excess Helmholtz free energy is then defined as [14]

$$A^E(V, T) = \int_{\infty}^V \left(\frac{nRT}{V} - p \right) dV \quad (32)$$

Substituting equation 24 into equation 32 and integrating yields

$$A^E(V, T) = RT \sum_{\ell=2}^J \left(\frac{1}{\ell-1} \right) \frac{J_{\ell} n^{\ell}}{V^{\ell-1}} \quad (33)$$

so that the total Helmholtz free energy of a real gas mixture is

$$A = \sum_{\alpha} n_{\alpha} \mu_{\alpha}^* + RT \sum_{\alpha} n_{\alpha} \left[\ln \left(\frac{n_{\alpha} RT}{V} \right) - 1 \right] + RT \sum_{\ell=2}^J \left(\frac{1}{\ell-1} \right) \frac{J_{\ell} n^{\ell}}{V^{\ell-1}} \quad (34)$$

The chemical potential is found by differentiating equation 34 with respect to n_a at constant volume and constant number of moles for all components other than a . The differentiation of the term containing the virial coefficients is done as follows:

$$\left(\frac{\partial}{\partial n_a}\right)_{n_b, n_c, \dots} [J_\ell n^\ell] = n^\ell \left(\frac{\partial J_\ell}{\partial n_a}\right)_{n_b, n_c, \dots} + \ell n^{\ell-1} J_\ell = \ell n^{\ell-1} J_\ell^a \quad (35)$$

where

$$J_2^a = \sum_{\alpha} x_{\alpha} B_{a\alpha} \quad (36)$$

$$J_3^a = \sum_{\alpha\beta} x_{\alpha} x_{\beta} C_{a\alpha\beta} \quad (37)$$

$$J_4^a = \sum_{\alpha\beta} x_{\alpha} x_{\beta} x_{\gamma} D_{a\alpha\beta\gamma} \text{ etc.}, \quad (38)$$

For component b of a binary mixture, equations 36 through 38 become

$$J_2^b = x_a B_{ab} + x_b B_{bb} \quad (39)$$

$$J_3^b = x_a^2 C_{aab} + x_a x_b C_{abb} + x_b^2 C_{bbb} \quad (40)$$

$$J_4^b = x_a^3 D_{aaab} + x_a^2 x_b D_{aabb} + x_a x_b^2 D_{abbb} + x_b^3 D_{bbbb} \quad (41)$$

For the general case, the chemical potential of component a in a gas mixture is therefore given by [14]

$$\mu_a = \mu_a^* + RT \ln \left(\frac{n_a RT}{V} \right) + RT \sum_{\ell=2}^{\infty} \left(\frac{\ell}{\ell-1} \right) \frac{J_{\ell}^a n^{\ell-1}}{V^{\ell-1}} \quad (42)$$

In the case of binary gas mixture, the chemical potential of component 2 (component b) is given by

$$\mu_2(\text{gas}) = \mu_2^*(\text{gas}) + RT \ln \left(\frac{n_2 RT}{V} \right) + \frac{2nRT}{V} (x_1 B_{12} + x_2 B_{22}) +$$

$$\frac{3n^2 RT}{2V^2} (x_1^2 C_{112} + x_1 x_2 C_{122} + x_2^2 C_{222}) +$$

$$\frac{4n^3 RT}{3V^3} (x_1^3 D_{1112} + x_1^2 x_2 D_{1122} + x_1 x_2^2 D_{1222} + x_2^3 D_{2222}) +$$

. . . .

(43)

Henceforward, the discussion will be restricted to binary systems so that the component subscripts a and b have been changed to 1 and 2 in keeping with more common usage.

The chemical potential of a pure condensed phase under the confining pressure of an inert gas has been derived from statistical mechanics by Fowler and Guggenheim [15] and is given by

$$\mu_2(\text{condensed}) = \mu_2^*(\text{condensed}) + pv_2^c \quad (44)$$

where $\mu_2^*(\text{condensed})$ is the chemical potential in the standard state (pure condensed phase at unit pressure), p is the total pressure, and v_2^c is the molar volume of the condensed phase. The above equation assumes that none of the confining gas dissolves in the condensed phase and that the condensed phase is incompressible. Equation 25 can be used to substitute for p so that equation 44 becomes

$$\begin{aligned} \mu_2(\text{condensed}) = \mu_2^*(\text{condensed}) + v_2^c \left[\frac{nRT}{V} + \frac{n^2RT}{V^2} (x_1^2 B_{11} + 2x_1 x_2 B_{12} + \right. \\ x_2^2 B_{22}) + \frac{n^3RT}{V^3} (x_1^3 C_{111} + 3x_1^2 x_2 C_{112} + 3x_1 x_2^2 C_{122} + x_2^3 C_{222}) + \\ \left. \frac{n^4RT}{V^4} (x_1^4 D_{1111} + 4x_1^3 x_2 D_{1112} + 6x_1^2 x_2^2 D_{1122} + 4x_1 x_2^3 D_{1222} + \right. \\ \left. x_2^4 D_{2222}) + \dots \right] \quad (45) \end{aligned}$$

The condition for equilibrium is the equality of the chemical potential, in both phases, of the component present in the pure condensed phase [13]:

$$\mu_2(\text{condensed}) = \mu_2(\text{gas}) \quad (46)$$

Equating these potentials for the case when there is no added gas ($x_1 = 0, x_2 = 1$) yields

$$\begin{aligned} \mu_2^*(\text{gas}) + RT \ln \left(\frac{n_2^0 RT}{V_2} \right) + \frac{2n_2^0 RT}{V_2} B_{22} + \frac{3n_2^{0^2} RT}{2V_2^2} 222 + \\ \frac{4n_2^{0^3} RT}{3V_2^3} D_{222} + \dots = \mu_2^*(\text{condensed}) + v_2^c \left(\frac{n_2^0 RT}{V_2} + \right. \\ \left. \frac{n_2^{0^2} RT}{V_2^2} B_{22} + \frac{n_2^{0^3} RT}{V_2^3} C_{222} + \frac{n_2^{0^4} RT}{V_2^4} D_{2222} + \dots \right) \end{aligned} \quad (47)$$

where $\frac{V_2}{n_2^0}$ is the molar molume of the pure saturated vapor. Then, if the added gas is present at such high concentration that x_1 is about equal to zero)

$$\begin{aligned}
& \mu_2^*(\text{gas}) + RT \ln \left(\frac{n_2 RT}{V} \right) + \frac{2nRT}{V} B_{12} + \frac{3n^2 RT}{2V^2} C_{112} + \\
& \frac{4n^3 RT}{3V^3} D_{1112} + \dots = \mu_2^*(\text{condensed}) + v_2^c \left(\frac{nRT}{V} + \right. \\
& \left. \frac{n^2 RT}{V^2} B_{11} + \frac{n^3 RT}{V^3} C_{111} + \frac{n^4 RT}{V^4} D_{1111} + \dots \right) \quad (48)
\end{aligned}$$

Subtracting equation 47 from equation 48 and neglecting terms in $\frac{n_2^0}{V_2}$ and its powers, except for the term $RT \ln \frac{n_2^0 RT}{V_2}$, since $\frac{n_2^0}{V_2} \ll \frac{n}{V}$, yields

$$\begin{aligned}
& RT \ln \left(\frac{n_2 RT}{V} \right) - RT \ln \left(\frac{n_2^0 RT}{V_2} \right) + \frac{2nRT}{V} B_{12} + \frac{3n^2 RT}{2V^2} C_{112} + \\
& \frac{4n^3 RT}{3V^3} D_{1112} + \dots = v_2^c \left(\frac{nRT}{V} + \frac{n^2 RT}{V^2} B_{11} + \frac{n^3 RT}{V^3} C_{111} + \dots \right) \quad (49)
\end{aligned}$$

which, upon rearrangement, becomes

$$\begin{aligned}
\ln \left(\frac{c_2}{c_2^0} \right) &= \frac{v_2^c}{v} - \frac{2B_{12}}{v} + \frac{v_2^c B_{11}}{v^2} - \frac{3C_{112}}{2v^2} + \\
& \frac{v_2^c C_{111}}{v^3} - \frac{4D_{1112}}{3v^3} + \dots \quad (50)
\end{aligned}$$

where c_2 is the concentration of component 2 in the gas phase (n_2/V), c_2^0 is the concentration which component 2 would have in the gas phase if it were present as a pure saturated vapor, and v is the molar volume of the gas mixture. Equation 50 may be written in another form which separates the Poynting effect from the solubility effect:

$$\ln\left(\frac{c_2}{c_2^0}\right) = \frac{pv_2^c}{RT} - \frac{2B_{12}}{v} - \frac{\frac{3}{2}C_{112}}{v^2} - \frac{\frac{4}{3}D_{1112}}{v^3} - \dots \quad (51)$$

The first term on the right side of the equation represents the Poynting effect and the remaining terms represent the solubility effect. The coefficient B_{12} is often large and negative and it is the term which represents the greater part of the enhancement of concentration shown by many of the systems of the type discussed above [16]. The higher coefficients are probably positive in almost all cases [17]. Equation 50 rather than equation 51 is used in this work.

The assumptions made in the derivation of equation 50 are as follows:

1. None of the gas (component 1) dissolves in the condensed phase (component 2).
2. The condensed phase is incompressible.
3. The molar volume of the saturated vapor of the condensed phase at its vapor pressure is much

larger than the molar volume of the compressed gas mixture at the same temperature ($v_2 \gg v$).

4. The mole fraction of component 2 in the gas mixture is very small ($x_2 \ll 1$).

In order to use equation 50, it is necessary to obtain either experimental or calculated values for the virial coefficients of interaction. Virial coefficients may be calculated from a knowledge of intermolecular forces. In general, molecules can be classified as either nonpolar or polar, depending upon the absence or presence of permanent electrical forces.

Nonpolar, or angle-independent, molecules do not possess any permanent charge distributions. All potential functions for these molecules must take into account the fact that molecules are attracted to one another at large separations but repel at small separations. Of all the potential functions suggested, the simplest and most widely used is of the bireciprocal form

$$\varphi(r) = Ar^{-n} - Br^{-m} \quad . \quad (52)$$

The first term accounts for the repulsive potential energy and the second for the attractive contribution. Equation 52 has two constants and has spherical symmetry. If the choice of n and m is 12 and 6, one obtains the 12-6 Lennard-Jones potential given as

$$\varphi(r) = 4\epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right] \quad (53)$$

where ϵ is the energy parameter (depth of the energy well) and σ is the collision diameter. Equation 53 is a reasonable approximation for simple nonpolar molecules.

Virial coefficients may be calculated once the potential function is chosen. For a Lennard-Jones potential, Hirschfelder, Curtiss, and Bird [18] have shown that the second virial coefficient $B(T)$ is

$$B(T) = f(T^*, b_0) \quad (54)$$

where T^* is a dimensionless temperature and is defined as

$$T^* = \frac{T}{\frac{\epsilon}{k}} = \frac{kT}{\epsilon} \quad (55)$$

and b_0 is the "hard-sphere" volume defined as

$$b_0 = \frac{2}{3} \pi N \sigma^3 \quad (56)$$

Then

$$B^*(T) = \frac{B(T)}{b_0} = f(T^*) \quad (57)$$

Hirschfelder, et al. [18] have tabulated values of $B^*(T)$ versus T^* so that $B(T)$ may be easily calculated from ϵ and σ .

Forces between polar molecules also consist of electron-cloud repulsion and London dispersion forces of attraction. In addition, polarity is manifested by a permanent unsymmetrical charge distribution which gives rise to an electrostatic contribution to the potential energy. The description of the charge distribution is given in terms called multipoles. The most commonly used polar potential is the Stockmayer potential. This function assumes that the only significant charge distribution results from dipole-dipole interactions and that it may be expressed in a convenient manner by

$$\varphi(r) = 4\epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 - \left(\frac{\mu^2}{r^3} \right) g(\theta) \right] \quad (58)$$

Here ϵ and σ are the Stockmayer-potential parameters and are not numerically equal to the Lennard-Jones potentials. The first two bracketed terms are similar in form to the Lennard-Jones 12-6 potential in that they account for repulsive and attractive potential energies; the third term involves the molecular dipole moment and a function of the angles between molecules. Hirschfelder, et al. [18] describe how this potential function may be used to obtain second and third virial coefficients for polar molecules.

Binary mixtures of molecules may be either nonpolar-nonpolar, polar-polar, or nonpolar-polar. In order to calculate virial coefficients of interaction for these mixtures it is necessary to know the interaction parameters (force constants). All techniques for estimating the interaction parameters of mixtures from the potential parameters of the pure components are empirical in nature. Various combining rules have been proposed for each of the three possible types of binary mixtures [19].

CHAPTER III

RELATED LITERATURE

The expression for the solubility of a condensed phase in a compressed gas (equation 50) has a long history. Poynting [12] first showed that a hydrostatic pressure would increase the activity or the chemical potential of a condensed phase by the amount shown in equation 44, and for many years the "Poynting effect" was invoked to explain the increased volatility of solids in the presence of added gases. However, the molar volumes of most condensed phases, especially mercury, are small and the enhancement due to this effect alone is only a small part of the total effect. The terms in equation 50 containing the virial coefficients of interaction, B_{12} , etc, were added independently by Perkins [20] in 1937 (second coefficient only), by Robin, Vodar, and Bergeon [21-24] in 1951-53 (second coefficient only), by Ewald, Jepson, and Rowlinson [25] in 1953 (complete expansion), and by Dokoupil, van Soest, and Swenker [26] in 1955 (complete expansion and its inversion to a pressure expansion). Ewald [27] has given the more complete form of equation 50 in which x_2 is not assumed to be very small.

Previous work on the solubility of mercury in compressed gases is very limited, with all of the research having been done

by Rowlinson and his co-workers. In 1955, Jepson and Rowlinson [28] estimated B_{12} and C_{112} for binary systems of mercury and xenon, ethane, propane, or butane from intermolecular forces based on the usual Lennard-Jones 12:6 potential function. At 275° C and a density of 6 moles/liter, the values of (c_2/c_2^0) they calculated for mercury in ethane, propane, and butane are 3.30, 4.87, and 7.59, respectively. In 1957, Jepson, Richardson, and Rowlinson [29] measured the concentration of mercury in the gas phase when liquid mercury is in equilibrium with propane and n-butane at pressures up to 30 atm from 184 to 256° C. These concentrations were up to 35 percent greater than the concentrations in pure mercury vapor at the same temperature, thus confirming their previous calculations which showed that this increase in the mercury concentration must affect adversely the accuracy of gas isotherms measured in the presence of mercury. This work was extended by Richardson and Rowlinson [30] in 1959 when they measured the solubility of mercury in n-butane at temperatures of 215, 256, and 300° C and at pressures up to 400 atm. The concentration of mercury was found to exceed that calculated from the saturated vapor pressure by factors of up to 3.7. Their results show a continuous rise of (c_2/c_2^0) with gas density up to 7 moles per liter, with no sign of a maximum. The solubility of mercury in compressed argon was measured by Stubley and Rowlinson [31] in 1961. The temperature range was 184 to 305° C and pressures of argon up to 400 atm were used. The results were used to obtain B_{12} , the second virial coefficient for the interaction of an argon atom with a mercury atom. It was shown that the values of B_{12}

agree with those estimated from the known properties of pure argon and pure mercury vapor.

No data could be found in the literature on the solubility of mercury in the gases of polar compounds. Therefore, this study was undertaken to measure the solubility of mercury in methanol vapor and gas which exhibits hydrogen bonding, and the solubility of mercury in acetone vapor and gas, which has a high dipole moment.

CHAPTER IV

APPARATUS AND PROCEDURE

The apparatus and procedures used in the work are a modification of the radioactive tracer technique developed by Jepson, Richardson, and Rowlinson [29]. This method avoids the obvious difficulties of trying to sample and analyze a compressed gas mixture in which one of the components is present in very small amounts. The use of a radioactive tracer makes possible the quantitative determination of a mixture component at a sensitivity unattainable by any other means. Further details on radioactivity and radioactive mercury are given in Appendix A.

The concentration of mercury atoms in the gas-phase was measured in a sealed glass tube by a tracer technique. The concentration of mercury near the bottom of a vertical glass tube was determined first for a tube containing only mercury vapor and then for an identical tube containing the compressed gas saturated with mercury at the same temperature. Since the count-rate is directly proportional to the number of mercury atoms, the ratio of the two observed count-rates is a direct measurement of the solubility of the mercury vapor in the added gas. In each tube there was a small excess of liquid mercury at the top to ensure saturation at all temperatures. A photograph of the apparatus is shown in Figure 1 and a schematic diagram is shown in Figure 2.

FIGURE 1. CONSTANT TEMPERATURE APPARATUS

FIGURE 2. SCHEMATIC DIAGRAM OF CONSTANT TEMPERATURE APPARATUS.

The glass sample tube was made of Pyrex precision-bore tubing with an internal diameter of 5.00 mm, an external diameter of about 9 mm, and a length of about 40 cm. It contained about 27 mg of radioactive mercury in a cup near the top of the tube, and a closely fitting Mumetal (a highly magnetic iron-nickel alloy) stirrer, 30 mm long, sealed in a 4 mm O.D. glass tube. The stirrer could be moved over the whole length of the tube up to the mercury cup by two C-shaped 6 oz permanent magnets placed with opposing poles about 2-1/4 inches apart on the outside of a vapor bath. The magnets moved up and down continuously by means of axial bearings and a chain drive mechanism powered by a simple 25 rpm gear motor. During actual counting, the stirrer was held stationary near the top of the tube by the magnets.

The glass sample tube was placed in a nonmagnetic stainless steel tube, with a wall thickness of 1/16 inch and an outside diameter of 1/2 inch, which was sealed on the bottom by a welded plug and on the top by a 1/2-inch stainless steel Swagelok cap. The purpose of this tube was to catch the fragments of glass and the radioactive mercury if the glass tube should have burst under the pressure of the added gas. Calculations showed that the maximum hoop stress on the stainless steel tube, in the event that the glass tube should break, would be a small fraction of the yield strength of the stainless steel. The stainless steel tube did not, however, absorb any appreciable amount of the γ -rays from the mercury.

The glass sample tube and the stainless steel case were maintained at constant temperature by a vapor bath of benzophenone.

The vapor bath, shown schematically in Figure 3, was specially designed to position the sample tube for counting. The vapor bath consisted of a silvered vacuum jacket and a glass positioning tube. The stainless steel case was centered in the glass positioning tube with the aid of two Viton O-rings. The desired bath temperature was adjusted and maintained by regulation of the pressure in the system over the range 8.6 - 66.0 cm Hg absolute. Very fine pressure control was obtained because of the 15 gal capacitance in the system and the double pressure regulation chambers on the vacuum and pressure sides of the system. The temperature was measured with a calibrated copper-constantan thermocouple in conjunction with a Leeds and Northrup Type K-3 universal potentiometer and a hanging-wire optical galvanometer. The details of the thermocouple calibration are presented in Appendix B. The thermocouple junction was immersed in finely ground SiO_2 at the bottom of a thermocouple well and was located about 1 inch away from the mercury droplet in the sample tube. The mercury droplet was located in a cup near the top of the sample tube in order to prevent spurious condensations of mercury during startup and operation of the vapor bath. The temperature at the top of the vapor bath must be less than or equal to the temperature at the bottom of the vapor bath. Therefore, this arrangement ensured that the entire sample tube was at constant temperature before the mercury began to evaporate.

The concentration of the mercury was measured, in arbitrary units, by the NaI scintillation probe as shown in Figure 2. This probe was completely surrounded by lead brick shielding of 4-inch

FIGURE 3. SCHEMATIC DIAGRAM OF SAMPLE TUBE IN VAPOR BATH.

thickness, visible in the foreground of Figure 1. The counting face of the probe was shielded by 2 inches of lead but had a 1-inch square collimator so that it received almost all its radiation from the mercury in the gas phase and very little from the liquid mercury at top of the tube. The probe was maintained at a constant temperature of 28° C by a stream of water flowing through a copper coil wrapped around the former.

Mercury metal tagged with ^{203}Hg , having a half-life of 46.59 days, at a specific activity of about 50 mCi/g and a radiometric purity of greater than 99 percent, was purchased from New England Nuclear. This material was diluted with triple-distilled mercury to a specific activity of about 7.5 mCi/g for use in the sample tubes. ^{203}Hg emits both beta and gamma radiation; the gamma radiation, which is detected by the NaI scintillation crystal, is emitted at an energy of 0.279 Mev and occurs in 100 percent of the disintegrations. Calculations indicated that a specific activity of 7.5 mCi/g would yield the desired count-rate of 10,000 to 100,000 counts/min over the temperature range of this study. If the count-rate were too low, the experimental precision would be poor and if the count-rate were too high, the electro-mechanical counting equipment would be jammed. The observed count-rate was corrected for the laboratory background and for the background due to the excess liquid mercury at the top of the tube. The total background was never more than 10 percent of the total count-rate and was usually much less than this.

The glass sample tubes were loaded upside down, first by pipetting 2×10^{-3} ml of the radioactive mercury into the tube and

insuring that the droplet fell through the cup-hole and into the tip at the bottom of the tube. Next the stirrer was added and the sample tube was attached to a vacuum manifold by means of a 9 mm Fisher-Porter Solv-Seal joint so that the methanol or acetone vapor could be added by distillation in vacuo. A photograph of the vacuum manifold is shown in Figure 4 and a schematic diagram is shown in Figure 5. The high-purity methanol or acetone was stored, frozen by liquid nitrogen, in a 25 ml round-bottom flask at the bottom of the degassing apparatus (F). Details of the degassing procedure and information on the purity of these materials are presented in Appendix C. With cold traps (E) and (M) immersed in liquid nitrogen, the entire system was pumped down to a pressure of less than 4×10^{-6} mm of mercury, as indicated by McLeod gauge (O), by the vacuum pump-diffusion pump combination (A). An electronic vacuum gauge (B) was used to maintain a constant check on the system pressure. Vapor from the flask at the bottom of the degassing apparatus (F) was then allowed to distill into the calibrated and thermostatted reservoir (H) until the desired pressure in the range 3-10 cm Hg absolute was read on the mercury manometer (G) by removing the liquid nitrogen from this flask. The constant temperature bath (I) was maintained at 28.0° C and the manometer readings were made with a cathetometer. Each column of mercury in the manometer (G) was covered with a small quantity of silicone oil to prevent evaporation of the mercury. The vapor in reservoir (H) was transferred to sample tube (K) by freezing with liquid nitrogen, after which sample tube (K) was sealed off below

FIGURE 4. VACUUM MANIFOLD

FIGURE 5. SCHEMATIC DIAGRAM OF VACUUM MANIFOLD.

the Solv-Seal joint with a gas-oxygen torch and turned right side up. The mass of vapor loaded into sample tube (K) was determined from the equation of state up to the second virial coefficient. Details of these calculations are presented in Appendix D. In the case where the desired pressure read on the manometer (G) exceeded the vapor pressure of methanol at 28.0°C , the sample tube (K) was loaded in two approximately equal increments.

A filled tube was inserted in the stainless steel case and placed in the vapor bath which was then brought up to the desired temperature in the range $220\text{--}300^{\circ}\text{C}$. The sample was stirred continuously while the count-rate was measured on a continuously recording count-rate-meter. After the count-rate leveled off, which usually required two days time, counts were taken on a scaler at intervals of about 4 hours until the agreement between successive count-rates was less than the statistical error of 0.3 percent for an accumulated count of 100,000. Tubes containing only the mercury vapor were counted twice, once during the methanol series and once during the acetone series. Each series consisted of five tubes loaded with mercury and organic compound at different densities, and one tube loaded with mercury alone. Since the mercury concentration was measured at five temperatures for each tube, each series took from 60 to 75 days to complete. The count-rate-meter and scaler were plugged into a constant voltage transformer to minimize errors due to line voltage fluctuations.

The volume of the sample tubes was measured at the conclusion of the experiments with the aid of the apparatus shown

schematically in Figure 6. The top of the sample tube was broken open and, after the tube was emptied and weighed, held above the surface of distilled water by means of an iron collar and two 2-oz magnets. The entire apparatus was evacuated, after which the tip was lowered below the water surface and atmospheric pressure was used to force the water into the sample tube. The volume of the tube was determined from the weight and density of water contained in it. Further details on volume calibration for the sample tubes and for the reservoir (H) in Figure 5 are presented in Appendix E.

FIGURE 6. SCHEMATIC DIAGRAM OF APPARATUS FOR DETERMINING SAMPLE TUBE VOLUME.

CHAPTER V

EXPERIMENTAL RESULTS

The solubility of mercury in compressed methanol and acetone was determined at five densities from 0.25 to 0.75 moles per liter and five temperatures from 220 to 300° C. The solubilities are shown in Table 1 as the ratio c_2/c_2^0 , where c_2^0 is the concentration of mercury atoms in the pure saturated vapor and c_2 is the concentration in the presence of the added gas. A complete tabulation of the raw data is presented in Appendix F. The ratio c_2/c_2^0 is equal to the ratio of the net count-rates as discussed in Appendix A. The gas densities were determined from the volume of the sample tubes, the number of moles of methanol or acetone added to the sample tubes, and the number of moles of mercury in the gas phase as determined from the equation of state up to the second virial coefficient and the ratio c_2/c_2^0 . The calculation of gas densities is described in detail in Appendix D. The total gas pressures listed in Table 1 were also determined from the equation of state up to the second virial coefficient for the gas mixture. Details of this calculation are given in Chapter VII of this dissertation.

An inspection of Table 1 reveals that the ratio c_2/c_2^0 increases with increasing gas density at constant temperature and decreases with increasing temperature at constant gas density.

TABLE 1. SOLUBILITY OF MERCURY VAPOR IN COMPRESSED METHANOL AND ACETONE

	Sample Tube					
	1	2	3	4	5	6
<u>Methanol</u>						
220.0° C						
Gas density (1/v), moles/liter	0.00104	0.268	0.375	0.480	0.635	0.745
Pressure (p), atm	0.0423	10.1	13.8	17.1	21.6	24.5
Concentration ratio (c_2/c_2^0)	1.000	1.063	1.087	1.109	1.132	1.143
240.0° C						
1/v	0.00178	0.269	0.376	0.481	0.635	0.746
P	0.0748	10.7	14.5	18.1	23.0	26.3
c_2/c_2^0	1.000	1.059	1.083	1.105	1.125	1.136
260.0° C						
1/v	0.00290	0.270	0.377	0.482	0.637	0.747
P	0.1267	11.2	15.3	19.1	24.4	27.9
c_2/c_2^0	1.000	1.056	1.080	1.100	1.126	1.135
280.0° C						
1/v	0.00455	0.272	0.379	0.484	0.638	0.749
P	0.2064	11.8	16.1	20.1	25.8	29.6
c_2/c_2^0	1.000	1.055	1.081	1.099	0.120	1.131
300.0° C						
1/v	0.00691	0.274	0.382	0.486	0.641	0.752
P	0.3247	12.4	16.9	21.1	27.1	31.2
c_2/c_2^0	1.000	1.055	1.075	1.098	1.114	1.125
<u>Acetone</u>						
220.0° C						
1/v	0.00104	0.241	0.372	0.493	0.632	0.731
P	0.0423	8.8	12.8	16.1	19.1	21.0
c_2/c_2^0	1.000	1.077	1.115	1.154	1.191	1.216
240.0° C						
1/v	0.00178	0.242	0.373	0.494	0.633	0.732
P	0.0748	9.3	13.6	17.1	20.6	22.7
c_2/c_2^0	1.000	1.073	1.110	1.147	1.172	1.196
260.0° C						
1/v	0.00290	0.243	0.375	0.495	0.634	0.733
P	0.1267	9.8	14.4	18.2	22.0	24.5
c_2/c_2^0	1.000	1.068	1.104	1.140	1.165	1.185
280.0° C						
1/v	0.00455	0.245	0.376	0.497	0.636	0.735
P	0.2064	10.3	15.2	19.3	23.4	26.1
c_2/c_2^0	1.000	1.065	1.097	1.130	1.152	1.174
300.0° C						
1/v	0.00691	0.248	0.379	0.500	0.638	0.738
P	0.3247	10.9	16.0	20.4	24.9	27.8
c_2/c_2^0	1.000	1.058	1.089	1.123	1.146	1.164

Figures 7 and 8 show $\ln(c_2/c_2^0)$ as a function of the density of the gas. It was shown in Chapter II that at constant temperature

$$\ln\left(\frac{c_2}{c_2^0}\right) = \frac{v_2^{\ell} - 2B_{12}}{v} + \frac{v_2^{\ell} B_{11} - \frac{3}{2}C_{112}}{v^2} + \frac{v_2^{\ell} C_{111} - \frac{4}{3}D_{1112}}{v^3} + \dots \quad (50)$$

where v_2^{ℓ} is the molar volume of liquid mercury and the other terms remain as previously defined. The mixed second virial coefficient may be calculated from the initial slopes of the curves in Figures 7 and 8. In practice, the $\ln(c_2/c_2^0)$ versus $1/v$ data were subjected to a regression analysis to determine the most statistically significant least squares polynomial [32] using a computer program which is listed in Appendix G. In order to force the polynomial through the origin, the abscissa was translated by subtracting the density of pure saturated mercury vapor at each temperature from the total gas density at each pressure. At the highest temperature and lowest pressure, the density of pure mercury vapor was only about 2.8 percent of the total gas density. A discussion of the effect of the translation of the abscissa on the accuracy of the results is included in the next chapter.

The computer program calculated polynomials from first order up to fifth order which is an exact fit of the data since there are five data points at each temperature and the polynomials

FIGURE 7. THE CONCENTRATION OF MERCURY IN SATURATED GASEOUS MIXTURES WITH METHANOL

FIGURE 8. THE CONCENTRATION OF MERCURY IN SATURATED GASEOUS MIXTURES WITH ACETONE

were forced through the origin. The program also calculated the standard deviation of the fit, the standard deviation of each coefficient, and the F statistic for each polynomial. The F statistic was determined from an analysis of variance [32] and is a measure of the significance of a given order polynomial compared to the next lowest order polynomial with respect to fitting the data. F values are tabulated in the literature [33] according to confidence level, the order of the polynomial, and the degrees of freedom which is equal to the number of data points minus the order of the polynomial for polynomials passing through the origin. For statistical significance at a given confidence level, the calculated F value should be greater than the tabulated F value.

A summary of the standard deviations and the calculated F values for each polynomial is given in Table 2 along with tabulated F values for the 97.5, 99.0, and 99.5 percent confidence levels. The results shown in Table 2 indicate that in all but two cases, polynomials of order higher than two are not statistically significant at the 97.5 percent confidence level. Even in the two exceptional cases, methanol at 220 and 260° C, the second order polynomial is significant to a higher confidence level than the third order polynomial. Therefore, by choosing the 99 percent confidence level as the basis for the statistical hypothesis, the $\ln(c_2/c_2^0)$ versus $1/v$ data are best represented by a second order polynomial so that

TABLE 2. POLYNOMIAL REGRESSION ANALYSIS OF $\ln(c_2/c_2^0)$ vs. $1/v$

	Standard Deviation	Degrees of Freedom	Calculated F	Tabulated F at Given Confidence Level		
				97.5%	99.0%	99.5%
Methanol at 220.0° C						
1st order polynomial	1.03×10^{-2}	4	----	----	----	----
2nd " "	2.02×10^{-3}	3	100.	16.0	30.8	49.8
3rd " "	3.89×10^{-4}	2	79.1	32.2	99.2	199.0
4th " "	4.91×10^{-4}	1	0.253	900	5,630	22,500
5th " "	0	0	----	----	----	----
240.0° C						
1st order polynomial	9.78×10^{-3}	4	----	----	----	----
2nd " "	2.58×10^{-3}	3	54.4	16.0	30.8	49.8
3rd " "	1.42×10^{-3}	2	7.88	39.2	99.2	199.0
4th " "	9.27×10^{-4}	1	3.72	900	5,630	22,500
5th " "	0	0	----	----	----	----
260.0° C						
1st order polynomial	8.15×10^{-3}	4	----	----	----	----
2nd " "	2.87×10^{-3}	3	29.2	16.0	30.8	49.8
3rd " "	7.49×10^{-4}	2	42.1	39.2	99.2	199.0
4th " "	9.32×10^{-4}	1	0.295	900	5,630	22,500
5th " "	0	0	----	----	----	----
280.0° C						
1st order polynomial	9.30×10^{-3}	4	----	----	----	----
2nd " "	2.75×10^{-3}	3	42.9	16.0	30.8	49.8
3rd " "	1.97×10^{-3}	2	3.84	39.2	99.2	199.0
4th " "	1.41×10^{-3}	1	2.91	900	5,630	22,500
5th " "	0	0	----	----	----	----
300.0° C						
1st order polynomial	9.26×10^{-3}	4	----	----	----	----
2nd " "	2.61×10^{-3}	3	47.4	16.0	30.8	49.8
3rd " "	2.50×10^{-3}	2	12.6	39.2	99.2	199.0
4th " "	3.09×10^{-3}	1	0.311	900	5,630	22,500
5th " "	0	0	----	----	----	----

TABLE 2. (Cont.)

	Standard Deviation	Degrees of Freedom	Calculated F	Tabulated F at Given Confidence Level		
				97.5%	99.0%	99.5%
Acetone at 220.0° C						
1st order polynomial	6.55×10^{-3}	4	----	----	----	----
2nd " "	1.17×10^{-3}	3	122.0	16.0	30.8	49.8
3rd " "	1.31×10^{-3}	2	0.404	39.2	99.2	199.0
4th " "	1.67×10^{-3}	1	0.235	900	5,630	22,500
5th " "	0	0	----	----	----	----
240.0° C						
1st order polynomial	9.10×10^{-3}	4	----	----	----	----
2nd " "	2.82×10^{-3}	3	38.8	16.0	30.8	49.8
3rd " "	3.18×10^{-3}	2	0.360	39.2	99.2	199.0
4th " "	3.87×10^{-3}	1	0.345	900	5,630	22,500
5th " "	0	0	----	----	----	----
260.0° C						
1st order polynomial	8.82×10^{-3}	4	----	----	----	----
2nd " "	3.17×10^{-3}	3	28.0	16.0	30.8	49.8
3rd " "	2.58×10^{-3}	2	2.54	39.2	99.2	199.0
4th " "	3.24×10^{-3}	1	0.264	900	5,630	22,500
5th " "	0	0	----	----	----	----
280.0° C						
1st order polynomial	8.10×10^{-3}	4	----	----	----	----
2nd " "	2.46×10^{-3}	3	40.5	16.0	30.8	49.8
3rd " "	2.97×10^{-3}	2	0.053	39.2	99.2	199.0
4th " "	3.58×10^{-3}	1	0.376	900	5,630	22,500
5th " "	0	0	----	----	----	----
300.0° C						
1st order polynomial	6.43×10^{-3}	4	----	----	----	----
2nd " "	3.30×10^{-3}	3	122.0	16.0	30.8	49.8
3rd " "	2.65×10^{-3}	2	2.67	39.2	99.2	199.0
4th " "	3.61×10^{-3}	1	0.073	900	5,630	22,500
5th " "	0	0	----	----	----	----

$$\ln\left(\frac{c_2'}{c_2^o}\right) = \frac{a}{v} + \frac{b}{v^2} \quad (59)$$

From a comparison between equations 50 and 59, it is obvious that

$$a = v_2^\ell - 2B_{12} \quad (60)$$

$$b = \left(v_2^\ell B_{11} - \frac{3}{2}C_{112}\right) + \left(v_2^\ell C_{111} - \frac{4}{3}D_{1112}\right) + \dots \quad (61)$$

Equation 61 can be used to calculate B_{12} since the coefficient a is obtained from the regression analysis and values of v_2^ℓ are tabulated in the literature [34]. However, equation 61 can only be used to obtain an estimate of C_{112} because a second order polynomial is used to fit an infinite polynomial series and all terms of order higher than two in the infinite series must be assumed to equal zero in order to calculate C_{112} . The equations used to calculate the interaction virial coefficients are

$$B_{12} = \frac{v_2^\ell - a}{2} \quad (62)$$

$$C_{112} \approx \frac{2}{3}(B_{11}v_2^\ell - b) \quad (63)$$

Values of B_{11} , the second virial coefficient for pure methanol or acetone, in the range 220 to 300° C were obtained from Rowlinson [35] and Brown and Smith [36], respectively. Table 3 contains a listing of a , b , B_{12} , B_{11} , and C_{112} along with the standard deviations of a and b as determined from the regression analysis. The standard deviation of a was used to calculate the standard confidence interval for B_{12} . A detailed discussion on experimental precision and accuracy is presented in the next chapter. Also included in Table 3 are values of B_{22} , the second virial coefficient for pure mercury, as calculated by Douglass, Ball, and Ginnings [37] from measured thermodynamic data.

TABLE 3. POLYNOMIAL AND VIRIAL COEFFICIENTS FOR MERCURY-METHANOL
AND MERCURY-ACETONE SYSTEMS^(a)

Temperature, ° C	a, cm ³ /mole	b, cm ⁶ /mole ²	B ₁₂ cm ³ /mole	B ₁₁ ^(b) cm ³ /mole	C ₁₁₂ ^(c) cm ⁶ /mole ²	B ₂₂ ^(d) cm ³ /g-atom
Mercury-Methanol						
220.0	268±7	-116±12	-126±3	-250	75	-109
240.0	255±9	-109±15	-120±4	-220	71	-101
260.0	239±10	- 89±16	-112±5	-195	57	- 93
280.0	243±10	-103±16	-114±5	-175	67	- 87
300.0	236±9	-103±15	-110±5	-157	67	- 81
Mercury-Acetone						
220.0	327±4	- 79±7	-156±2	-398	49	-109
240.0	323±11	-107±17	-154±5	-360	68	-101
260.0	308±12	-102±19	-146±6	-326	65	- 93
380.0	288±9	- 95±15	-136±4	-298	60	- 87
300.0	261±12	- 70±20	-123±6	-273	44	- 81

(a) Mercury is component 2.

(b) Obtained from Rowlinson [35] and Brown and Smith [36].

(c) Estimated value.

(d) Calculated by Douglas, Ball, and Ginnings [37].

CHAPTER VI

PRECISION AND ACCURACY

At the outset it is necessary to define the term error and to distinguish between the terms accuracy and precision. The error of a measurement is the difference between the observed or measured value and the true value of the quantity measured. The error of a measurement is a measure of the accuracy of that measurement. In those cases in which the true value of a quantity is not known with any degree of exactness, it is necessary to express the exactness of a measurement in some way that does not involve a knowledge of the error. This may be done by obtaining the arithmetical mean of a number of measurements and finding the difference between the value of a given measurement and the average value. This difference may be called the deviation of that particular measured value. The magnitude of the deviations of a series of measurements is a measure of the precision of measurement. It is seen, then, that accuracy expresses the correctness of a measurement and precision the reproducibility of a measurement.

In physical chemistry experiments, it is often not practical to determine the precision of a measurement by repeating the measurement a number of times in order to find how much the values scatter about the mean. Therefore, it may be necessary to estimate the precision of a measurement from a single performance of that

measurement. The following paragraphs discuss the estimation of precision for each class of observed or measured values from the experimental work of this dissertation.

Count-Rate

The occurrence of nuclear disintegrations is a random phenomenon subject to established methods of statistical analysis. The standard deviation for a given number of disintegrations is equal to the square root of the number of disintegrations [38]. If a reasonably large number of counts has been obtained that number may be used in place of the number of disintegrations for the purpose of evaluating the standard deviation. In this work, 100,000 counts were accumulated for gross counting and 60,000 counts were accumulated for the background which remained constant at about 1,000 counts/min. The gross counting time varied from 1 to 10 minutes depending upon the concentration of mercury vapor in the gas phase. The error in counting time is negligible since the scaler was equipped with an electro-mechanical timer. Therefore, the gross counting rate ranged from $10,000 \pm 32$ to $100,000 \pm 316$ counts/min and the background was $1,000 \pm 4$ counts/min.

The standard deviation of the difference in two counting rates is given by the root-mean-square of the individual deviations [38]. The net count-rate ranged from 9,000 to 99,000 counts/min with standard deviations of $\sqrt{32^2 + 4^2}$ or 32 counts/min and $\sqrt{316^2 + 4^2}$ or 316 counts/min, respectively. Therefore, the fractional deviation in net count-rate is $32/9,000$ or 0.0036. To obtain the standard deviation of the ratio of two count-rates we must

assume that the two fractional deviations of the rates are not simply additive but on the average combine to give a root-mean-square deviation [38]. Therefore, the fractional deviation of the ratio is equal to $\sqrt{0.0036^2 + 0.0036^2}$ or 0.0051.

In calculating the ratio of two count-rates, it is necessary to correct for radioactive decay. The correction is an exponential function of the decay constant and the decay time as discussed in Appendix A. The error in decay time is negligible and the decay constant, which is inversely proportional to half-life, has an uncertainty of 0.4 percent [39]. Since both the numerator and denominator of the count-rate ratio must be corrected for radioactive decay, one can calculate the deviation that occurs when the decay time of one is x fraction of the decay time of the other. For this case, the ratio of decay corrections is $e^{-x\lambda t}/e^{-\lambda t}$, or $e^{-(x-1)\lambda t}$ where λ is the decay constant and t is the decay time. If one uses an uncertainty of 0.4 percent for the decay constant, the ratio of decay corrections can become $e^{-x(1.004\lambda)t}/e^{-1.004\lambda t}$ or $e^{-(x-1)1.004\lambda t}$. The fractional deviation caused by the uncertainty in the decay constant is then $e^{-(x-1)1.004\lambda t} - e^{-(x-1)\lambda t} / e^{-(x-1)\lambda t}$, or $e^{-(x-1)0.004\lambda t} - 1$. When x equals 1, the decay times are equal and the deviations cancel out. When x equals zero, one of the count-rates in the ratio is not corrected for decay and the fractional deviation is equal to $e^{0.004\lambda t} - 1$. Since the maximum decay time encountered during the experiments was 75 days, the maximum fractional deviation due to the uncertainty in the decay constant is $e^{0.004 \times \frac{0.693}{46.59d} \times 75d} - 1$, or 0.0045. The estimation of an average fractional deviation due to this

uncertainty is difficult because of the variability in both x and t . However, for the purpose of error estimation it is assumed that the average fractional deviation is the average of the maximum and minimum deviations, or 0.0023. Since the deviations due to counting statistics and decay corrections are probably not compensating errors, the total fractional deviation in the count-rate ratio is simply the sum of the two individual fractional deviations, or 0.0074.

$$\frac{\ln(c_2/c_2^0)}{}$$

The ratio, c_2/c_2^0 , where c_2 is the concentration of mercury in the compressed gas and c_2^0 is the concentration which mercury would have in the gas phase if it were present as a pure saturated vapor, is equal to the count-rate ratio as discussed in Appendix A. However, an additional deviation must be considered because of the variability of the inside diameter of the precision bore tubing since mercury concentrations were compared between two different tubes. The manufacturer's specification lists the tubing ID as 0.1968 ± 0.0002 in. for a fractional deviation of 0.0010. Since the tube volume is proportional to the square of the diameter, the fractional deviation in volume is 0.0020. Taking into account the possibility of compensating errors, the overall fractional deviation in c_2/c_2^0 is

$$\sqrt{0.0074^2 + 0.0020^2} = 0.0077.$$

In order to determine the fractional deviation in $\ln(c_2/c_2^0)$ it is useful to write the following inequality based on the fractional deviation in c_2/c_2^0 :

$$0.9923 \left(\frac{c_2}{c_2^0} \right) < \left(\frac{c_2}{c_2^0} \right) < 1.0077 \left(\frac{c_2}{c_2^0} \right) \quad (64)$$

Taking the natural logarithm of the above relation yields

$$\ln \left(\frac{c_2}{c_2^0} \right) + \ln 0.9923 < \ln \left(\frac{c_2}{c_2^0} \right) < \ln \left(\frac{c_2}{c_2^0} \right) + \ln 1.0077 \quad (65)$$

or

$$\ln \left(\frac{c_2}{c_2^0} \right) - 0.0077 < \ln \left(\frac{c_2}{c_2^0} \right) < \ln \left(\frac{c_2}{c_2^0} \right) + 0.0077 \quad (66)$$

In other words, the absolute deviation in the $\ln(c_2/c_2^0)$ is 0.0077. Since values of the $\ln(c_2/c_2^0)$ range from 0.0535 to 0.1956 (refer to Figures 7 and 8), the fractional deviation in the $\ln(c_2/c_2^0)$ ranges from 0.0594 to 0.144. It is interesting to note that a 0.8 percent deviation in c_2/c_2^0 can become a 14 percent deviation in $\ln(c_2/c_2^0)$. This fact points out the value of using a curve fitting technique to estimate the initial slopes of the $\ln(c_2/c_2^0)$ versus $1/v$ curves.

Pressure

Pressure measurements were made with a U-tube mercury manometer which was read with a 10-cm. Gaertner cathetometer. The precision of the cathetometer was experimentally determined to be

± 0.001 cm. Since each leg of the manometer had to be corrected for a zero reading, the overall precision of the pressure readings is ± 0.004 cm of Hg. The range of pressure values is from 3.211 to 9.670 cm of Hg so that the fractional deviation ranges from 0.004 to 0.0012. The accuracy of the pressure measurements should be about the same as the precision since the absolute pressure on the low pressure side of the manometer was determined to be 4×10^{-6} cm of Hg with a McLeod gauge.

Volume

Volumes were measured by the pycnometric method using water as the liquid as described in Appendix E. The precision and accuracy of this method is estimated to be about 0.3 percent.

Temperature

The temperature of the constant temperature bath and of the distilled water used for the pycnometric measurements was measured with a mercury thermometer graduated in tenths of a degree Centigrade. Therefore, the precision of these thermometer readings is estimated to be $\pm 0.05^{\circ}$ C. The accuracy of these thermometer readings was determined by taking readings in an ice bath and in a water bath at about 25° C alongside thermometer no. 5611221 which was calibrated by the National Bureau of Standards. This calibration technique indicated that the accuracy of the thermometer readings was about $\pm 0.07^{\circ}$ C.

The temperature of the vapor bath at the top of the sample tube was measured with a copper-constantan thermocouple in conjunction with a universal potentiometer and a hanging-wire galvanometer.

The thermocouple potential could be determined with a precision of ± 0.0005 mv so that the precision of the temperature readings is $\pm 0.01^{\circ}$ C. The accuracy of the temperature readings was determined by checking the thermocouple readings against five known temperature standards as described in Appendix B. This technique yielded a standard deviation of $\pm 0.06^{\circ}$ C for the accuracy of the corrected temperature readings.

The benzophenone used in the vapor bath was a high purity sample so that the vertical temperature gradient in the bath was probably very small. This fact was verified by the extreme care that had to be taken in order to prevent mercury vapor from condensing at the bottom of the sample tubes which contained mercury alone. If a temperature gradient would have existed in the bath, condensation of mercury vapor would be impossible because the liquid droplet of mercury was located at the top of the sample tube.

Gas Density

The gas density was determined from the moles of material loaded into the sample tube, the moles of mercury present in the vapor phase, and the volume of the sample tube. The uncertainty in the moles of mercury present in the vapor phase has a negligible effect on the gas density because the mole fraction of mercury in the added gas is very small. The moles of material loaded into the sample tube was determined from the equation of state up to the second virial coefficient as discussed in Appendix D. The precision of this calculation can be estimated from the precision of the pressure, volume,

and temperature measurements. Assuming that all errors are not simultaneously at their maximum value, the fractional deviation in the number of moles loaded into the sample tubes is $\sqrt{0.0012^2 + 0.0030^2 + 0.0002^2}$, or 0.0033. The accuracy of the equation of state method is difficult to determine. One approach is to compare results obtained using the ideal gas law with results obtained using the virial equation. In this case, the maximum deviation between the two methods is about 1 percent. Therefore, it is probably safe to assume that the fractional error in the number of moles loaded into the tubes is within 0.01.

The fractional error in the gas density, assuming compensating errors, can be determined from the fractional errors in n and v to be $\sqrt{0.010^2 + 0.0030^2}$, or 0.0104.

B_{12}

An estimate of the fractional deviation in B_{12} can be obtained from the fractional deviation in $\ln(c_2/c_2^0)$ and the fractional error in gas density by assuming a simple functional relationship among B_{12} , $\ln(c_2/c_2^0)$, and $1/v$. In this case, using an average value for the fractional deviation in $\ln(c_2/c_2^0)$, the fractional deviation in B_{12} is $\sqrt{0.0917^2 + 0.0104^2}$, or 0.0924. The fractional deviation in B_{12} determined from a statistical analysis of the least squares fit is about 0.05 in most cases. Therefore, the least squares second-order polynomial does a good job of fitting the data and B_{12} has a precision of about 5 percent.

Errors of Method

Errors arise as a result of approximations and assumptions made in the theoretical development of the equation used to calculate B_{12} (equation 50). These assumptions are listed near the end of Chapter II and an attempt will be made to estimate the error caused by each of them.

The first assumption is that none of the methanol or acetone gas (or vapor) dissolves in the liquid mercury. An exhaustive search of the literature failed to uncover data on the solubility of any gas in liquid mercury except for some work by Moss [40] in which he could detect no indication of helium in mercury after 4 days at 400 psia and 20° C. The sensitivity of Moss' method was such that the maximum solubility of helium in mercury under his experimental conditions is about 7×10^{-6} mole fraction. Johnson and Shuttleworth [41] performed a theoretical analysis of the solubility of gases in liquid metals and showed that the heat of solution can be estimated from the surface area of the gaseous atom or molecule and the surface tension of the liquid metal. The solubility is a negative exponential function of the heat of solution $\left[f(e^{-H/RT}) \right]$ so that methanol and acetone could be expected to be much less soluble in mercury than helium, since the surface area of these molecules is much greater than the surface area of a helium atom. Although solubility increases with absolute temperature, the increase in going from 20° C to 300° C is more than compensated for by the increase in molecular size of methanol or acetone compared to helium. By combining the work of Moss with that

of Johnson and Shuttleworth, it is possible to approximate the maximum solubility of methanol or acetone at 30 atm and 300° C in liquid mercury to be about 4×10^{-7} mole fraction. Obviously, any error introduced by a solubility of this magnitude would be negligible.

The second assumption is that liquid mercury is incompressible. Smith and Keyes [42] measured the mean compressibility coefficient, $\frac{1}{V} \frac{\Delta V}{\Delta p}$, of mercury and obtained a value of 6.97×10^{-6} at 300° C over a pressure range of 1 to 50 atm. Therefore, the fractional change in the volume of liquid mercury compressed from 1 to 30 atm is 2.09×10^{-4} . Such a small fractional change in volume should have a negligible effect on the accuracy of the data.

The third assumption is that the molar volume of saturated mercury vapor at its vapor pressure, v_2 , is much larger than the molar volume of the compressed gas mixture, v (methanol and mercury or acetone and mercury) at the same temperature. In the derivation of equation 50, if the terms in $1/v_2$ are not neglected the equation becomes

$$\ln\left(\frac{c_2}{c_2^0}\right) = \frac{v_2^L - 2B_{12}}{v} - \frac{v_2^L - 2B_{22}}{v_2} + \frac{v_2^L B_{11} - \frac{3}{2} C_{112}}{v^2} -$$

$$\frac{v_2^L B_{22} - \frac{3}{2} C_{222}}{v_2^2} + \frac{v_2^L C_{111} - \frac{4}{3} D_{1112}}{v^3} - \frac{v_2^L C_{222} - \frac{4}{3} D_{1112}}{v_2^3} + \dots \quad (67)$$

As was mentioned previously, in the worst case $1/v_2$ is only 2.79 percent of $1/v$, and in most cases $1/v_2$ is a much smaller fraction of $1/v$. Furthermore, since B_{22} is the same order of magnitude as B_{12} (refer to Table 3), subtracting $1/v_2$ from $1/v$ (translation of the abscissa) should reduce the error in the initial slope of the $\ln(c_2/c_2^0)$ versus $1/v$ curve, caused by neglecting terms in $1/v_2$ and its powers, to a negligible amount.

The fourth and final assumption is that the mole fraction of mercury vapor, x_2 , in the gas mixture is very small. The largest value of x_2 obtained under the experimental conditions is about 0.03 at a temperature of 300°C and a pressure of 10.9 atm. At lower temperatures and higher gas pressures, x_2 is much smaller. By substituting values of 0.03 for x_2 and 0.97 for x_1 in the derivation of equation 50, the first part of the equation becomes

$$\ln\left(\frac{c_2}{c_2^0}\right) = \frac{v_2^2 - 2(0.97B_{12} + 0.03B_{22})}{v} + \dots \quad (68)$$

Since B_{12} equals $-123\text{cm}^3/\text{mole}$ and B_{22} equals $-81\text{cm}^3/\text{g-atom}$, the maximum error introduced by assuming x_2 equal to zero is $[123 - 0.97(123) - 0.03(81)]/123$, or 1.03 percent.

Other Sources of Error

Any impurities that may be present in the pure components (mercury, methanol, and acetone) can cause an error in the results. However, because of the nature of the starting materials and the

procedures used in loading the sample tubes, it is believed that impurities were reduced to negligible levels. A detailed discussion on sample purity is given in Appendix C.

CHAPTER VII
DISCUSSION OF RESULTS

Second Virial Coefficient of Interaction

The experimental values of the second virial coefficients of interaction, listed in Table 3, may be compared with those calculated by various methods. Prausnitz and Gunn [43] showed that for ideal binary mixtures, where the volumes of the pure components are additive at constant pressure and temperature (Amagat's law), the virial coefficients of interaction become

$$B_{12} = \frac{1}{2}(B_{11} + B_{22}) \quad (69)$$

$$C_{112} = 1/3(2C_{111} + C_{222}) - (B_{11} - B_{22})^2 \quad (70)$$

$$C_{112} = 1/3(C_{111} + 2C_{222}) - (B_{11} - B_{22})^2 \quad (71)$$

Equations 69, 70, and 71 lead to the following for the virial coefficients of the mixture:

$$B_m = x_1 B_{11} + x_2 B_{22} \quad (72)$$

$$C_m = x_1 C_{111} + x_2 C_{222} - 3x_1 x_2 (B_{11} - B_{22})^2 \quad (73)$$

Equations 72 and 73 and similar equations for the higher virial coefficients are equivalent to Amagat's law of additive volumes or to the identical statement that the compressibility factor of a mixture at constant temperature and pressure is a straight-line function of the composition. Unfortunately, this ideal solution case is very rarely valid even for simple gases, and the more general approach has been to attempt a formulation of an intermolecular potential function applicable to unlike molecules. Values of B_{12} calculated from equation 69 using the values of B_{11} and B_{22} shown in Table 3 are plotted as a function of temperature in Figures 9 and 10 (curve a in both figures) for mercury-methanol and mercury-acetone, respectively, along with the experimental values of B_{12} . The lack of agreement is obvious.

Mercury-methanol and mercury-acetone are nonpolar-polar mixtures. These systems are characterized by the fact that the polar molecule (methanol or acetone) polarizes the nonpolar component (mercury). In order to calculate interaction virial coefficients for mixtures, it is necessary to know the force constants between unlike molecules in the mixture. Unfortunately, the best we can do is to make use of empirical combining laws which relate the force constants between unlike molecules to those between like molecules.

FIGURE 9. SECOND VIRIAL COEFFICIENTS OF INTERACTION FOR MERCURY-METHANOL SYSTEM

FIGURE 10. SECOND VIRIAL COEFFICIENTS OF INTERACTION FOR MERCURY-ACETONE SYSTEM

Hirschfelder, Curtiss, and Bird [18] have shown that the effective total energy of interaction between a polar and a nonpolar molecule has the same form as that between two nonpolar molecules. Therefore, for calculation of B_{12} , the tables of $B^*(T)$ as a function of T^* for the Lennard-Jones potential may be used.

The force constants describing the potential of interaction between a polar (subscript p) and a nonpolar (subscript n) molecule may be obtained from the following empirical combining laws given by Hirschfelder, et al. [18]:

$$\sigma_{np} = \frac{1}{2}(\sigma_n + \sigma_p) \xi^{-1/6} \quad (74)$$

$$\epsilon_{np} = \sqrt{\epsilon_n \epsilon_p} \xi^2 \quad (75)$$

The factor ξ is given by

$$\xi = \left[1 + \frac{1}{2} \frac{\alpha_n \mu_p^*}{\sigma_n^3} \sqrt{\frac{\epsilon_p}{\epsilon_n}} \right] = \left[1 + 0.892 \frac{\alpha_n t_p^*}{(b_0)_n} \sqrt{\frac{\epsilon_p}{\epsilon_n}} \right] \quad (76)$$

since

$$t_p^* = \frac{\mu_p^*}{\sqrt{8}} \quad (77)$$

and in which α is the polarizability of the nonpolar molecule in cubic angstroms, σ_n is the collision diameter of the nonpolar

molecule in angstroms, and $(b_o)_n$ is expressed in cm^3 per g-mole.

The values of the various parameters used in equations 74, 75, and 76 are summarized in Table 4 along with some additional data which is needed later. Except for mercury, the force constants were determined from experimental values of second virial coefficients. The force constants for mercury were calculated by Stubbley and Rowlinson [31] from the work of Douglas, Ball, and Ginnings [37] on the thermodynamic properties of mercury. The polarizability of mercury was calculated from the dielectric constant of mercury vapor [34] by the Clausius-Mosotti relation [18].

Values of B_{12} calculated from the interaction force constants obtained from equations 74, 75, and 76 are shown plotted as curve b for mercury-methanol and mercury-acetone in Figures 9 and 10, respectively. The agreement between experimental and calculated values is very good for the mercury-methanol system, but not as good for the mercury-acetone system.

Reid and Sherwood [19] use a slightly different definition for the empirical factor ξ . They define the factor, ξ' , as

$$\xi' = \left[1 + \frac{1}{4} \frac{\alpha_n \mu_p^2}{\left(\frac{\sigma_n + \sigma_p}{2} \right)^6 \sqrt{\epsilon_n \epsilon_p}} \right] \quad (78)$$

TABLE 4. MOLECULAR FORCE CONSTANTS^(a)

Item	Mercury	Methanol	Acetone	Ethane	Propane
Lennard-Jones potential					
$\epsilon_n/k, ^\circ K$	610 [31, 37]			243 [18]	242 [18]
$\sigma_n, \text{\AA}$	2.85 [31, 37]				
$(b_0)_n, \text{cm}^3/\text{g-mole}$	29.19 [31, 37]				
Polarizability (α_n), cm^3	5.39×10^{-24} [18, 34]				
Stockmayer potential					
$\epsilon_p/k, ^\circ K$		634 [35]	479 [36]		
$\sigma_p, \text{\AA}$		2.40 [35]	3.68 [36]		
t_p^*		0.8 [35]	0.8 [36]		
Collision diameter due to nonpolar forces only (σ_p^1), $\text{\AA}$		4.12 [19]	5.00 [19]		

(a) Numbers in brackets are references.

Since

$$\mu_p^{*2} = \frac{\mu_p^2}{\epsilon_p \sigma_p^3} \quad (79)$$

$$\xi' = \left[1 + \frac{1}{2} \frac{\alpha_n \mu_p^{*2} \sigma_p^3}{\left(\frac{\sigma_n + \sigma_p}{2} \right)^6 \sqrt{\frac{\epsilon_p}{\epsilon_n}}} \right] =$$

$$\left[1 + 0.892 \frac{\alpha_n t_p^{*} (b_o)_p}{\left\{ \frac{(b_o)_n^{1/3} + (b_o)_p^{1/3}}{2} \right\}^6 \sqrt{\frac{\epsilon_p}{\epsilon_n}}} \right] \quad (80)$$

However, for the systems mercury-methanol and mercury-acetone, values of ξ' and ξ differ by only about four parts in ten thousand so that the simple form of equation 76 is much more preferable than equation 80.

Blanks and Prausnitz [44] have presented a method for calculating B_{12} for polar-nonpolar binary mixture which corrects for the displacement of the dipole from the center of the polar molecule and which emphasizes many of the nonpolar characteristics of the polar material. In such systems, interaction parameters are estimated from modified Lennard-Jones parameters as

$$\sigma_{np}' = \frac{1}{2}(\sigma_n + \sigma_p') \xi'^{-1/6} \quad (81)$$

$$\epsilon'_{np} = \epsilon_n \epsilon'_p \xi'^{1,2} \quad (82)$$

$$\xi'^{1,2} = \left[1 + \frac{1}{2} \frac{K_p \alpha_n \mu_p^2}{\left(\frac{\sigma_n + \sigma'_p}{2} \right)^6 \sqrt{\epsilon_n \epsilon'_p}} \right] \quad (83)$$

The constant K_p reflects the displacement of the polar dipole from the center of the molecule. K_p is often assumed to be unity, but this can be a very poor assumption. The parameters σ'_p and ϵ'_p are hybrids in that they apply to polar molecules but emphasize nonpolar intermolecular forces of the species.

Blanks and Prausnitz [44] define σ'_p as

$$\sigma'_p = 0.84 v_c^{1/3} \quad (84)$$

where v_c is the critical molar volume of the polar molecule in $\text{cm}^3/\text{g-mole}$. Equation 84 is the same form as the empirical correlation for nonpolar molecules. Since polar forces do not seriously affect the molar volume at the critical point, equation 84 is an approximate method for estimating the collision diameter due to nonpolar forces only.

The term ϵ'_p is defined by Blanks and Prausnitz [44] as the Lennard-Jones energy parameter of the hydrocarbon homomorph of the polar molecule. The homomorph of a polar molecule is a nonpolar molecule having very nearly the same size and shape as those of the polar molecule. Figures 11 and 12 depict Stuart models of methanol

and ethane, and propane, acetone, and isobutane, respectively. In these models, the atoms are represented by spheres of appropriate relative diameters and facings on a scale proportional to the actual interatomic distances. It is clear from Figures 11 and 12 that ethane is the hydrocarbon homomorph of methanol and propane is the hydrocarbon homomorph of acetone. Appropriate values of σ_p' and ϵ_p'/k (ϵ_n/k of the hydrocarbon homomorph) for methanol and acetone are listed in Table 4.

Values of B_{12} calculated from the interaction force constants of Blanks and Prausnitz [44] with K_p equal to unity are shown plotted as curve c for mercury-methanol and mercury-acetone in Figures 9 and 10, respectively. In both cases, calculated absolute values of B_{12} are considerably less than experimental absolute B_{12} values. A possible explanation for this discrepancy is the fact that a dipole is not located at the center of a polar molecule. An exposed dipole will always have a larger induction energy associated with it than a central dipole. To a very good first approximation, the increase in induction energy is a function only of the dipole displacement from the molecular center and not of the temperature. Therefore, Blanks and Prausnitz [44] justify the use of an empirical, temperature-independent correction factor, K_p , which must never be less than unity. It will be equal to unity in those cases where the dipole is at the molecular center and will be larger than unity for all other cases, but it will always depend only on the properties of the polar molecule and not on those of the nonpolar molecule.

METHANOL

ETHANE

FIGURE II. STUART MODELS OF METHANOL AND ETHANE

PROPANE

ACETONE

ISOBUTANE

FIGURE 12. STUART MODELS OF PROPANE , ACETONE , AND ISOBUTANE

A trial-and-error calculational procedure was used to determine which value of K_p for methanol and acetone gave the best fit to the experimental data. The results yielded a value of 1.8 for K_p for methanol and 1.4 for K_p for acetone and the appropriate calculated values of B_{12} for mercury-methanol and mercury-acetone are shown plotted as curve d in Figures 9 and 10, respectively. In both cases, the agreement between experimental and calculated values of B_{12} is about within the experimental error. Blanks and Prausnitz [44] determined K_p for acetone to be about 13 from experimental data on second virial coefficients of mixtures. In view of the very limited data available, not much confidence can as yet be placed on the reliability of values for K_p .

A plot of experimental values of B_{12} versus temperature for binary systems with mercury as one component is shown in Figure 13. Thus far, only five systems have been studied including the two systems described in this work. As one would expect, absolute values of B_{12} decrease with increasing temperature. In general, absolute values of B_{12} increase with increasing molecular size of the second component. Also, for molecules of about the same size, a polar molecule exhibits a much larger absolute value of B_{12} than a nonpolar molecule (acetone versus propane) because of the larger intermolecular forces caused by induction of the mercury atoms by the polar molecules.

Third Virial Coefficient of Interaction

The coefficient C_{112} , which represents the interaction of two molecules of methanol or acetone with an atom of mercury, is

FIGURE 13. EXPERIMENTAL DETERMINATIONS OF INTERACTION SECOND VIRIAL COEFFICIENTS FOR BINARY SYSTEMS WITH MERCURY AS ONE COMPONENT

positive in the mercury-methanol and mercury-acetone systems. The positive value of C_{112} is partially responsible for the fact that the solubility of mercury in compressed methanol or acetone falls off from a linear proportionality to density with increasing density. The fact that the solubility increases more slowly as the density rises is also due to the added gas being imperfect so that its pressure does not increase linearly with its density; hence, the Poynting term is lower. However, the Poynting effect is small in comparison to the effect of C_{112} . The positive sign of C_{112} is also indicative of the fact that when the number of methanol or acetone molecules clustering around a mercury atom increases, then their mutual interactions will hinder the clustering process. The forces responsible for the mutual interactions could be either dipole formation or hydrogen bonding, both of which can cause dimerization. However, hydrogen bonding would be expected only with methanol which could form dimers of structure

Dipole interaction can, of course, occur with all polar molecules. Lambert, et al. [45] have proposed dimerization as an alternative to the Stockmayer potential for the treatment of intermolecular forces between polar molecules.

Pressure Correction

The effect of mercury on the observed gas pressure may be calculated by comparing the virial expansions for the pressure p_1 of n_1 moles of gas in a volume V in the absence of mercury with the pressure p of n_1 moles of gas and n_2 moles of mercury in the same volume V at the same temperature T . These pressures are given by

$$p_1 = \frac{n_1 RT}{V} + \frac{n_1^2 B_{11} RT}{V^2} + \frac{n_1^3 C_{111} RT}{V^3} + \dots \quad (85)$$

$$p = \frac{(n_1 + n_2) RT}{V} + \frac{(n_1 + n_2)^2 B_m RT}{V^2} + \frac{(n_1 + n_2)^3 C_m RT}{V^3} + \dots \quad (86)$$

From equations 29 and 30 and the fact that $x_1 = \frac{n_1}{n_1 + n_2}$ and $x_2 = \frac{n_2}{n_1 + n_2}$, equation 86 can be transformed into

$$p = \frac{(n_1 + n_2) RT}{V} + \frac{n_1^2 B_{11} + 2n_1 n_2 B_{12} + n_2^2 B_{22}}{V^2} RT + \frac{(n_1^3 C_{111} + 3n_1^2 n_2 C_{112} + 3n_1 n_2^2 C_{122} + n_2^3 C_{222}) RT}{V^3} + \dots \quad (87)$$

Neglecting powers of n_2 high than the first, the correction, Δp , which must be applied to compensate for the presence of mercury is given by

$$\Delta p = p - p_1 = \frac{n_2 RT}{V} + \frac{2n_1 n_2 B_{12} RT}{V^2} + \frac{3n_1^2 n_2 C_{112} RT}{V^3} + \dots \quad (88)$$

The fractional correction in pressure is given by

$$\frac{\Delta p}{p} = \frac{n_2 + \frac{2n_1 n_2 B_{12}}{V} + \frac{3n_1^2 n_2 C_{112}}{V^2} + \dots}{n_1 + n_2 + \frac{n_1^2 B_{11} + 2n_1 n_2 B_{12}}{V} + \frac{n_1^3 C_{111} + 3n_1^2 n_2 C_{112}}{V^2} + \dots} \quad (89)$$

or

$$\frac{\Delta p}{p} = x_2 \left[\frac{1 + \frac{2B_{12}}{v_1} + \frac{3C_{112}}{v_1^2} + \dots}{1 + \frac{n_1 B_{11} + 2n_2 B_{12}}{(n_1 + n_2)v_1} + \frac{n_1 C_{111} + 3n_2 C_{112}}{(n_1 + n_2)v_1^2} + \dots} \right] \quad (90)$$

where $v_1 = V/n_1$, and so is the experimentally observed molar volume of the gas. By making use of the approximations $n_1/n_1 + n_2$ equals one and $n_2/n_1 + n_2$ equals zero, equation 90 can be simplified to

$$\frac{\Delta p}{p} = x_2 \left(\frac{1 + \frac{2B_{12}}{v_1} + \frac{3C_{112}}{v_1^2} + \dots}{1 + \frac{B_{11}}{v_1} + \frac{C_{111}}{v_1^2} + \dots} \right) \quad (91)$$

which can be mathematically approximated as

$$\frac{\Delta p}{p} = -x_2 \left(1 + \frac{2B_{12} - B_{11}}{v_1} + \frac{3C_{112} - C_{111} + B_{11}^2 - 2B_{11}B_{12} + \dots}{v_1^2} \right) \quad (92)$$

The minus sign in front of x_2 is added to indicate that Δp must be subtracted from the pressure reading, p , to obtain the pressure, p_1 , of the gas alone. The first term of this series, $-x_2$, is the correction for an ideal gas mixture of this composition, but even this differs from the correction usually applied which is $-x_2^0$, the mole fraction of mercury in the gas phase, calculated on the assumption that the concentration is that of the pure saturated vapor at the same temperature. Values of x_2 may be calculated from equation 50 since, for small values of n_2 , x_2/x_2^0 is about equal to c_2/c_2^0 .

Equation 92 was used to calculate $\Delta p/p$ for methanol and acetone at 260° C (above the critical temperatures) in the presence of mercury up to a gas density of one mole/liter. Unfortunately, values of C_{111} and C_{112} are not known with enough accuracy to perform the calculation at higher densities. Values of C_{111} were calculated from literature values of the Stockmayer force constants [35, 36] and all other necessary values for the virial coefficients were obtained from Table 3. Comparative values of $\Delta p/p$ are listed in Tables 5 and 6, for methanol and acetone, respectively, calculated

TABLE 5. PRESSURE CORRECTION FOR METHANOL ISOTHERM
IN THE PRESENCE OF MERCURY AT 260° C

Gas Density($\frac{1}{V}$), moles/liter	Measured Pressure(p), atm	$(\Delta p/p)_1^{(a)}$ ($\times 10^3$)	$(\Delta p/p)_2^{(b)}$ ($\times 10^3$)	$(\Delta p/p)_3^{(c)}$ ($\times 10^3$)	Percent Error In Corrected Pressure $(\Delta p/p)_3 - (\Delta p/p)_1$
0.1	4.290	-29.54	-29.58	-30.19	0.07
0.2	8.409	-15.07	-15.11	-15.76	0.07
0.3	12.359	-10.25	-10.30	-10.99	0.07
0.4	16.140	- 7.85	- 7.89	- 8.64	0.08
0.5	19.753	- 6.41	- 6.46	- 7.26	0.09
0.6	23.197	- 5.46	- 5.51	- 6.36	0.09
0.7	26.474	- 4.79	- 4.83	- 5.74	0.10
0.8	29.584	- 4.28	- 4.33	- 5.30	0.10
0.9	32.528	- 3.90	- 3.94	- 4.98	0.11
1.0	35.306	- 3.59	- 3.63	- 4.73	0.11

(a) From the normal vapor pressure of mercury.

(b) From the Poynting effect.

(c) From the equation 92.

TABLE 6. PRESSURE CORRECTION FOR ACETONE ISOTHERM
IN THE PRESENCE OF MERCURY AT 260° C

Gas Density ($\frac{1}{V}$), moles/liter	Measured Pressure (p), atm	$(\Delta p/p)_1^{(a)}$ ($\times 10^3$)	$(\Delta p/p)_2^{(b)}$ ($\times 10^3$)	$(\Delta p/p)_3^{(c)}$ ($\times 10^3$)	Percent Error in Corrected Pressure $(\Delta p/p)_3 - (\Delta p/p)_1$
0.1	4.233	-29.93	-29.98	-31.00	0.11
0.2	8.186	-15.48	-15.52	-16.63	0.12
0.3	11.862	-10.68	-10.73	-11.92	0.12
0.4	15.268	- 8.30	- 8.34	- 9.63	0.13
0.5	18.407	- 6.88	- 6.93	- 8.32	0.14
0.6	21.285	- 5.95	- 6.00	- 7.51	0.16
0.7	23.906	- 5.30	- 5.34	- 6.98	0.17
0.8	26.275	- 4.82	- 4.87	- 6.63	0.18
0.9	28.396	- 4.46	- 4.46	- 6.41	0.20
1.0	30.274	- 4.19	- 4.23	- 6.28	0.21

- (a) From the normal vapor pressure of mercury
(b) From the Poynting effect.
(c) From equation 92.

from the normal vapor pressure of mercury, from the Poynting effect, and from equation 92. An inspection of Tables 5 and 6 reveals that at a pressure of 35 atm, an error of about 0.1% is introduced into the methanol isotherm (the corrected pressure is 0.1% too high) if the pressure reading is corrected in the usual way, while for acetone at 30 atm, the error is about 0.2%. Thus, the effect of mercury solubility on measured gas isotherms at moderate pressures becomes significant only when the experimental error is less than 1 part in 500.

The question arises as to the effect of mercury solubility on gas isotherms at higher pressures. As can be seen from Tables 5 and 6, the error in pressure increases with increasing pressure. Jepson and Rowlinson [28] used equation 92 to calculate $\Delta p/p$ for ethane, propane, and butane at 275° C up to a gas density of 8 moles/liter. They used calculated values of B_{12} and C_{112} and found that at high densities (about 5 moles/liter) $\Delta p/p$ can become large and positive. A positive sign for $\Delta p/p$ means that the addition of mercury atoms at constant volume to the pure compressed gas results in a diminution of the pressure, that is, the partial molal volume of mercury in this region is negative. However, these results are open to question for two reasons. First of all, calculated rather than experimental values of B_{12} and C_{112} were used. Second, and more important, equation 92 was truncated after the $1/v^2$ term; at high gas densities it is very probable that virial coefficients higher than the third (terms in $1/v^3$) contribute significantly to the value of $\Delta p/p$. These points need to be resolved through experimental data

at gas densities up to 10 moles/liter.

Effect of Critical Temperature on Mercury Solubility

The critical temperature of methanol is 240.0° C [46] and that of acetone is 235.9° C [47]. Since mercury solubility was measured from 220 to 300° C in 20° intervals, the critical temperature was crossed in each case. However, no difference in behavior was detected for methanol and acetone vapor as compared to methanol and acetone gas (refer to Figures 7 and 8). Evidently, all the experiments were performed far enough away from the two-phase region of methanol and acetone so that the virial equation of state was always valid.

CHAPTER VIII

CONCLUSIONS

The concentration of mercury in compressed methanol is 14.3 percent greater than the concentration in pure mercury vapor at a temperature of 220° C and a methanol pressure of 24.5 atm. In compressed acetone, the concentration of mercury is 21.6 percent greater at the same temperature and an acetone pressure of 21.0 atm. The concentration ratios are accurate to within 1 percent. The solubility of mercury vapor in compressed methanol or acetone increases with increasing pressure and decreases with increasing temperature. There is no discontinuity in mercury solubility in crossing from methanol or acetone vapor to gas when the methanol or acetone is not near the two-phase region.

The second virial coefficient of interaction, B_{12} for the system mercury-methanol ranges from -126 to -110 cm³/g-mole in the temperature range of 220 to 300° C. For the same temperature range, B_{12} ranges from -156 to -123 cm³/g-mole for the system mercury-acetone. The values of B_{12} are precise to within 5 percent and accurate to within 10 percent. B_{12} for the mercury-methanol and mercury-acetone systems may be accurately estimated by the method of Blanks and Prausnitz [44] using values of 1.8 and 1.4 for the empirical constant, K_p , for methanol and acetone, respectively.

The solubility of mercury in methanol can cause an error of about 0.1 percent in the corrected pressure at 35 atm for the methanol isotherm at 260° C; that is, unless a correction is made for mercury solubility, the pressure determined by subtracting the normal vapor pressure of mercury from the gauge reading will be 0.1 percent too high. For acetone at 260° C and 30 atm, the error in pressure is about 0.2 percent. Therefore, the effect of mercury solubility on measured acetone isotherms at moderate pressures is significant only in cases where the experimental error is less than 1 part in 500.

The effect of mercury solubility on the accuracy of measured gas isotherms for other compounds depends upon the value of the second virial coefficient of interaction B_{12} for these compounds with mercury. Thus far, B_{12} has been experimentally determined for only five binary systems in which mercury is one component. Absolute values of B_{12} increase with increasing molecular size of the second component, and for molecules of about the same size, a polar molecule exhibits a much larger absolute value of B_{12} than a nonpolar molecule. The greater the absolute value of B_{12} , the larger the error to be expected in the gas isotherm measurements. The largest error at moderate pressures attributable to mercury solubility from the available experimental values of B_{12} is about 0.2 percent.

CHAPTER IX

RECOMMENDATIONS

The effect of mercury solubility on the accuracy of methanol and acetone isotherms at high pressures (> 35 atm) is still not known. The solubility measurements described in this dissertation should be extended to higher pressures to obtain accurate values of the third virial coefficients of interaction, C_{112} , and estimates of the fourth virial coefficients of interaction, D_{1112} . The method of Kay [48] should be used with gallium as the confining liquid to obtain very accurate p-V-T data for methanol and acetone so that accurate values of pure component third virial coefficients, C_{111} may be determined. The above data should then be used to calculate $\Delta p/p$ at high pressures. Of particular interest is whether $\Delta p/p$ becomes positive at high pressures.

APPENDIX A
RADIOACTIVITY AND RADIOACTIVE MERCURY

RADIOACTIVITY AND RADIOACTIVE MERCURY

Radioactivity

Radioactivity was accidentally discovered in 1895 by Becquerel as a consequence of experiments he was performing with uranium salts. Uranium is one of many natural occurring radioactive substances. All elements found in natural sources with atomic number greater than 83 (bismuth) are radioactive. Additional natural radioactivities have been discovered in potassium, rubidium, indium, platinum, and several of the rare earths. However, in these elements the particular isotope responsible for the radioactivity occurs in very small abundance or the half-lives are extremely long, making the activities very difficult to detect. Artificial radioactivity has been produced by bombarding stable elements with nuclear particles. At least one radioactive isotope is now known for every element in the periodic table, and some elements have as many as 20 or more. The measured half-lives range from a small fraction of a microsecond to many millions of years. Many artificially produced radioactivities have found important applications in research.

Radioactivity is the disintegration of an atomic nucleus and the disintegration process follows the laws of probability. If one considers a large initial number of radioactive atoms, N_0 , then the fraction remaining unchanged after time t may be taken as

$$\frac{N}{N_0} = e^{-\lambda t} \quad (93)$$

where N is the number of unchanged atoms after time t , and λ is a constant characteristic of the particular radioactive species. It can be shown by differentiation of equation 93 that the number of disintegrations per unit time is given by

$$-\frac{dN}{dt} = \lambda N \quad (94)$$

The unit of radioactivity is the curie which is defined as that quantity of a radioactive substance in which there are 3.700×10^{10} disintegrations per second.

The constant λ is known as the decay constant for the radioactive species and has units of reciprocal time. For most radioactive substances, no attempt to alter λ through variation of ordinary experimental conditions, such as temperature, pressure, chemical change, and gravitational, magnetic, or electric fields, has ever given a detectable effect. The characteristic rate of radioactive decay may conveniently be given in terms of the half-life, $t_{1/2}$, which is the time required for an initial large number of atoms to be reduced to half that number by decay. Thus, at the time

$t = t_{1/2}$, $N = N_0/2$ and

$$e^{-\lambda t_{1/2}} = \frac{1}{2} \quad (95)$$

or

$$t_{1/2} = \frac{\ln 2}{\lambda} = \frac{0.69315}{\lambda} \quad (96)$$

In practical work with radioactive materials the number of atoms N is not directly evaluated, and even the rate of change, dN/dt , is usually not measured absolutely. The usual procedure is to determine, through an effect of the radioactivity, a quantity proportional to N . This quantity, termed the activity A , is equal to $k N$ or $k(-dN/dt)$ and has units of counts per unit time. The coefficient k , will depend on the nature of the detection instrument, the efficiency for the recording of the particular radiation in that particular instrument, and the geometrical arrangement of sample and detector. A usual feature of experimentation is careful precaution to keep all these factors under control.

The two most common forms of radioactive decay are α emissions and β emissions. An alpha particle is a helium nucleus and, as such, consists of two protons and two neutrons. Alpha emission, which occurs only among the heavier elements, always results in a reduction of the atomic number by 2 and of the mass number by 4.

Ordinary β decay is commonly found throughout the range of the periodic table. In this type of decay negative electrons are emitted and the atomic number is increased by one unit while the mass number remains constant. Two other types of β decay result in a decrease by one unit in atomic number; these are positron emission and capture of an orbital electron from the K shell by the nucleus. A positron is identical to a negative electron except that it has a positive charge. Most α - and β -decay processes leave the resulting nuclei in an excited state and are therefore followed by γ radiation. γ radiation is electromagnetic radiation given up by a nucleus in an excited state as it returns to the ground state. Since γ radiation has a much greater range (ability to penetrate matter) than α or β particles, in many studies in which a radioactive isotope is used as a tracer, it is the γ radiation which is detected.

Gamma radiation is commonly detected by an inorganic-crystal scintillator in which the absorbed radiation is converted to light energy through the luminescence process. Most commercial inorganic-crystal scintillators are sodium iodide activated with thallium to create fluorescent centers. The light is transmitted to a photo-multiplier tube in which it is converted to a current which is fed to succeeding electronic equipment for analysis. The electronic equipment usually consists of a preamplifier, an amplifier, and a scaler or a count-rate meter. Scintillation detectors have the advantage of higher efficiency for gamma counting and higher counting rates and shorter resolving times than are possible with other

detectors. Further details on radioactivity and radiation detection may be found elsewhere [49, 50, 51, 52].

Radioactive Mercury

The element mercury, atomic number 80, has seven stable isotopes and over twelve radioactive isotopes [53]. Of the radioactive isotopes, the one most suitable for tracer studies is ^{203}Hg (mass number of 203) because of its availability, half-life, and decay mode. The decay scheme for ^{203}Hg is shown in Figure 14 [39]. ^{203}Hg decays entirely by negative electron emission with a half-life of 46.59 days. Each β disintegration is accompanied by the emission of 0.279 million electron-volts (Mev) of γ radiation as the resulting thallium nucleus is transformed from an excited state to its ground state.

^{203}Hg was purchased from New England Nuclear as mercury metal with a specific activity of 53 millicuries/g. The method of preparation is neutron bombardment of ^{202}Hg and the radiochemical purity is listed as greater than 99 percent with the principal radioactive contaminant being ^{197}Hg [54]. No information is given on the chemical purity of the mercury metal, but the method of preparation suggests that it should be as least as good as the radiochemical purity.

The radioactive mercury metal was diluted with triple distilled stable mercury metal to a specific activity of 7.5 millicuries/g (dillution factor of about 7) because calculations and preliminary experiments indicated that this specific activity would

FIGURE 14. DECAY SCHEME FOR ^{203}Hg

yield a count-rate of from 10,000 to 100,000 count/min from mercury vapor in the temperature range 220 to 300° C in the apparatus shown in Figure 2. The tagged mercury metal was prepared about one week before use so that the ^{197}Hg activity ($t_{1/2} = 65$ hours) was reduced by about a factor of 10. Therefore, the ^{203}Hg tagged mercury metal used in the experiments described in this dissertation had a chemical and radiochemical purity of greater than 99.9 percent. Even if all the ^{203}Hg present in the tagged mercury had decayed to ^{203}Tl , the mole fraction of thallium in the sample would only be about 5×10^{-7} so that its effect on the experimental results would be insignificant.

In the experiments described in this dissertation, the measured parameter was the activity of ^{203}Hg . Since activity A , is equal to $k\lambda N$, and k remained constant throughout the experiments because of the fixed geometry of the radiation detector in relation to the sample tubes, it is obvious that the ratio of activities between sample tubes is equal to the ratio of mercury atoms. Furthermore, because of the fixed geometry and the use of precision bore sample tubes, the volume of the sample tube "visible" to the detector remained constant. Therefore, the ratio of activities between sample tubes is also equal to the ratio of mercury concentration, c_2/c_2^0 . The only additional precautions that needed to be taken was to use tagged mercury from the same batch (exactly the same specific activity) and to correct the count rates for radiation decay from an arbitrary base time according to equation 93. The delay of one week between

preparation and use of tagged mercury also insured that the sample was of uniform specific activity because enough time had been allowed for mixing by diffusion to occur.

APPENDIX B
THERMOCOUPLE CALIBRATION

THERMOCOUPLE CALIBRATION

The copper-constantan thermocouple was calibrated against five known temperature standards. These included the melting points of ice, tin, and lead, and a water bath at room temperature and a silicone oil bath at 111° C. The thermocouple was calibrated in the same type of glass tube as the well on the vapor bath, with the bead immersed in finely ground SiO₂. The precision potentiometer reading for the melting point of ice was determined by immersing the thermocouple in a slush bath of ice. The readings for the melting point of tin and lead were obtained by immersing the thermocouple in specially constructed furnaces which contained ultra-high purity samples of tin and lead in graphite crucibles. The melting points were certified as 231.88° C for tin and 327.43° C for lead by the National Bureau of Standards. The furnaces were able to maintain the metals at their melting points for about 10 minutes. The temperature of the water bath was determined by placing the bulb of thermometer no. 5611221 adjacent to the thermocouple junction, and the temperature of the silicone oil bath was similarly determined with thermometer no. 5907065. Both of these thermometers had been calibrated to the nearest 0.01° C by the National Bureau of Standards. In all cases, the thermocouple reference junction was immersed in a slush bath of ice.

The potentiometer readings for the five true temperatures were converted into temperature readings with the aid of a conversion

table [55], with the following results:

True Temperature, °C	Potentiometer Reading, mv	Temperature from Conversion Table, °C	Correction, °C
0.00	-0.0005	-0.01	+0.01
24.50	0.9648	24.39	+0.11
111.20	4.7887	110.84	+0.36
231.88	10.9555	230.86	+1.02
327.43	16.349	325.32	+2.11

The above data were used to fit the temperature correction to a polynomial function of the potentiometer reading in millivolts using a least squares computer technique. A second degree polynomial was found to be the most statistically significant with a standard deviation of 0.06° C. This polynomial was then used to calculate the appropriate potentiometer readings for the desired true vapor bath temperatures. The results are as follows:

True Vapor Bath Temperature, °C	Potentiometer Reading, mv
220.00	10.3132
240.00	11.3986
260.00	12.5029
280.00	13.6256
300.00	14.7632

APPENDIX C
PREPARATION OF METHANOL AND ACETONE

PREPARATION OF METHANOL AND ACETONE

The methanol and acetone used in the experiments described in this dissertation were purchased from Burdick & Jackson Laboratories, Inc., Muskegon, Michigan. These solvents, termed "Distilled-in-Glass" grade by the supplier, are spectrographic grade and are prepared by appropriate physical and chemical pretreatment followed by distillation in glass systems through efficient columns operated at high reflux ratios. The products are essentially pure and dry and contain no residue. They are shipped in amberglass bottles, under nitrogen. The supplier lists the maximum moisture content as 0.08% for methanol and 0.1% for acetone, as determined by the Karl-Fischer method.

Prior to loading the solvent into the sample tubes, a 5 ml portion was placed in the 25 ml round-bottom flask at the bottom of the degassing apparatus (F in Figure 5) along with 1 g of activated Linde Molecular Sieve Type 5A. The molecular sieve was activated at a temperature of 350° C under a vacuum of less than 10 microns Hg. Under these activation conditions, the water adsorption isotherm at 25° C indicates that at a loading of 1 g of H₂O/10 g of Type 5A molecular sieve the water partial pressure is about 1.8×10^{-2} mm of Hg [56]. Since the highest pressure used for loading the calibrated volume (H in Figure 5) with methanol or acetone was about 10 cm of Hg which corresponds to the vapor pressure of methanol at about 25° C, the maximum amount of water that could have been transferred to the

calibrated volume was about 1.8×10^{-4} mole fraction, even if the organic material contained as much as 2.5% moisture. At lower loading pressures and, therefore, lower solvent temperatures, the mole fraction of moisture that could have been transferred would be lower because the partial pressure of water vapor above the molecular sieve decreases rapidly with temperature at a constant sieve loading.

The precision of virial coefficient measurements depends in part upon the efficiency with which the liquid systems are degassed. The usual procedure consists of freezing the liquid, pumping away the noncondensable gases, melting, and refreezing. This process has to be repeated for many cycles and consequently is tedious and time consuming. Bell, et al. [57] have described a method which is similar to the technique of freeze drying and one cycle is sufficient to completely degas most organic liquids. Bell's method was used in this dissertation and the apparatus (F in Figure 5) consists of a Pyrex glass dewar and a detachable sample flask. The liquid to be degassed is frozen in the sample flask by liquid nitrogen and the entire apparatus is evacuated. Liquid nitrogen is placed in the central compartment of the dewar and removed from the sample flask. The frozen liquid slowly sublimates onto the cold glass surface, while noncondensable gases are continuously pumped away. These gases do not redissolve unless the sublimate thaws. A sample of 5 to 10 ml of liquid takes about 30 minutes to be degassed and less than 5 percent of the sample is lost in the process. After degassing, the frozen liquid is allowed to melt and refreeze at the bottom of the sample flask. The results of static measurements of the vapor pressure of

liquids degassed in this manner agree exactly with the literature values. [57]

APPENDIX D

**CALCULATION OF MASS OF METHANOL OR ACETONE
LOADED INTO SAMPLE TUBES AND GAS DENSITY**

CALCULATION OF MASS OF METHANOL OR ACETONE
LOADED INTO SAMPLE TUBES AND GAS DENSITY

The number of moles of methanol or acetone loaded into the sample tubes were calculated from the virial equation of state up to the second virial coefficient. Therefore,

$$n_1 = \frac{pV}{RT + B_{11}p} \quad (97)$$

Values of B_{11} for methanol and acetone at 28° C, the temperature of the constant temperature bath (I) (refer to Figure 5) were obtained from Lambert, et al. [45] The pressure was determined with the mercury manometer (G) and the volume was determined from the calibrated reservoir (H).

The gas density in a sample tube was calculated from the volume of the tube, the number of moles of organic material loaded into the tube, and the number of moles of mercury present in the vapor phase. The moles of mercury present in the vapor phase was also determined from the virial equation of state, so that

$$n_2^0 = \frac{pV}{RT + B_{22}p} \quad (98)$$

In equation 98, T is the absolute temperature of the benzophenone vapor bath, p is the vapor pressure of mercury at the appropriate temperature, and V is the volume of the sample tube. Values of B_{22} were obtained from Table 3. n_2^0 had to be corrected for the solubility of mercury in the compressed gas according to the following equation:

$$n_2 = n_2^0(c_2/c_2^0) \quad . \quad (99)$$

Values of (c_2/c_2^0) were obtained from Table 1. The gas density is then

$$\frac{1}{V} = \frac{n_1 + n_2}{V} \quad (100)$$

where $\frac{1}{V}$ is the density in moles/liter (reciprocal molar volume), n_1 is the moles of organic material present in the tube, n_2 is the moles of mercury present in the vapor phase, and V is the volume of the sample tube in liters.

APPENDIX E
VOLUME CALIBRATION

VOLUME CALIBRATION

The volume of the reservoir (H) (refer to Figure 5) and the sample tubes were determined in the same way that pycnometers are calibrated [58]. The method consists of filling the volume with deionized, double distilled water and weighing to determine the amount of water in the volumes. The volume is then calculated from the density of water at the appropriate temperature. The temperature of the water was kept constant by using distilled water that had been standing in the laboratory for a long period of time. For water at room temperature, the density decreases by about 0.03 percent per degree C rise in temperature. Changes in laboratory air pressure were insignificant because the density of pure water at room temperature and pressure is increased only by about 0.005 percent for a pressure increase of 1 atm. The effect of dissolved air on the density of water at room temperature is noticeable only in the 7th decimal place and is therefore insignificant for this work.

The cleaned vessels were weighed before and after filling with water. The vessels were filled by evacuation and subsequent immersion in a reservoir of distilled water. Small air bubbles were eliminated by injection of distilled water with a hypodermic needle and syringe. The effect of water adsorption on the outside surface of the vessel was standardized by wiping the glass surface carefully

with a lintless cloth and then allowing the vessel to stand for 15 to 20 minutes before each weighing. The cleaned vessels were flushed with balance room air prior to weighing, and the empty vessel weight was corrected for the weight of air contained in it. By taking these precautions, it is estimated that the volume determinations are accurate to within 0.3 percent.

The question arises as to how the measured volume of the sample tubes is affected by the internal gas pressure developed under the experimental conditions. The radial and axial tensile stresses in a cylinder of wall thickness t are given by [59]

$$s_{\text{radial}} = \frac{pr}{t} \quad (101)$$

$$s_{\text{axial}} = \frac{pr}{2t} \quad (102)$$

where r is the tube radius, p is the internal pressure, and s is the stress. Since the sample tube radius is 4.5 mm, the wall thickness is 2 mm, and the maximum internal gas pressure is 445 psig (31.2 atm absolute), the maximum radial stress is 1,000 psi and the maximum axial stress is 500 psi. According to the theory of elasticity,

$$y = \frac{\text{tensile stress}}{\text{tensile strain}}$$

or

$$Y = \frac{s_{\text{radial}}}{\Delta r/r} \quad (103)$$

$$Y = \frac{s_{\text{axial}}}{\Delta h/h} \quad (104)$$

where Y is Young's modulus. Using a value of 9.1×10^6 psi for Young's modulus for borosilicate glass [60], one obtains a $\Delta r/r$ of 1.1×10^{-4} and a $\Delta h/h$ of 0.5×10^{-4} . Since

$$\frac{\Delta V}{V} = \frac{2\Delta r}{r} + \frac{\Delta h}{h} \quad (105)$$

the maximum increase in tube volume due to internal gas pressure is only about 0.03 percent.

APPENDIX F
EXPERIMENTAL DATA

EXPERIMENTAL DATA

VOLUME OF CALIBRATED RESERVOIR

Weight of chamber filled with air = 342.8 g

Weight of chamber filled with water = 1399.0 g

Water temperature = 23.3° C

VOLUME OF SAMPLE TUBES

Tube No.	Weight Filled With Air, g	Weight Filled With Water, g	Water Temperature, °C
<u>Methanol Series</u>			
12	40.7562	48.0692	25.88
14	40.4179	47.7003	25.88
15	40.5480	47.7768	25.88
17	40.4250	47.7272	25.88
18	40.8995	48.2378	25.88
<u>Acetone Series</u>			
19	40.7438	48.2422	24.78
20	39.7225	46.9947	24.78
21	40.4538	47.7455	24.78
22	40.4755	47.7148	24.78
23	40.8479	48.2351	24.78

CATHETOMETER READINGS

Tube No.	Left Leg, cm	Right Leg, cm	Reservoir Temperature, °C
Methanol Series			
zero reading	4.6330	4.6332	27.95
14	6.3652	2.8999	27.95
18	7.0702	2.1828	27.95
12	7.7357	1.5161	27.95
15	8.6869	0.5652	27.95
17A	7.0069	2.2772	27.95
17B	7.1038	2.1636	27.95
11(mercury alone)	----	----	----
Acetone Series			
zero reading	4.8598	4.8511	28.00
19	6.4547	3.2349	28.00
20	7.2438	2.4318	28.00
21	8.0240	1.6437	28.00
22	8.8811	0.7808	28.00
23	9.6063	0.0521	28.00
16(mercury alone)	----	----	----

COUNTING DATA

Tube No.	Date	Time	Gross Counts	Counting Time, min.	Potentiometer Reading mv
Methanol Series					
Bkgd	3/21/72	10:30 am	61,561	60	-----
11	3/15/72	4:45 pm	90,809	5	10.3132
11	3/15/72	10:20 pm	90,285	5	10.3132
11	3/21/72	11:08 pm	110,028	4	11.3986
11	3/21/72	11:15 pm	109,881	4	11.3986
11	3/22/72	9:15 pm	130,541	3	12.5029
11	3/22/72	9:21 pm	130,788	3	12.5029
11	3/23/72	10:06 am	134,118	2	13.6256
11	3/23/72	10:09 am	133,861	2	13.6256
11	3/23/72	12:40 pm	100,489	1	14.7632
Bkgd	3/23/72	12:45 pm	100,209	1	14.7632
14	3/24/72	4:55 pm	57,387	60	-----
14	3/24/72	8:55 am	77,800	5	10.3132
14	3/24/72	12:02 pm	80,129	5	10.3132
14	3/24/72	1:55 pm	81,147	5	10.3132
14	3/24/72	4:04 pm	82,863	5	10.3132
14	3/25/72	8:30 pm	82,434	5	10.3132
14	3/25/72	8:35 pm	82,810	5	10.3132
14	3/26/72	1:00 pm	105,305	4	11.3986
14	3/26/72	1:07 pm	106,075	4	11.3986
14	3/26/72	1:12 pm	105,930	4	11.3986
14	3/26/72	8:35 pm	106,700	4	11.3986
14	3/26/72	8:44 pm	107,884	4	11.3986
14	3/27/72	11:10 am	125,310	3	12.5029
14	3/27/72	2:12 pm	126,366	3	12.5029
14	3/27/72	4:55 pm	126,907	3	12.5029
14	3/27/72	5:00 pm	127,296	3	12.5029
14	3/28/72	8:55 am	128,632	2	13.6256
14	3/28/72	11:30 am	129,991	2	13.6256
14	3/28/72	2:00 pm	129,842	2	13.6256
14	3/29/72	8:43 am	96,402	1	14.7632
14	3/29/72	11:22 am	96,579	1	14.7632
Bkgd	4/ 4/72	10:00 am	55,233	60	-----
18	4/ 6/72	9:48 pm	71,349	5	10.3132
18	4/ 6/72	10:00 pm	142,567	10	10.3132
18	4/ 7/72	11:35 am	109,020	5	11.3986
18	4/ 7/72	2:15 pm	111,332	5	11.3986
18	4/ 7/72	4:25 pm	112,371	5	11.3986
18	4/ 8/72	8:20 pm	91,422	4	11.3986
18	4/ 9/72	9:05 pm	107,047	3	12.5029
18	4/ 9/72	9:08 pm	107,361	3	12.5029
18	4/10/72	12:23 pm	106,535	2	13.6256
18	4/10/72	4:33 pm	107,862	2	13.6256
18	4/10/72	9:15 pm	108,790	2	13.6256

COUNTING DATA (Cont.)

Tube No.	Date	Time	Gross Counts	Counting Time min.	Potentiometer Reading mv
18	4/11/72	8:50 am	108,614	2	13.6256
18	4/12/72	9:23 am	159,827	2	14.7632
18	4/12/72	12:10 pm	159,910	2	14.7632
Bkgd	4/13/72	11:00 am	53,452	60	-----
12	4/15/72	9:30 pm	127,863	10	10.3132
12	4/15/72	10:45 pm	127,855	10	10.3132
12	4/17/72	9:55 pm	101,882	5	11.3986
12	4/17/72	10:00 pm	102,227	5	11.3986
12	4/19/72	8:25 am	93,376	3	12.5029
12	4/19/72	12:30 pm	94,953	3	12.5029
12	4/20/72	9:12 am	92,766	2	13.6256
12	4/20/72	1:27 pm	94,344	2	13.6256
12	4/20/72	4:32 pm	94,851	2	13.6256
12	4/21/72	9:18 am	136,647	2	14.7632
12	4/25/72	9:20 pm	134,003	2	14.7632
Bkgd	4/26/72	11:15 am	49,410	60	-----
15	4/28/72	8:55 am	109,732	10	10.3132
15	4/28/72	11:10 am	109,314	10	10.3132
15	4/28/72	3:20 pm	108,806	10	10.3132
15	4/29/72	9:20 pm	87,806	5	11.3986
15	4/29/72	9:30 pm	87,459	5	11.3986
15	4/30/72	9:50 pm	105,076	4	12.5029
15	4/ 1/72	9:10 am	107,567	4	12.5029
15	5/ 1/72	3:10 pm	108,488	4	12.5029
15	5/ 2/72	9:32 am	118,902	3	13.6256
15	5/ 2/72	11:15 am	118,382	3	13.6256
15	5/ 2/72	3:55 pm	119,553	3	13.6256
15	5/ 3/72	8:55 am	121,784	3	13.6256
15	5/ 3/72	10:40 am	121,928	3	13.6256
15	5/ 4/72	9:53 am	116,000	2	14.7632
15	5/ 5/72	4:23 am	117,506	2	14.7632
15	5/ 5/72	8:52 am	118,180	2	14.7632
Bkgd	5/ 5/72	2:30 pm	51,038	60	-----
17	5/ 7/72	1:55 pm	96,565	10	10.3132
17	5/ 7/72	6:00 pm	96,708	10	10.3132
17	5/ 8/72	9:10 am	96,259	10	10.3132
17	5/ 9/72	10:40 am	148,200	10	11.3986
17	5/ 9/72	4:55 pm	150,425	10	11.3986
17	5/10/72	9:05 am	152,395	10	11.3986
17	5/11/72	4:25 pm	92,663	4	12.5029
17	5/12/72	8:45 am	93,713	4	12.5029
17	5/13/72	10:20 pm	104,696	3	13.6256
17	5/14/72	10:10 am	104,906	3	13.6256
17	5/15/72	11:15 am	100,183	2	14.7632
17	5/16/72	8:25 pm	101,671	2	14.7632

COUNTING DATA (Cont.)

Tube No.	Date	Time	Gross Counts	Counting Time, min	Potentiometer Reading, mv
Acetone Series					
Bkgd	6/15/72	11:40 am	58,472	60	-----
19	6/16/72	9:00 am	93,317	10	10.3132
19	6/16/72	3:15 pm	93,440	10	11.3986
19	6/17/72	10:50 pm	120,630	4	11.3986
19	6/19/72	12:23 pm	139,094	3	12.5029
19	6/19/72	4:22 pm	139,495	3	12.5029
19	6/19/72	10:30 pm	140,805	3	12.5029
19	6/20/72	10:12 pm	141,513	2	13.6256
19	6/21/72	9:23 am	142,284	2	13.6256
19	6/22/72	8:52 am	103,460	1	14.7632
19	6/22/72	4:15 pm	104,372	1	14.7632
19	6/22/72	9:52 pm	104,147	1	14.7632
Bkgd	6/26/72	2:30 pm	66,520	60	-----
20	6/28/72	9:45 am	154,858	10	10.3132
20	6/28/72	4:30 pm	157,733	10	10.3132
20	6/28/72	8:15 pm	163,898	10	10.3132
20	6/29/72	8:12 pm	100,065	4	11.3986
20	6/30/72	9:40 am	101,348	4	11.3986
20	6/30/72	3:35 pm	105,164	4	11.3986
20	7/ 1/72	10:25 pm	117,760	3	12.5029
20	7/ 2/72	8:45 am	120,882	3	12.5029
20	7/ 3/72	4:24 pm	112,990	2	13.6256
20	7/ 4/72	6:30 pm	120,672	2	13.6256
20	7/ 5/72	5:37 pm	85,612	1	14.7632
20	7/ 6/72	9:27 am	87,608	1	14.7632
20	7/ 6/72	3:47 pm	175,320	2	14.7632
Bkgd	7/ 7/72	3:10 pm	57,930	60	-----
21	7/ 9/72	2:40 pm	138,490	10	10.3132
21	7/ 9/72	10:00 pm	140,465	10	10.3132
21	7/10/72	10:30 am	141,553	10	10.3132
21	7/12/72	11:45 am	110,344	5	11.3986
21	7/12/72	9:12 pm	111,107	5	11.3986
21	7/13/72	9:00 am	112,412	5	11.3986
21	7/14/72	4:48 pm	100,376	3	12.5029
21	7/15/72	10:20 pm	102,885	3	12.5029
21	7/16/72	9:32 pm	99,371	2	13.6256
21	7/17/72	9:05 am	100,653	2	13.6256
21	7/17/72	5:35 pm	101,236	2	13.6256
21	7/17/72	10:26 pm	102,077	2	13.6256
21	7/18/72	4:47 pm	138,037	2	14.7632
21	7/19/72	8:52 am	146,259	2	14.7632
21	7/19/72	4:50 pm	148,236	2	14.7632
21	7/20/72	9:17 am	147,451	2	14.7632

COUNTING DATA (Cont.)

Tube No.	Date	Time	Gross Counts	Counting Time, Potentiometer Reading,	
				min	mv
Bkgd	7/20/72	4:20 pm	53,432	60	-----
22	7/23/72	1:40 pm	118,946	10	10.3132
22	7/24/72	9:00 am	120,855	10	10.3132
22	7/26/72	10:17 pm	112,715	6	11.3986
22	7/27/72	9:25 am	112,655	6	11.3986
22	7/28/72	5:30 pm	108,644	4	12.5029
22	7/29/72	10:28 pm	114,263	4	12.5029
22	7/31/72	10:20 am	122,661	3	13.6256
22	7/31/72	5:00 pm	124,160	3	13.6256
22	8/ 1/72	9:10 am	126,437	3	13.6256
22	8/ 2/72	5:09 pm	117,933	2	14.7632
22	8/ 3/72	10:47 am	120,983	2	14.7632
22	8/ 3/72	6:04 pm	121,551	2	14.7632
Bkgd	8/ 4/72	11:50 am	43,526	60	-----
16	8/ 6/72	2:37 pm	138,197	10	11.3986
16	8/ 6/72	6:47 pm	110,113	5	12.5029
16	8/ 6/72	10:55 pm	101,986	3	13.6256
16	8/ 6/72	11:14 pm	101,368	2	14.7632
16	8/ 7/72	2:02 pm	83,280	10	10.3132
Bkgd	8/ 9/72	12:15 pm	42,862	60	-----
23	8/14/72	4:15 pm	84,669	10	10.3132
23	8/15/72	8:50 am	85,499	10	10.3132
23	8/16/72	8:50 am	88,093	10	10.3132
23	8/18/72	8:45 am	107,285	8	11.3986
23	8/19/72	10:00 pm	108,376	8	11.3986
23	8/22/72	8:50 am	102,187	5	12.5029
23	8/22/72	4:50 pm	102,250	5	12.5029
23	8/24/72	8:40 am	118,928	4	13.6256
23	8/25/72	8:45 am	119,733	4	13.6256
23	8/25/72	5:05 pm	119,860	4	13.6256
23	8/27/72	7:20 pm	128,634	3	14.7632
23	8/28/72	8:40 am	128,817	3	14.7632

APPENDIX G
COMPUTER PROGRAM FOR
POLYNOMIAL REGRESSION ANALYSIS

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PROGRAM SIMREG(INPUT,OUTPUT,TAPE5=INPUT,TAPE6=OUTPUT)
DIMENSION X(132),Y(1000),SLMX(21),SLMY(11),B(11),A(11,11),
1 IDENT(1),LTEMP(11),LPR(11),LPC(11),R(10),YC(1000),DF(1000),
1 S(11)
000003 DOUBLE X,Y,SLMX,SUMY,A,B,P,CET,FIV,SCRL,F,F,YC,CF,STOV,S
000003 100 FORMAT (4D18.8)
000003 200 FORMAT (3I5)
000003 300 FORMAT (8A10)
000003 400 FORMAT (1H1,23X,8A10///10X,9F-THERE ARE,15,36H DATA POINTS, FOR WHIC
1H SUM(Y**2) IS,1P020.8,35H, TO FIT POLYNOMIALS OF DEGREE 1 TO,13//
1 15X,1HY,2(19X,1HY,19X,1HY),19X,1HY/(5X,6D20.8))
000003 500 FORMAT (1H1,23X,8A10///10X,1HX,2(19X,1HY,19X,1HY),19X,1HY/(5X,
1 6D20.8))
000003 600 FORMAT (1H1,23X,8A10///10X,24HTHE SQUARED MATRIX FOR A,13,21H DEGR
1EE POLYNOMIAL IS)
000003 700 FORMAT (///10X,21HTHE SQUARED VECTOR IS)
000003 800 FORMAT (/(5X,1P020.8))
000003 900 FORMAT (///10X,34H*** ERROR IN MATRIX SOLUTION ****)
000003 1000 FORMAT (///10X,40HTHE POLYNOMIAL COEFFICIENTS (AX + BX2 + ...) ARE)
000003 1100 FORMAT (1H1,23X,8A10///10X,38HTHE STANDARD DEVIATION FOR THIS FIT
1IS,1P020.8,10X,56HTHE F STATISTIC BETWEEN THIS FIT AND THE PREVIOUS
1S FIT IS,012.3,10X,15,19H DEGREES OF FREEDOM/10X,14HTHE VALUES ARE
1//20X,1HX,19X,1HY,13X,13HY(CALCULATED),7X,10HDIFFERENCE/(15X,4D20.
1A))
000003 1200 FORMAT (1H1,23X,8A10///20X,1HX,19X,1HY,13X,13HY(CALCULATED),7X,
1 11HDIFFERENCE/(15X,1P4D20.8))
000003 1300 FORMAT (///10X,60HTHE STANDARD DEVIATION ESTIMATES FOR THE POLYNOMI
1AL COEFFICIENTS ARE)
C
C READ INPUT DATA
C
000003 1900 READ (5,200) NDATA,MAXDEG,IFEND
000015 READ (5,300) (IDENT(I),I=1,8)
000027 READ (5,100) (X(I),Y(I),I=1,NDATA)
C
C COMPUTE SUM(Y**2)
C
000045 SCPL=0.0
000047 DO 1 I=1,NDATA
C
C PRINT HEADING,NCATA,SUM(Y**2),MAXDEG,X,Y
C
000050 1 SCRL=SCPL+Y(I)**2
000065 ISTOP=NCATA
000066 IF(NDATA.LE.132) GO TO 2
000070 ISTOP=132
000072 2 WRITE (6,400) (IDENT(I),I=1,8),NDATA,SCRL,MAXDEG,(X(I),Y(I),
1 I=1,ISTOP)
C
C IF DATA TAKE MORE THAN ONE PAGE, RESET HEADING AND CONTINUE PRINTING
C
000123 3 IF(NDATA.LE.ISTOP) GO TO 5
000126 ISTART=ISTOP+1
000139 ISTOP=ISTOP+139

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```

002131 IF (NDATA,GE,ISTOP) GO TO 4
002132 ISTOP=NDATA
002133 4 WRITE (6,5:0) (IDENT(I),I=1,0),(X(I),Y(I),I=ISTART,ISTOP)
002134 GO TO 3
002135
C
C
C COMPUTE SUMS NEEDED IN MATRICES
C
002161 5 MATRX=MAXDEG
002162 N2DGE=MAXDEG+NMTRX-1
002163 DO 6 N=1,N2DGE
002164 SU4Y(N)=0.0
002165 6 SU4Y(N)=0.0
002166 DO 7 I=1,NDATA
002167 P=Y(I)
002168 DO 7 N=1,N2DGE
002169 IF (N,GT,NMTRX) GO TO 61
002170 SU4Y(I)=SUMY(N)+P*Y(I)
002171 61 P=P*Y(I)
002172 7 SUMY(N)=SUMX(N)+P
002173 8 CONTINUE
C
C
C LOOP FOR DEGRE=1,MAXDEG
C
002245 DO 20 N=1,NMTRX
C
C FORM AND PRINT A MATRIX AND S VECTOR
C
002246 NDGRE=N
002247 WRITE (6,600) (IDENT(I),I=1,0),NDGRE
002248 DO 10 I=1,N
002249 S(I)=SUMY(I)
002250 DO 3 J=1,N
002251 3 A(I,J)=SUMX(I+J-1)
002252 10 WRITE (6,900) (A(I,J),J=1,N)
002253 WRITE (6,700)
002254 WRITE (6,800) (SUMY(I),I=1,N)
002255
C
C SOLVE MATRIX EQUATION AND PRINT SOLUTION
C
002344 CALL INVT(1,N,1,0,0,LTERR,ERR,DET,NPIV,PIV,LPR,LPC)
002345 IF (ERR,EQ,0) GO TO 11
002346 WRITE (6,900)
002347 GO TO 21
002348 11 WRITE (6,1000)
002349 DO 11 I=1,N
002350 R(I)=1.0
002351 DO 11 J=1,N
002352 11 B(I)=B(I)+A(I,J)*S(J)
002353 WRITE (6,400) (B(I),I=1,N)
C
C COMPUTE R
C
002436 PRINT*REI=0.0
002441 DO 12 I=1,N

```

```

C      FORM AND PRINT YC, DF, STDV OF E, AND STDV OF FIT
C
003442 12 R(NDGRE)=P(NDGRE)+B(I)*SLMY(I)
003443 STDV=J.C
003444 DO 14 I=1,NDATA
003445 YC(I)=C.C
003446 P=1.0
003447 DO 13 J=1,N
003448 P=P*X(I)
003449 13 YC(I)=YC(I)+P*B(J)
003450 PF(I)=YC(I)-Y(I)
003451 14 STDV=STDV+PF(I)**2
003452 NDFF=NDATA-NDGRE
003453 IF(NDFF.GT.0) GO TO 142
003454 STDV=J.C
003455 GO TO 143
003456 142 STDV=SQRT(STDV/NDFF)
003457 DO 1421 I=1,N
003458 1421 SLI=STDV*SQRT(A(I,I))
003459 WRITE (6,130)
003460 WRITE (6,130) (SLI,I=1,N)
C
C      COMPUTE F STATISTIC
C
003630 143 F=0.1
003631 18 IF(NDGRE.LE.1.OR.NDFF.LE.0) GO TO 141
003632 SSE=SQRT(P(NDGRE))
003633 XMSD=SSE/NDFF
003634 NDUM=NDGRE-1
003635 XMSR=(NDGRE)-R(NDUM)
003636 F=XMSD/XMSR
003637 141 ISTOP=NDATA
003638 IF(NDATA.LE.44) GO TO 15
003639 ISTOP=44
003640 15 WRITE (6,1100) (IDENT(I),I=1,8),STDV,F,NDFF,(X(I),Y(I),YC(I),DF(I),
1      .I=1,ISTOP)
C
C      CHECK IF DATA TAKE MORE THAN ONE PAGE
C
003734 16 IF(NDATA.LE.ISTOP) GO TO 20
003735 ISTART=ISTOP+1
003736 ISTOP=ISTOP+46
003737 IF(NDATA.GE.ISTOP) GO TO 17
003738 ISTOP=NDATA
003739 17 WRITE (6,1200) (IDENT(I),I=1,8),(X(I),Y(I),YC(I),DF(I),I=ISTART,
1      ISTOP)
003740 GO TO 16
003741 20 CONTINUE
003742 21 IF(IFEND.FQ.0) GO TO 1900
003743 CALL EXIT
003744 END

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052316	SUBROUTINE INVT(A,N,NN,EPS,LTEMP,IERR,DET,NPIV,PIV,LPR,LPC)	8045A001
072316	DIMENSION A(NN,N)	8045A002
302316	DIMENSION LTEMP(1),LPR(1),LPC(1)	8045A003
	DOUBLE A,EPS,DET,PIV,TEMP	
C		8045A004
C	DECK 9345A	8045A005
C		8045A006
C	SUBROUTINES CALLED - NONE	8045A007
C		8045A008
C	THIS ROUTINE INVERTS MATRIX A IN ITS OWN SPACE. IT ALSO COMPUTES THE	8045A009
C	THE DETERMINANT OF A.	8045A010
C		8045A011
C	THE METHOD IS THE USUAL GAUSSIAN EXCHANGE PROCESS. BOTH ROWS AND	8045A012
C	COLUMNS ARE SEARCHED FOR MAXIMAL PIVOTS. THERE IS NO UNNECESSARY	8045A013
C	INTERCHANGING OF ROWS OR COLUMNS, ALL SUCH INTERCHANGES BEING CARRIED	8045A014
C	OUT AFTER THE EXCHANGE PROCESS IS COMPLETE. CHAPTER 1 OF E.L. STIEFEL,	8045A015
C	INTRODUCTION TO NUMERICAL MATHEMATICS, ACADEMIC PRESS, N.Y., 1963, SHOULD	8045A016
C	BE HELPFUL IN FOLLOWING THE CODE.	8045A017
C		8045A018
C	THE CALLING PROGRAM MUST SET A,N,NN,EPS,AND LTEMP TO-	8045A019
C		8045A020
C	A-THE MATRIX TO BE INVERTED	8045A021
C		8045A022
C	N-THE ORDER OF A	8045A023
C		8045A024
C	NN-THE NUMBER OF WORDS OF STORAGE PROVIDED FOR EACH COLUMN	8045A025
C	OF ARRAY A BY THE CALLING PROGRAM	8045A026
C		8045A027
C	EPS-A NON-NEGATIVE NUMBER WHICH EACH PIVOT IS REQUIRED TO EXCEED	8045A028
C	IN ABSOLUTE VALUE (CUSTOMARILY ZERO)	8045A029
C		8045A030
C	LTEMP-A BLOCK OF AT LEAST N WORDS OF TEMPORARY INTEGER STORAGE	8045A031
C		8045A032
C	IN ADDITION TO OVERWRITING A WITH ITS INVERSE,THE ROUTINE ALSO SETS	8045A033
C	IERR,DET,NPIV,PIV,LPR,AND LPC TO-	8045A034
C		8045A035
C	IERR- 0 IF INVERSION IS COMPLETED AND NO TROUBLE IS DETECTED	8045A036
C		8045A037
C	2 IF MAGNITUDE OF CURRENT PIVOT FAILS TO EXCEED EPS	8045A038
C	(INVERSION WILL NOT BE COMPLETED)	8045A039
C		8045A040
C	DET-PLUS OR MINUS THE PRODUCT OF THE CURRENT AND ALL PREVIOUS	8045A041
C	PIVOTS	8045A042
C		8045A043
C	NPIV-THE NUMBER OF THE CURRENT PIVOT (FIRST,SECOND,ETC.)	8045A044
C		8045A045
C	PIV-THE CURRENT PIVOT	8045A046
C		8045A047
C	LPR-THE FIRST NPIV POSITIONS LIST THE PIVOT ROW INDICES IN ORDER	8045A048
C	OF USE	8045A049
C		8045A050
C	LPC-THE FIRST NPIV POSITIONS LIST THE PIVOT COLUMN INDICES IN	8045A051
C	ORDER OF USE	8045A052
C		8045A053


```

C DO INITIALIZATIONS
C
000016      ERR=0
000017      SET=1
000018      DO 2 I=1,N
000019      LP=0
000020      2 LP(I)=I
000021
C
000022      DO 17 NO=1,N
000023      KPIV=NP
C BEGIN EXCHANGE PROCESS
C
000024      DO 17 NO=1,N
000025      KPIV=NP
C SELECT PIVOT
C
000026      PIV=0
000027      DO 4 K=NP,N
000028      IF LP(K)
000029      DO 4 L=NP,N
000030      J=LP(K)
000031      IF (ABS(R(I,J))-DABS(PIV)) 4,3,3
000032      3 PIV=K
000033      LP(K)=J
000034      J=PIV
000035      PIV=K
000036      4 CONTINUE
C UPDATE DETERMINANT AND PIVOT ROW AND COLUMN LISTS
C
000037      DET=DET*PIV
000038      IF (DET<0) DET=-DET
000039      LP2(NP)=LP(KPIV)
000040      LP(KPIV)=ITEMP
000041      IF (ITEMP=LP(KPIV))
000042      LP(KPIV)=LP(KPIV)
000043      LP(KPIV)=ITEMP
000044      IF (ITEMP=LP(KPIV))
000045      LP(KPIV)=LP(KPIV)
000046      LP(KPIV)=ITEMP
C
C EXIT IF PIVOT TOO SMALL
C
000047      IF (ABS(PIV)-DABS(PIV)) 8,7,7
000048      7 ERR=2
000049      RETURN
C MODIFY PIVOT ROW
C
000050      DO 9 J=1,N
000051      9 A(IPIV,J)=A(IPIV,J)/PIV
C MODIFY OTHER ROWS
C
000052      DO 14 I=1,N
000053      IF (I-PIV) 10,14,10
000054      10 TEMP=A(I,PIV)

```

000221	IF (TEMP)11,14,11	8045A109
000223	11 DO 13 J=1,N	8045A110
000225	IF (J-JPIV)12,13,12	8045A111
000227	12 A(I,J)=A(I,J)+A(IPIV,J)*TEMP	8045A112
000246	13 CONTINUE	8045A113
000251	14 CONTINUE	8045A114
	C	8045A115
	C MODIFY PIVOT COLUMN	8045A116
	C	8045A117
000254	DO 15 I=1,N	8045A118
000255	15 A(I,JPIV)=A(I,JPIV)/PIV	8045A119
000277	A(I=IV,JPIV)=-A(IPIV,JPIV)	8045A120
000355	17 CONTINUE	8045A121
	C	8045A122
	C END EXCHANGE PROCESS	8045A123
	C	8045A124
	C UNSCRAMBLE ROWS OF INVERSE AND ADJUST SIGN OF DETERMINANT	8045A125
	C	8045A126
000310	DO 18 I=1,N	8045A127
000311	L=LFC(I)	8045A128
000314	18 LTEMP(I)=LPC(I)	8045A129
000321	DO 22 I=1,N	8045A130
000322	19 K=LTEMP(I)	8045A131
000325	IF (I-K)20,22,20	8045A132
000326	20 DET=-DET	8045A133
000331	DO 21 J=1,N	8045A134
000333	TEMP=A(I,J)	8045A135
000341	A(I,J)=A(K,J)	8045A136
000351	21 A(K,J)=TEMP	8045A137
000352	LTEMP(I)=LTEMP(K)	8045A138
000365	LTEMP(K)=K	8045A139
000366	GO TO 19	8045A140
000367	22 CONTINUE	8045A141
	C	8045A142
	C UNSCRAMBLE COLUMNS OF INVERSE	8045A143
	C	8045A144
000372	DO 23 I=1,N	8045A145
000373	L=LFC(I)	8045A146
000376	23 LTEMP(I)=LPP(I)	8045A147
000403	DO 27 J=1,N	8045A148
000404	24 K=LTEMP(I)	8045A149
000407	IF (I-K)25,27,25	8045A150
000410	25 DO 26 J=1,N	8045A151
000412	TEMP=A(J,I)	8045A152
000425	A(J,I)=A(J,K)	8045A153
000432	26 A(J,K)=TEMP	8045A154
000442	LTEMP(I)=LTEMP(K)	8045A155
000445	LTEMP(K)=K	8045A156
000446	GO TO 24	8045A157
000447	27 CONTINUE	8045A158
000452	RETURN	8045A159
000452	END	8045A160

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