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Forty years of calorimetry at Brigham Young University

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Abstract

A history of the development of calorimetry at Brigham Young University is given. Short biographies of the faculty involved in calorimetric research are given, descriptions of the calorimeters developed at the university are presented, and a number of examples of experiments performed are presented, using calorimeters available at the university. © 1997 Elsevier Science B.V.

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1. Introduction

A recent census indicates that the following calorimeters are available at Brigham Young University (BYU): Ten titration calorimeters, ten flow calorimeters, two cryogenic calorimeters, five differential scanning calorimeters, two heat conduction calorimeters, and one pressure scanning calorimeter. Table 1 summarizes in more detail the characteristics of these calorimeters and lends credence to the claim that the calorimeter density (calorimeters/m^2) is probably as high or higher in Provo UT, than anywhere else on earth. The purpose of this paper is to review the development of calorimetry at BYU, describe some of the calorimeters developed at the university and provide examples of the application of these calorimeters to a wide variety of chemical processes.

2. Development of calorimetry

Credit must go to J. Rex Goates as the pioneer in calorimetry at BYU. Rex joined the Chemistry Department in 1947 after completing a Ph.D. at the University of Wisconsin at Madison. He joined the faculty at BYU at a time when teaching assignments were heavy, and resources and support facilities almost nonexistent. Nevertheless, he soon developed a research program in thermodynamics, involving the determination of the solubility product constants of silver and mercuric sulfides. His results revealed some very serious errors in the values of the solubility products of these compounds as reported in the literature, with the value of K_{sp} off by orders of magnitude. He also became involved in the determination of the thermodynamics of adsorption on clays and other types of soil minerals. His research turned to calorimetry after spending a sabbatical leave at the Massachusetts Institute of Technology (MIT) with George Scatchard in 1949, where he used a very simple calorimeter to determine the heat of mixing for binary

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Table 1
Calorimeters currently at Brigham Young University

Number	Type	Manufacturer	Temperature range/K	Pressure range/(MPa)	Special characteristics	Operable [a]
4	Titration/isoperibol	Tronac	285–305	Ambient	—	Yes
1	Titration/isoperibol	Tronac	285–305	Ambient	—	No
5	Titration/Isoperibol	Tronac	280–350	Ambient	—	Yes
2	Flow/isothermal	BYU [b]	250–375	0.4–15	—	Yes
1	Flow/isothermal	BYU [b]	250–475	0.4–15	—	Yes
2	Flow/isothermal	BYU [b]	325–475	0.4–15	Pt/Rh insert [c]	Yes
1	Flow/isothermal	BYU [b]	325–525	0.4–20	Pt/Rh insert [c]	Yes
1	Flow/Isothermal	BYU [b]	500–575	0.4–25	Pt/Ir insert [c]	Yes
1	Flow/Isothermal	BYU [b]	500–675	0.4–50	Pt/Rh insert [c]	Yes
1	Heat conduction	Hart	290–475	Ambient	—	Yes
1	Heat conduction	Setaram	275–575	0.1–300	Pressure scanning	Yes
1	Adiabatic cryogenic	BYU [d]	5–350	—	—	Yes
1	Adiabatic cryogenic	BYU	5–350	—	0.5 cm^3 sample	No
4	Differential scanning	Hart	250–375	0.1–15	—	Yes
1	Differential scanning	Seiko	125–775	Ambient	—	Yes
1	Flow/counter flow	Picker	275–325	Ambient	—	No
1	Heat capacity flow	Picker	275–325	Ambient	—	No
1	Oxygen combustion	Parr	Ambient	—	—	No

[a] Calorimeters counted as not operable are those that could not be made operable with minimal work.
[b] Flow calorimeters include components manufactured by Hart Scientific, such as controllers, constant-temperature baths, and inserts.
[c] Corrosion-resistant insert.
[d] Westrum design.

and ternary mixtures. The MIT calorimeter, which is indicative of the sophistication of many of the heat of mixing calorimeters available at the time, consisted of a glass tube bent into an oval. The tube was mounted on a wheel and placed in the center of a Dewar flask in a room, air conditioned to 20°C. The two arms of the tube were isolated from one another by a layer of mercury. The liquids to be mixed were placed in the two arms and equilibrated to room temperature. Rotating the tube by turning the wheel mixed the liquids. A thermocouple placed in a well in one of the arms measured the temperature change and an electrical heater in a well in the other arm provided electrical calibration. This apparatus allowed Rex and his coworkers at MIT to measure the heats of mixing (or excess molar enthalpies as we now call them) for mixtures of methanol, tetrachloromethane, benzene, cyclohexane, *n*-hexane, and *n*-hexadecane [1].

By 1955, Rex found a graduate student, Max Hill, who was interested in the properties of nonelectrolyte mixtures, and they decided to build a calorimeter at BYU to study the heat effects when simple nonelectrolyte liquids are mixed. Max helped with the design and fabrication of the mixing vessel and started the assembly of the apparatus, but left for the University of California, at Berkeley, to work on a Ph.D. in nuclear chemistry, before completing the project.

The design and construction of the electrical measuring circuits and the completion of the housing around the mixing vessel, along with the assembly and testing of the final apparatus, were left to the next graduate student, Bevan Ott. A schematic of the resulting calorimeter is shown in Fig. 1 [2]. The liquids to be mixed were loaded into the two chambers of the calorimeter, which were separated by an aluminum foil diaphragm and sealed at the top with a plug. The apparatus was placed in a glass tube that was sealed with a neoprene stopper and evacuated through a stopcock. The assembly was equilibrated in a constant temperature bath, and mixing was accomplished by inverting the apparatus. This caused a metal weight in the bottom compartment to fall, which pierced the aluminum foil diaphragm and stirred the mixture. Changing the size of the weight varied the composition of the resultant mixture.

The temperature change due to mixing was measured by a thermocouple placed on the side of the mixing vessel. The thermocouple emf, resulting from

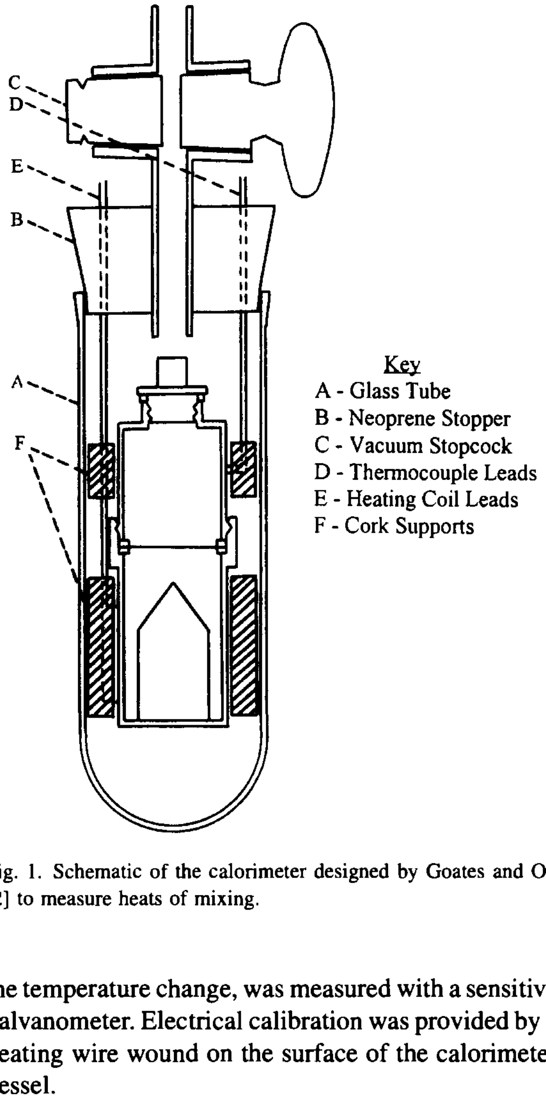

Fig. 1. Schematic of the calorimeter designed by Goates and Ott [2] to measure heats of mixing.

the temperature change, was measured with a sensitive galvanometer. Electrical calibration was provided by a heating wire wound on the surface of the calorimeter vessel.

(Benzene + cyclohexane), (benzene + tetrachloromethane), and (cyclohexane + tetrachloromethane) were the first three systems studied. Fig. 2 summarizes the heats of mixing or excess enthalpies H^E_m obtained for $\{xC_6H_6 + (1-x)c-C_6H_{12}\}$ at 298.15 K [3]. This mixture has now been studied very carefully and is used as a system for testing mixing calorimeters. The curve shows the 'test results' expected for this system [4]. The agreement between the curve and these very early results is not 'great', but considering the crude nature of the calorimeter, it is not too bad either.

Another graduate student, Ralph Sullivan, took over the calorimeter after Bevan Ott left. He studied H^E_m for the (benzene + cyclohexane) system as a function of temperature and combined the H^E_m results with G^E_m, the excess molar Gibbs energy, measured by Scatchard et al. at MIT [5] to calculate S^E_m, the excess molar entropy, from the relation

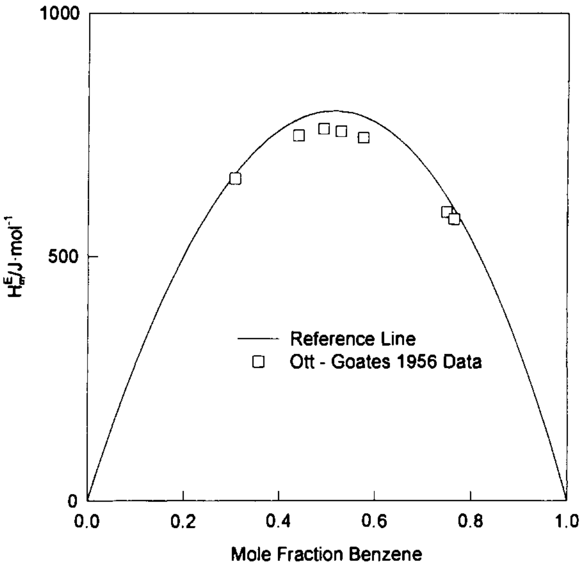

Fig. 2. Comparison of the H^E_m results for $\{xC_6H_6 + (1-x)c-C_6H_{12}\}$ at 298.15 K [3] obtained with the Goates–Ott calorimeter, with the curve representing the accepted values [4].

$$G^E_m = H^E_m - TS^E_m \tag{1}$$

Fig. 3 summarizes H^E_m, G^E_m, and TS^E_m for this system. H^E_m is larger than for mixtures of aliphatic hydrocarbons and has a negative $C^E_{p,m}$. The π-π interactions in the benzene that are broken when the cyclohexane is added probably make a major contribution to H^E_m. G^E_m is small and positive so that S^E_m is also positive, indicating an increased disorder in the mixture over that for an ideal mixture.

3. Calorimetrists at BYU

The Goates–Ott calorimeter was simple and not of high accuracy nor easy to operate, but was typical of mixing calorimeters of the day. No one had yet figured out a way to eliminate the vapor space above the liquid mixture, and changes in vapor composition upon mixing can cause serious errors when volatile liquids are mixed. Isothermal operation to minimize heat

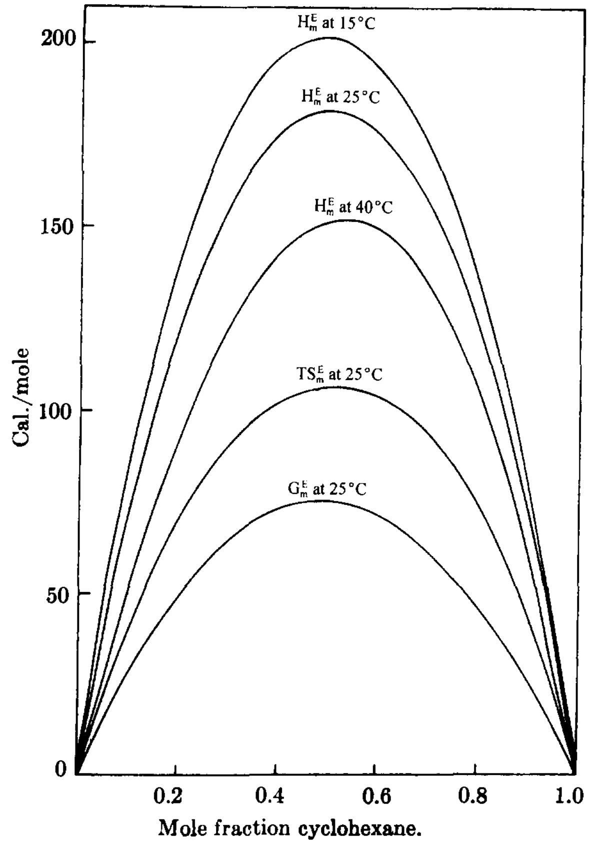

Fig. 3. Comparison of excess molar enthalpies for $xC_6H_6+(1-x)c-C_6H_{12}\}$ [3] with excess molar Gibbs energies reported by Skatchard et al. [5] and excess molar entropies calculated from the difference. Reprinted with permission from Ref. [3].

leaks had not been developed, and the measurement of each data point was a major operation, requiring disassembly, loading, and assembly of the calorimeter.[1] By 1960, other types of calorimetry, most notably cryogenic and combustion calorimeters, were well developed and producing accurate results, but a check of the literature shows less than 200 papers published before 1960 reporting heats of mixing for nonelectrolyte mixtures, with many of the results highly suspect.

Calorimetry at BYU was in its infancy in 1956 and probably would not have matured at the university were it not for the arrival of James J. (Jim) Christensen and Reed M. Izatt. Reed completed his Ph.D. in the Chemistry Department at Pennsylvania State University, in 1954, where he worked with W.C. Fernelius on the thermodynamics of interactions of acetylacetone with metal ions. He then accepted a post-doctoral appointment at the Mellon Institute in Pittsburgh, where he worked with T. Hatch and W.A. Hamor, studying aerosols and settling rates. It was while at Mellon that Reed met Jim Christensen, who was a graduate student at the Carnegie Institute. (Since that time, the two schools have merged to form Carnegie-Mellon University.)

Reed accepted an appointment in 1956 in the Chemistry Department at Brigham Young University, where he has been ever since. His retirement in 1993 did not signal an end to Reed's professional activity – he still carries on an active research program in the department.

Jim Christensen received his Ph.D. in Chemical Engineering from the Carnegie Institute of Technology in 1957. His graduate work with C.C. Monrad involved a study of heat transfer and pressure drops inside coiled tubes. This work did not involve calorimetry directly, but prepared him for later work in developing mixing calorimeters.

Jim joined the Chemistry Department at BYU as a chemical engineer in 1957. When chemical engineering became a separate department a few years later, Jim became a member of that department. Except for sabbatical leaves in 1964–65 at Oxford University, in 1973–74, at the Center for Advanced Studies at the National Polytechnical Institute in Mexico City, Mexico, and shorter leaves at the Energy and Technology Center in Bartlesville, OK, and the EXXON Corporation Research Labs in Linden, NJ, he remained at BYU until his untimely death in 1987.

Reed and Jim actually met at a church in Pittsburgh. They became good friends and discovered that they had common interests that involved the interactions of protons with anions and ligands with metal ions. When they both ended up at BYU, they decided to join their research programs. An important part of the studies

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[1] A notable exception was the Hirobe calorimeter. Hajismi Hirobe was a lecturer at the Imperial University of Tokyo. He died in 1914 without publishing his work, which was later published (in 1925) from manuscripts he had written [6]. He reported the heat of neutralization of HCl(aq) with NaOH(aq) and the heats of mixing as a function of composition for 51 nonelectrolyte mixtures. His work, which has survived the scrutiny of more modern measurements, was made with an ingenious titration calorimeter that was kept isothermal by adding drops of hot or cold mercury during the mixing process.

involved knowing about the energetics of the formation of metal ion complexes and proton ionizations. This led them to the task of constructing reliable calorimeters to measure these energy effects. The development of these calorimeters, which will be described more fully later in this paper, were the beginnings of modern calorimetry at BYU.

Over the next 25 years, a number of other thermodynamicists, who had an interest in using calorimeters in their research programs, joined the faculty at BYU. The ranks were swollen with visiting scientists, research associates, post-doctoral fellows, and graduate and undergraduate students, several of whom eventually became faculty members at BYU. In 1969, Jim and Reed organized the Thermochemical Institute at BYU. This organization, with a charter to bring together faculty from across campus with a common interest in thermodynamics and calorimetry, played an important catalytic role in the growth of research using calorimeters, although some faculty members who made thermodynamic measurements did not affiliate with the Institute. Space will not allow for a report of all who contributed to calorimetric studies at BYU, even though it is recognized that many did make major contributions to the programs. The following summary recognizes only those with faculty appointments at the university.

Bevan Ott completed the excess molar enthalpy measurements described earlier, obtained his M.S. degree at BYU in 1956, and left for California where he worked with W.F. Giauque at the University of California, at Berkeley, on a cryogenic calorimetry problem. He completed his Ph.D. in 1959, spent a year as a faculty member at Utah State University, and joined the Chemistry Department at BYU in 1960. He has been at BYU since that time, except for sabbatical leaves that included eight months in 1977–78 working with Robin Stokes and Ken Marsh at the University of New England in New South Wales, Australia, measuring excess molar volumes, excess molar enthalpies, and excess molar Gibbs energies for hydrocarbon mixtures, and a semester during the fall of 1984 working with Gerhard Schneider on high-pressure (liquid + liquid) equilibrium at Ruhr-Universität in Bochum, Germany. At BYU, Bevan re-established ties with Rex Goates and they collaborated on thermodynamic research for 30 years. The early work involved mostly (solid + liquid) equilibrium studies, but later, excess enthalpy and excess volume measurements were added, first with a Picker flow calorimeter and then with one of the high-pressure high-temperature flow calorimeters that will be described later.

Earl Woolley and Delbert Eatough were the next on the scene. Both joined the BYU faculty in 1970, with Earl in Chemistry and Delbert with an appointment in the Thermochemical Institute.

Earl completed his Ph.D. in physical chemistry at BYU in 1967, working with K.P. Anderson on a thermodynamic study of complex ion solubility of silver halides in water and mixed aqueous solvents. A post-doctoral appointment at the University of Lethbridge working with Loren Helper got him started in calorimetry. They used an LKB batch/titration calorimeter to study hydrogen bonding of phenol in non-aqueous solvents, and the thermodynamics of acid-base neutralizations. Earl's work at BYU has included the calorimetric study of carboxylic acid hydrogen bonding in non-aqueous solvents, calorimetric heat capacities of simple aqueous electrolytes, and more recently, the thermodynamics of aqueous surfactant systems. He spent the past year as a visiting scientist at Oak Ridge National Laboratories, using the superb high-temperature high-pressure flow calorimeter available there to study the thermodynamics of aqueous sodium chloride, sodium carbonate, and sodium bicarbonate.

Delbert Eatough also did his graduate work at BYU, receiving a Ph.D. in physical chemistry in 1967 working with Reed Izatt (and Jim Christensen). As a part of his graduate work, he helped develop the technique to be described later for using a titration calorimeter to determine equilibrium constants for chemical reactions. He used the technique to study the complexation of sulfate and cyanide ions with metal ions.

Delbert worked for Shell Development Corporation in Emeryville CA, from 1967–1970, at which time he returned to BYU as the Director of the Thermochemical Institute. His appointment was changed to professor in the Chemistry Department when the Thermochemical Institute was disbanded. In recent years, he has focused his research on environmental chemistry, where he has become a world authority, but he has used calorimeters for such diverse applications as the determination of different forms of sulfur in atmospheric samples and for the chemical characterization of coal liquids.

Lee Hansen also received his start in calorimetry, working as an undergraduate at BYU with Reed Izatt and Jim Christensen. Lee stayed at BYU for his graduate work and received his Ph.D. in inorganic chemistry, working with Reed (and Jim). He was deeply involved in the development and construction of the high-precision titration calorimeter that will be described later. He automated the data analysis system and used the calorimeter to determine equilibrium constants, primarily for the dissociation of the proton from weak acids, protonated amines, and protonated nitrogen heterocycles.

After completing his Ph.D. in 1965, Lee joined the Chemistry Department at the University of New Mexico, where he remained actively involved in calorimetry. He spent the summer of 1971 with Loren Hepler at the University of Lethbridge, then the winter of 1971–72 with Gary Watt at the Kettering Research Institute in Yellow Springs OH, and the spring of 1972 with Frank Millero at the University of Miami, studying the thermodynamics of sea water. He never returned to the University of New Mexico, joining the Chemistry Department at BYU in the fall of 1972. Since returning to BYU, he has worked closely with Jim Christensen in developing and commercializing the titration and flow calorimeters that will be described later, and has used calorimeters to study a wide variety of chemical processes. A recent emphasis has been the study of plant metabolism, using a heat conduction differential scanning calorimeter.

John Oscarson joined the BYU Chemical Engineering Department in 1974 after working on his Ph.D. from 1971–74 at the University of Michigan, studying transport phenomena. His early work as a faculty member at BYU involved (vapor + liquid) and (liquid + liquid) measurements. His interest in calorimeters goes back to his undergraduate days at BYU in the 1960's, when he worked with Jim Christensen and Reed Izatt. He became seriously involved in calorimeters again in the early 1980's. Sabbatical leaves at Tronac, in 1983–84, at Oak Ridge National Laboratories in 1990, and at the Electric Power Research Institute in Palo Alto CA, in 1992–93, have strengthened his interest in calorimetry. He is now heavily involved in the study of high temperature aqueous systems (mostly electrolyte solutes), including measurements near the critical temperature of water.

Ed Lewis joined the Thermochemical Institute in 1981 as Research Professor of Chemistry. Ed received his Ph.D. in 1972 from the University of New Mexico, working under the direction of Lee Hansen. He worked on a variety of calorimetry related projects, including the study of inclusion compounds of cyclodextrins, determination of the enthalpy of formation of samarium oxide (Sm_2O_3), developing techniques that used thermometric titrations for analysis of binary mixtures, and using TRIS as a calorimeter titration standard.

After New Mexico, Ed worked as a post-doctoral fellow at the University of Texas Health Science Center, in San Antonio, and then joined the Chemistry Department at the University of Alabama, where he remained until moving to BYU. In 1992, he left BYU to accept a position as the Executive Vice President of Calorimetry Sciences Corporation (formerly Hart Scientific) in Provo UT, where he supervises the research, development, and improvement of instrumentation, including calorimetric equipment.

Juliana Boerio-Goates completed her Ph.D. in 1979, working with Edward Westrum at the University of Michigan on a cryogenic calorimetric study of phase transitions in π molecular complexes. She stayed at Michigan for an extra year in a post-doctoral position, working with A.H. Frances on an electronic spectroscopy study of energy transfer in transition-metal compounds.

Julie joined the Chemistry Department at BYU in 1982, bringing with her a cryogenic calorimeter of the Ed Westrum design that was fabricated in the University of Michigan machine shops. Julie has modified and automated this calorimeter and used it to measure heat capacities and phase transitions for a variety of substances, including iodoform and the langbeinites. A focus of her work at present involves the measurement of entropies and free energies of formation of mono- and di-saccharides. Julie spent a sabbatical leave at MIT in 1989 working with Carl Garland, using AC Calorimetry to study phase transitions in systems containing chiral liquid crystal molecules.

Jadwiga (Dottie) Sipowska, Phil Brown, and Sue Gillespie all came to BYU as research associates and, subsequently, became research faculty members. Dottie obtained her Ph.D. in 1986 from the Institute of Physical Chemistry at the Polish Academy of Sciences. Her work with Jan Stecki principally involved the measurement of excess volumes and (vapor + liquid) equilibrium for (alkanol + hydrocarbon) systems. After her Ph.D., she remained at the Polish Academy until 1988, with appointments as assistant and then Associate Professor, while continuing her work with Professor Stecki.

Dottie came to BYU in 1988 where she collaborated, principally with Bevan Ott, on calorimetric measurements of excess enthalpies and volumes for mixtures of simple alkanes and alkanols. In 1993, she accepted a position as Assistant Professor of Chemistry at the University of Michigan – Flint. She is now collaborating with Ed Westrum at the University of Michigan – Ann Arbor, using cryogenic calorimetry to study the phase properties and heat capacities of metal halides and platinum and copper selenides.

Phil Brown returned to BYU in 1993 to take up where Dotti Sipowska left-off, in measuring excess enthalpies and volumes for mixtures of simple alkanes with one another and with alkanols. Phil is originally from Australia. A number of years ago, he moved to the United States and BYU, where he completed his B.S. degree in chemistry. He continued his graduate studies at BYU and received his Ph.D. in Physical/Inorganic chemistry in 1986, working with Reed Izatt (and Jim Christensen), using high-temperature high-pressure flow calorimeters to study the thermodynamics of aqueous hydrochloric and sulfuric acids at high temperatures. He spent a year (1986–87) as a post-doctoral fellow working with Richard Bartsch at Texas Tech University on the thermodynamics of supported membranes. He then accepted a position as research scientist with Tronac, where he was responsible for designing, troubleshooting, application development, and customer support for the calorimeters sold by Tronac. He stayed with Tronac until moving to BYU. In 1995, Phil began a teaching faculty appointment at BYU. This position requires a heavy commitment to teaching but does allow him some time to continue collaboration on calorimetric research.

Sue Gillespie started working for Jim Christensen in 1986 as a research assistant. She also worked on her graduate degree, first with Jim Christensen as her major professor, and then with John Oscarson after Jim passed away in 1987, and obtained her M.S. in Chemical Engineering in 1988. She has continued her collaboration with John Oscarson and Reed Izatt. At present, her appointment is as a part-time research faculty member in the Chemistry Department. She supervises the operation of one of the major calorimetry laboratories in the university (six working calorimeters) and is deeply involved in the interpretation of the data relating to high-temperature high-pressure heats of mixing and of dilution, obtained for aqueous electrolyte mixtures.

Several other faculty members at BYU were involved with calorimetry earlier in their careers, but their research has since taken them in other directions. Included in this list are John Lamb and Gary Watt from the Chemistry Department, and Richard Rowley and Calvin Bartholomew from the Chemical Engineering Department.

4. Calorimeters at BYU

Two different types of precision calorimeters with various modifications were developed at Brigham Young University. The descriptions are as follows:

Titration calorimeters: Fig. 4 shows the construction of the isoperibol titration calorimeter developed by Jim Christensen, Reed Izatt and their students [7].

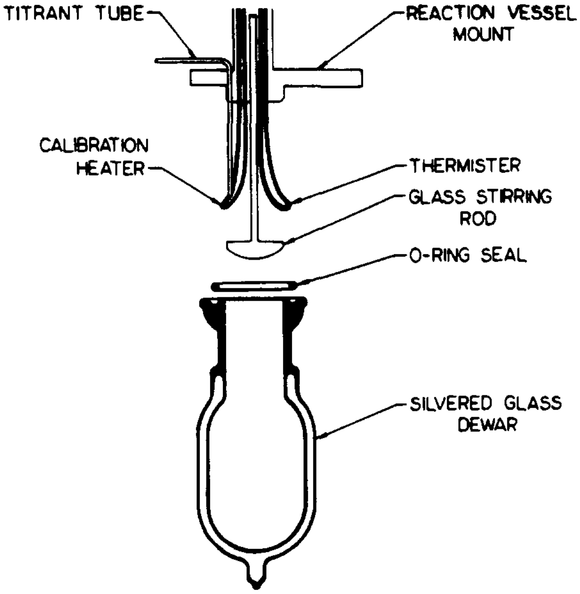


Fig. 4. Schematic of the isoperibol titration calorimeter insert [7].

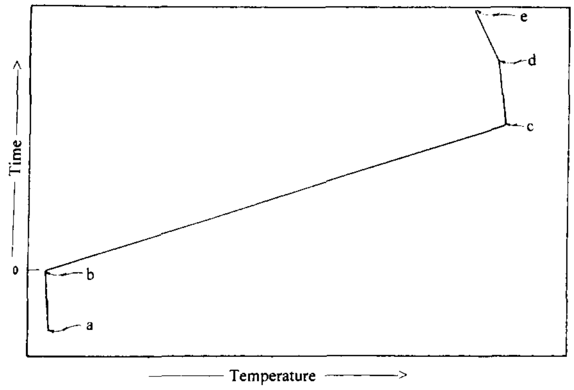


Fig. 5. A typical titration plot of temperature against time for the isoperibol titration calorimeter.

The reaction vessel is a silvered glass dewar flask, made with thin walls to reduce the heat capacity. It usually has a volume of ≈25 or 50 mL, although reaction vessels as small as 1.5 mL have been used. Titrant is added with a motor driven buret that can be used in an incremental mode or with a constant delivery rate that is variable over a wide range of flow rates. The temperature change during reaction is measured with a Teflon encased thermistor immersed in the reaction fluid; a Teflon encased heater, also immersed in the liquid, is used for calibration. Both the calorimeter and the buret containing the titrant are placed in a constant temperature (±0.0002 K) water bath.

A typical titration run is shown in Fig. 5. Titrant is added starting at point b. At point c, the reaction is complete. The addition of titrant is stopped at point d. A calibration run at the end of the titration (after point e), after cooling the reaction mixture to the initial temperature, gives the heat capacity of the system after reaction, from which the heat of reaction can be calculated from the temperature change. With care, such an apparatus can be used to measure heat effects with an accuracy of ±0.2%. It is important to note that, in one titration run, the heat effect at any point along the titration curve can be calculated accurately. One titration run thus gives data equivalent to a large number of batch calorimeter measurements.

A later modification allows the titration calorimeter to be run in an isothermal rather than an isoperibol mode [8,9]. The schematic design is shown in Fig. 6. A Peltier cooler mounted on the bottom of the reaction vessel removes heat at a constant rate. To keep the temperature constant, the heat removal is balanced by a pulsed control heater that is also mounted on the bottom of the reaction vessel. The isothermal condition is maintained by changing the frequency of the pulses from the control heater. A typical time vs. power (frequency) curve is shown in Fig. 7. Integration of the area under the curve during the titration gives the total heat effect.

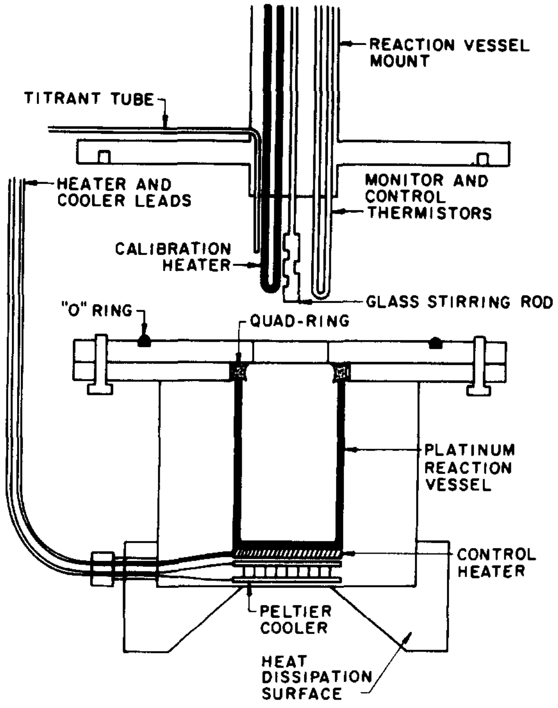


Fig. 6. Schematic of the titration calorimeter designed for isothermal operation. Reprinted by permission from Ref. [9].

Both the isoperibol and the isothermal calorimeters have been manufactured commercially both by Tronac and Calorimetry Sciences, and can be purchased with various accessories and data input/output devices.

High-temperature high-pressure flow calorimeters: In this flow calorimeter, fluids are mixed in a capillary tube inside the calorimeter. Over the years, the flow cell has gone through several modifications. The design of the cell in the earliest calorimeter [10,11] is shown in Fig. 8. A control heater is sandwiched between a coiled metal capillary tube and a Peltier cooler that is attached to a flat plate. This entire

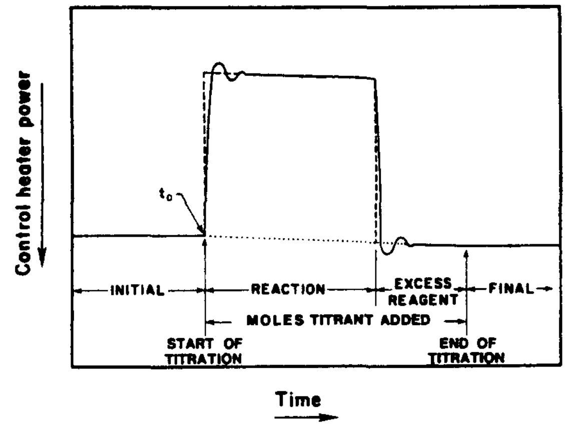


Fig. 7. A plot of power (or frequency) vs. time during the operation of the isothermal titration calorimeter. Integration of the area under the curve gives the total heat effect.

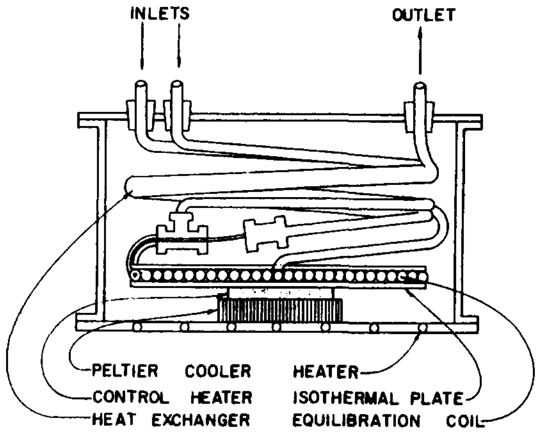


Fig. 8. Design of the early 'flat-plate' isothermal flow calorimeter. Reprinted with permission from Ref. [11].

assembly is enclosed in a metal container and immersed in a constant temperature bath controlled to ±0.002 K. Heat removed by the Peltier device is balanced by adjusting the frequency of electrical pulses through the control heater. High-pressure pumps are used to flow the reactants into the reaction vessel. Concentric tubes are used to separately carry the reactants to the coil, where they mix on the flat plate. A heater wound between the turns of the coil is used for electrical calibration. A back pressure regulator placed in the capillary tube after it exits the reaction vessel controls the pressure, with an upper limit of ≈20 MPa.

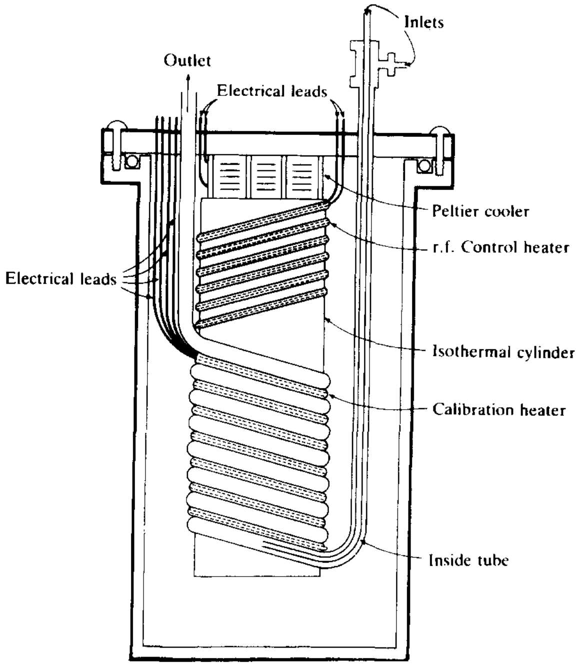


Fig. 9. Design of the isothermal flow calorimeter with the flat-plate replaced by a cylinder.

A later modification of the reaction vessel replaced the flat plate with a copper cylinder as shown in Fig. 9 [12]. Mixing is accomplished in a metal capillary tube wound around the bottom half of the cylinder. Isothermal temperature control is obtained by balancing the cooling from a Peltier device mounted on the top of the cylinder, with a pulsed electrical heater wound around the upper part of the cylinder. An electrical calibration heater is wound between the turns of the capillary mixing coil.

The change of frequency with time during a typical endothermic mixing measurement is shown in Fig. 10. A measurement of $\Delta\nu_{\mathrm{mix}}$ and $\Delta\nu_{\mathrm{e}}$, and the changes in frequency during mixing and during calibration that are required to maintain isothermal conditions, allows calculation of Q_{mix}, the heat of mixing, from Q_{e}, the electrical heat, using the relationship $Q_{\mathrm{mix}} = (\Delta\nu_{\mathrm{mix}}/\Delta\nu_{\mathrm{e}})Q_{\mathrm{e}}$.

Liquid baths and Peltier devices limit the upper temperature of the previous calorimeter to ≈475 K. Fig. 11 shows a modification of the calorimeter [13] designed for operation to temperatures as high as 675 K and pressures to 40 MPa. The Peltier cooler

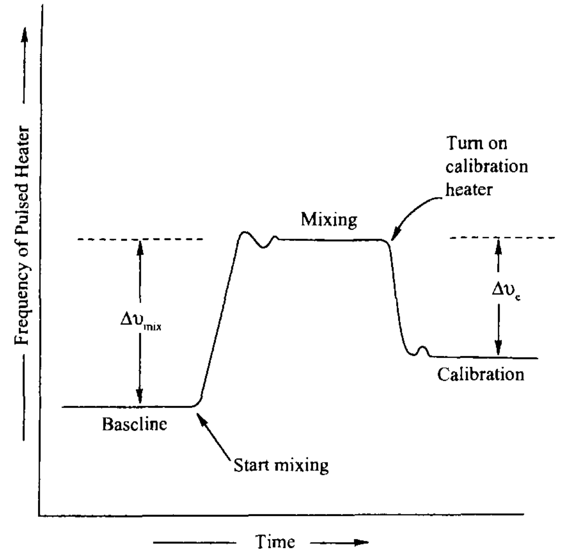


Fig. 10. Graph of frequency vs. time for a typical endothermic mixing measurement using the isothermal flow calorimeter.

in the earlier version is replaced by a constant heat leak, obtained by controlling the bottom plate of the calorimeter insert at a lower temperature than the mixing cylinder (see Fig. 11). The entire apparatus is placed in a constant temperature air bath, with concentric shields controlling the temperature environment around the mixing vessel and equilibrating the fluids to be mixed to the temperature of the mixing vessel (see Fig. 11).

Other modifications of the apparatus include construction of the capillary tubes from tantalum and later from platinum–iridium alloys for use with corrosive chemicals. When necessary, Teflon bags containing the chemicals are also used in the pumping system to isolate the pumps from the corrosive chemicals. For aqueous systems, where incomplete mixing is not a problem, the fluids to be mixed are brought together in a 'Y'-joint instead of using concentric tubes. This version is the one shown in Fig. 11[14].

In addition to the calorimeters developed at Brigham Young University, many of the calorimeters available at the university (as summarized in Table 1), but not developed at BYU, have been modified and accessories added to improve their effectiveness, versatility, and accuracy. These additions and changes

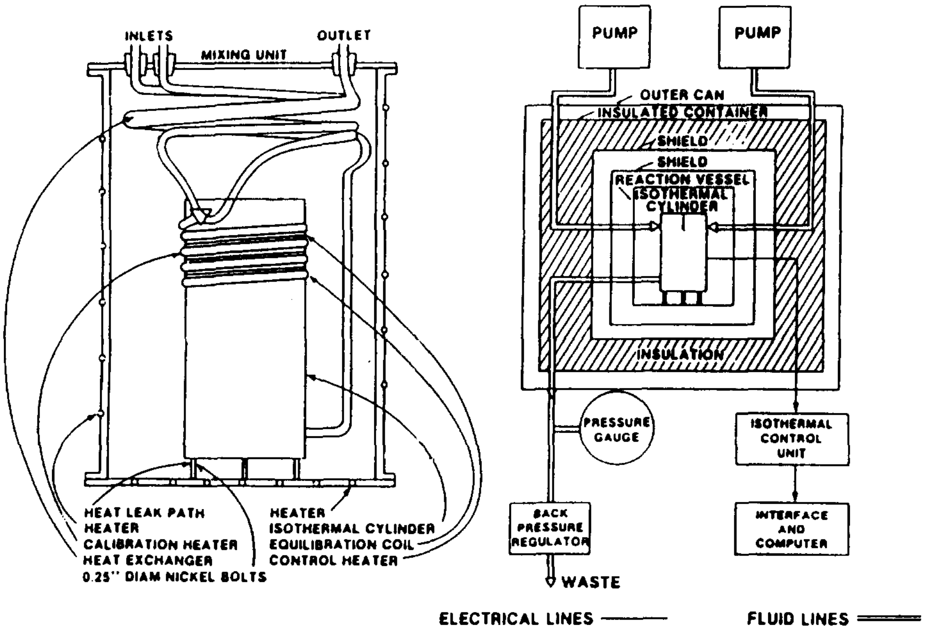


Fig. 11. The high-temperature modification of the isothermal flow calorimeter in which the Peltier cooler has been replaced by a constant heat leak and mixing occurs in a 'Y'-joint instead of concentric tubes [14]. Shown are the insert on the left and the concentric heat shields around the insert on the right. Reprinted by permission from Ref. [14].

were important and necessary for making the many different types of calorimetric measurements reported over the past 40 years.

5. Examples of experiments using calorimeters

The following are examples of experiments performed at Brigham Young University using calorimeters. The examples, some of which involve measurements that were made a number of years ago, are not meant to represent an exhaustive list, but were chosen to demonstrate the importance and versatility of calorimetry as a tool for studying chemical processes and to give an indication of the variety of experiments performed at BYU using calorimeters. It is also of interest to note the degree of collaboration on the various projects, with faculty working together in different combinations in which each faculty member brings a particular expertise to the solution of the problem. The examples are listed, at least approximately, in chronological order, and no attempt has been made to rank them in terms of importance.

5.1. The heat of ionization of water [15]

$\Delta_r H^0$ for the reaction

$$H^+(aq) + OH^-(aq) = H_2O(l) \qquad (2)$$

is an important quantity, since this reaction is often used to calibrate calorimeters and it serves as the basis for the calculation of $\Delta_f H^0$, the enthalpy of formation, for the OH^- ion. About 1960, Jim Christensen and Reed Izatt checked the literature and found that a considerable range of values of $\Delta_r H^0$ for the reaction in Eq. (2) had been reported, leading to an unacceptable uncertainty in the value of $\Delta_r H^0$. (Values ranged from -13.52 to -13.22 kcal mol^{-1}) The values reported are summarized in Fig. 12.

As a consequence of this uncertainty, measurements of $\Delta_r H$ were made for the neutralization of NaOH(aq) with perchloric acid(aq) and with HCl(aq). The measurements were made by graduate student J.D. Hale. The extrapolation of these results to zero ionic strength as shown in Fig. 12 gave a value of -13.335 ± 0.015 kcal mol^{-1} (-55.794 kJ mol^{-1}) for the reaction in Eq. (2). At almost the same time, Cecil Vanderzee, and his student J.A. Swanson, at the University of Nebraska made similar measurements. Their value [24] of -13.336 ± 0.009 kcal mol^{-1} is in excellent agreement with the BYU value. The combination of these two sets of measurements, made with high accuracy in independent laboratories, significantly reduced the uncertainty in $\Delta_r H^0$ for the reaction in Eq. (2) and led the National Bureau of Standards [25] to adopt a value for $\Delta_f H^0$ of OH^- of -229.994 kJ mol^{-1}, which is based on a value of

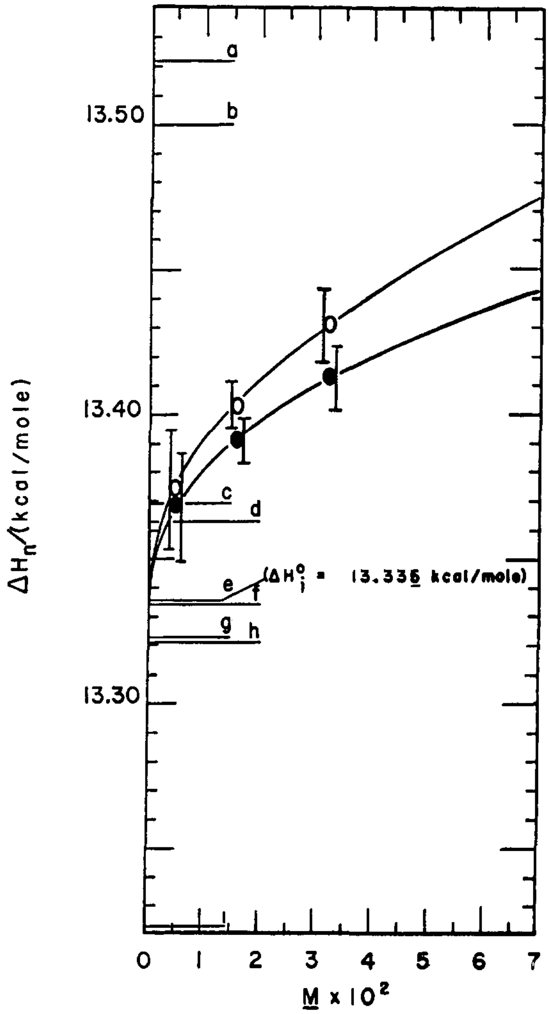


Fig. 12. Comparison of $\Delta_r H$ (expressed as ΔH_n in the figure) for the reaction in Eq. (2). The references for the various values reported are as follows: (a) – [16]; (b) –, [17]; (c) – [18]; (d) – [19]; (e) – [15] (present study); (f) – [20]; (g) – [21]; (h) – [22]; (i) – [23]. The values from this study are shown extrapolated to molarity $M = 0$ using NaOH as the base; and ○ – HCl and • – $HClO_4$ as the acid. Fig. 12 is reprinted with permission from Ref. [15].

-55.836 kJ mol^{-1} (-13.345 kcal mol^{-1}) for the reaction in Eq. (2). This value averages in results of other investigators, but is strongly influenced by the results at BYU and at Nebraska.

5.2. Calorimetric determination of equilibrium constants [26,27]

Fig. 5, which was given earlier as an example of a typical time vs. temperature curve obtained during a titration in a calorimeter, is obtained when the reaction has a large equilibrium constant and essentially goes to completion. However, when the reaction does not go to completion, a time vs. temperature titration curve represented by the one in Fig. 13 is obtained.

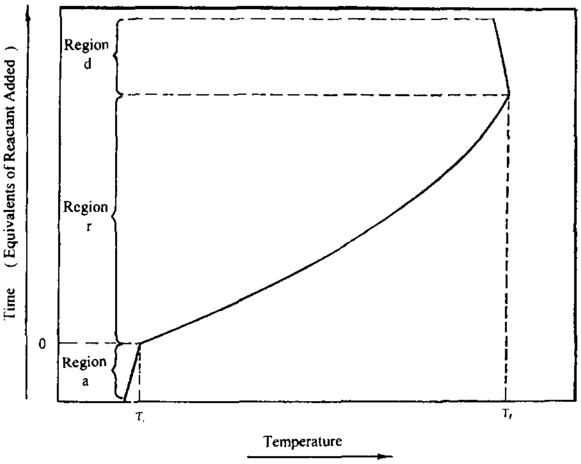


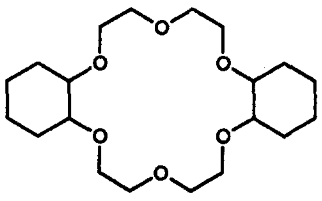
Fig. 13. A typical titration plot of temperature T vs. time t in the isoperibol titration calorimeter for a reaction with an equilibrium constant small enough that significant amounts of reactants remain at the equivalence point. In region 'a', titrant is not being added, and the temperature change is due to stirring, heating by the thermister, and heat transfer. In region 'r', titrant is being added, and the temperature change is due to heats of reaction, heats of dilution of titrant and solution, addition of titrant at a different temperature than in the reaction vessel, and the effects in 'a'. In region 'd', the titrant has been turned off and the temperature change is due to the same effects as in 'a'.

The curvature in region 'r' occurs because the reaction does not go to completion. Lee Hansen (as a graduate student) worked with Jim Christensen and Reed Izatt to devise a method for calculating the equilibrium constant for the reaction from the curvature of the titration curve. This application was originally called an entropy titration by the authors because it allows for the simultaneous determination of $\Delta_r H$ and $\Delta_r G$, from which $\Delta_r S$ can be calculated. Table 2 compares the pK values for two reactions as obtained from this calorimetric method, with literature values obtained from other types of measurements. The agreement in the values provides verification of the method.

This procedure has since been applied to a large variety of chemical reactions and has proven to be a useful and reliable technique for determining equilibrium constants.

5.3. Ion binding by synthetic macrocyclic compounds [31]

Macrocyclic compounds such as dicyclohexyl-18-crown-6 shown below form complexes with many cations.



dicyclohexyl-18-crown-6

In most instances, the complex results from inclusion of the cation in the center of the macrocyclic ring, while forming coordinate bonds with the heteroatoms in the ring.

Reed Izatt, Jim Christensen, and co-workers have used the calorimetric technique described in Section 5.2 to determine the equilibrium constants for the binding of various metal ions to a number of different macrocycles. As an example, Fig. 14

Table 2

Comparison of the pK for two chemical reactions obtained from calorimetric titration curves with values obtained by other methods

Reaction	pK (present study)	pK (from literature)	Reference
$HSO_4^- = H^+ + SO_4^{2-}$	1.90	1.98	[28,29]
$HPO_4^{2-} + OH^- = PO_4^{3-} + H_2O$	−1.61	−1.625	[30]

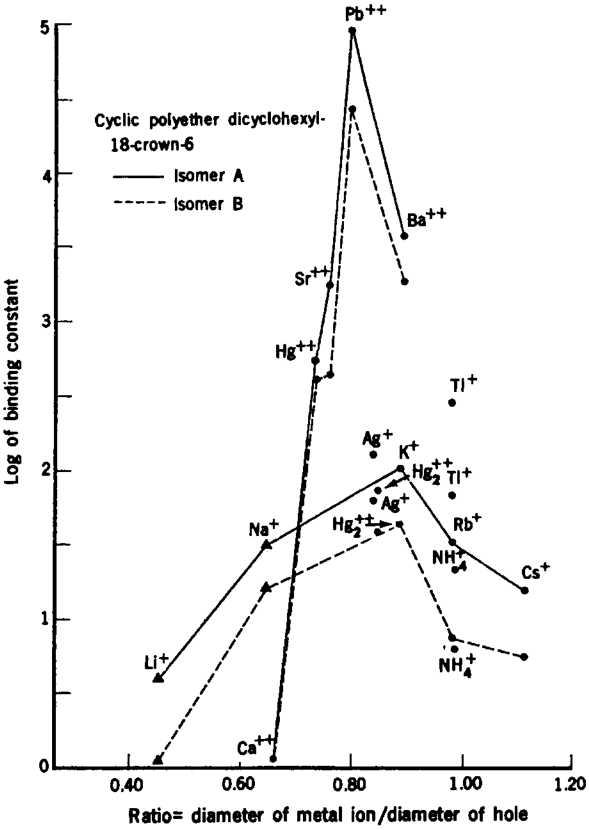


Fig. 14. Graph of the log of the equilibrium constant for the binding of a metal ion to the dicyclohexyl-18-crown-6 macrocycle against the ratio of the diameter of the metal ion to the diameter of the hole in the macrocycle. The diameter of the hole in dicyclohexyl-18-crown-6 is assumed to be 3.0 Å. Dicyclohexyl-18-crown-6 exists as two different geometric isomers. The equilibrium constants for the formation of complexes with both isomers are shown by the solid lines and the dashed lines, respectively. Reprinted by permission from Ref. [31].

compares the log of the equilibrium constant for the complexing of a number of different metal ions with dicyclohexyl-18-crown-6, as a function of the ratio of the diameters of the metal ion to the diameter of the hole (assumed to be 3.0 Å for this macrocycle). Fig. 14 demonstrates that the strength of the complex depends on the size of the ion, and very strongly on the charge on the ion. It is evident from this figure that dicyclohexyl-18-crown-6 selectively complexes Pb^{2+} over other ions. Other macrocyles can be designed with different cavity sizes and a variety of heteroatoms that will selectively complex specific cations. This selectivity is the basis for several techniques of ion separation. Since this initial work, a large number of macrocyclic complexing systems have been studied. Jerald Bradshaw, a faculty member in the chemistry department at BYU whose research involves synthesis of organic compounds, makes the macrocycles while Reed Izatt and coworkers study the complexing ability. A company (IBC Advanced Technologies, Inc.) has been formed and spun out of the university to commercialize separation processes using macrocycles.

5.4. Determination of sulfur in aerosols [32]

As a part of their environmental studies, Delbert Eatough and a host of co-workers have been involved for a number of years in the study of airborne aerosols in the atmosphere. In studies of environmental pollution, it is important to know the amount of sulfur (IV) and sulfur (VI) in the aerosols, since pulmonary effects apparently depend upon the amounts of both.

A thermometric titration procedure was developed at BYU to determine in one titration, the sulfur (IV) and total sulfur in an environmental sample. The procedure can be understood by referring to Fig. 15. Sulfur (along with a number of other components) is extracted (at low temperature to avoid oxidation) from the environmental sample using an acidic $FeCl_3$ solution, and an aliquot of the extractant solu-

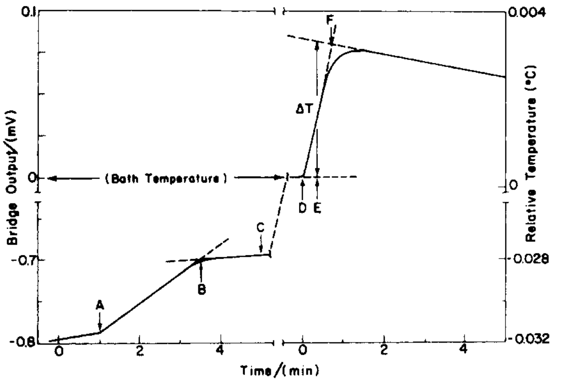


Fig. 15. Typical curves for the thermometric titrations used to determine the amount of sulfur(IV) and sulfate in the extractant solution from an aerosol sample. Reprinted with permission from Ref. [32].

tion is put in the calorimeter. A standard $K_2Cr_2O_7$ solution is added as titrant during the time from point 'A' to point 'C' in Fig. 15. The heat generated results from the oxidation of sulfur(IV) to sulfur(VI). From the endpoint of the redox titration at 'B' the amount of sulfur(IV) can be calculated. Since other reducing agents such as Fe(II) and As(III) may also be present, the portion of the thermogram representing the sulfur(IV) oxidation must be identified. This can be done from the slope of the thermogram from 'A' to 'B', since this slope is proportional to the heat of the reaction and hence, would be different for different redox reactions.

Between times 'C' and 'D', the temperature in the reaction vessel is adjusted to the bath temperature. At point 'D', a $BaCl_2$ solution is injected. The temperature change ΔT, which results from the precipitation of $BaSO_4$, can then be used to calculate total sulfur as sulfate.

The procedure is selective, in that there are no major interferences with other types of contaminants. An analysis of the sources of error in determining the small amounts of sulfur present indicate that the precision of the technique is ±(5% of total S(IV) +3 nmol) and ±(10% of total sulfate +30 nmol) in 2.25 ml of extractant solution.

5.5. *Stability of the pinacol hexahydrate [33]*

Pinacol $[C(CH_3)_2OH]_2$ is a diol related to ethylene glycol. A graduate student, Jeffrey Priest, working with Bevan Ott and Rex Goates determined the (solid + liquid) phase diagram for the (pinacol + water) system given in Fig. 16, and showed that pinacol monohydrate $\{[C(CH_3)_2OH]_2{\cdot}H_2O\}$ and pinacol hexahydrate $\{[C(CH_3)_2OH]_2{\cdot}6H_2O\}$ freeze from liquid solution. DSC measurements showed that the solid pinacol hexahydrate has an exceptionally large enthalpy of fusion per gram of solid [33]. The reasons can be understood by considering ΔH for the following processes which add together to give ΔH for the formation of the pinacol hexahydrate(s) from pinacol(s) and water(s).

$$[C(CH_3)_2OH]_2(l) + 6H_2O(l) = [C(CH_3)_2OH]_2{\cdot}6H_2O(l);\ \Delta H_1 = -5.33\,kJ\,mol^{-1}$$

$$6H_2O(s) = 6H_2O(l);\ \Delta H_2 = 45.49\,kJ\,mol^{-1}$$

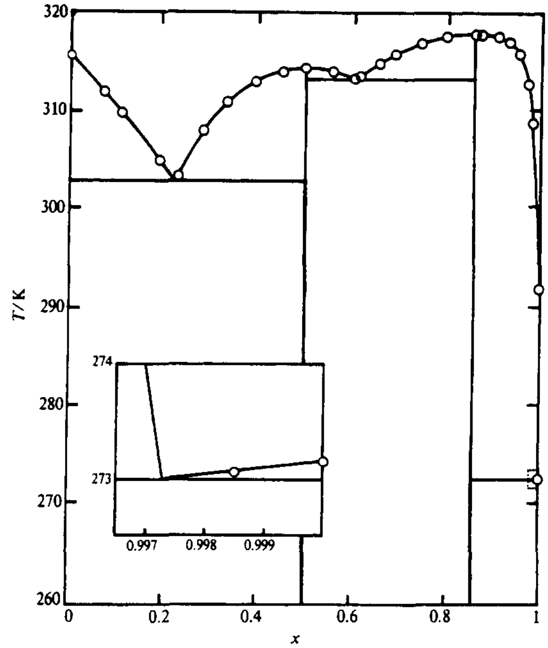


Fig. 16. (Solid + liquid) phase diagram for $\{xH_2O + (1-x)[C(CH_3)_2OH]_2\}$. Reprinted with permission from reference [33].

$$[C(CH_3)_2OH]_2(s) = [C(CH_3)_2OH]_2(l);\ \Delta H_3 = 14.9\,kJ\,mol^{-1}$$

$$[C(CH_3)_2OH]_2\cdot 6H_2O(l) = [C(CH_3)_2OH]_2{\cdot}6H_2O(s);\ \Delta H_4 = -67.7\,kJ\,mol^{-1}$$

$$[C(CH_3)_2OH]_2(s) + 6H_2O(s) = [C(CH_3)_2OH]_2{\cdot}6H_2O(s);\ \Delta H_5 = -(12.5 \pm 0.5)kJmol^{-1}$$

The values of ΔH_1, ΔH_2, ΔH_3, and ΔH_4 were obtained at a common temperature, $T = 318.78$ K, the melting temperature of the pinacol hexahydrate, as follows. Earl Woolley measured the excess molar enthalpies for $\{xH_2O + (1-x)[C(CH_3)_2OH]_2\}$ at 320 and 325 K using a Tronac titration calorimeter. (A commercial version of the Christensen–Izatt–Hansen calorimeter described earlier.) The results are shown in Fig. 17. Note that the minimum in H_m^E occurs near $x = 0.8571$, the composition corresponding to the stoichiometric ratio of water to pinacol in $[C(CH_3)_2OH]_2{\cdot}6H_2O$, suggesting that complexes may be forming in the liquid mixture as well as in the solid. ΔH_1 was calculated from these measurements by taking the

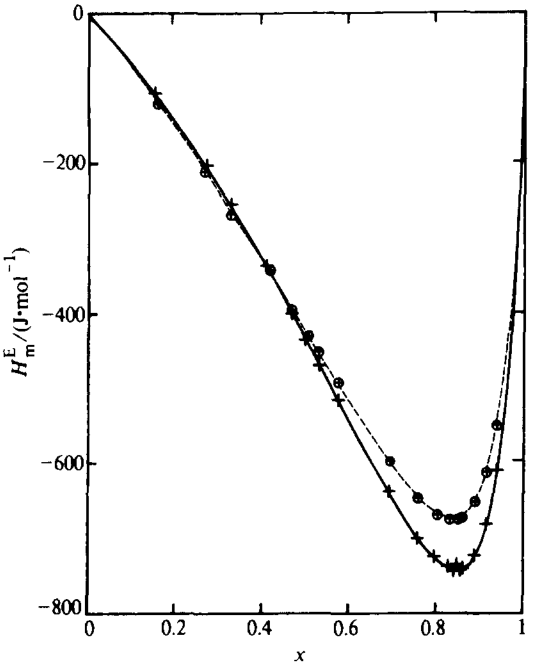


Fig. 17. Excess molar enthalpies H^E_m for $\{xH_2O + (1-x)\ C(CH_3)_2OH]_2\}$. The temperatures are as follows: + ———, 320 K; and ○ - - -, 325 K. Reprinted with permission from reference [33].

H^E_m values at the two temperatures at $x = 0.8571$ and extrapolating to $T = 318.78K$. ΔH_2 was obtained from values for $\Delta_{fus}H$ and $\Delta_{fus}C_p$ of water summarized in an earlier paper [34] and corrected to $T = 318.78K$ using the equation $(\partial\Delta_{fus}H/\partial T)_p = \Delta_{fus}C_p$. ΔH_3 and ΔH_4 were obtained from DSC measurements made by Jeffrey Priest, again corrected to $T = 318.78K$ using ΔC_p results obtained from the DSC measurements.

The large negative ΔH_5 indicates a significant energy stabilization when pinacol(s) and water(s) combine to form the pinacol hexahydrate(s). Kim and Jeffrey [35] have reported the structure of the pinacol hexahydrate(s) using X-ray diffraction studies. They describe the structure as being very similar to a clathrate, with the pinacol molecules in voids within a hydrogen bonded framework structure of water molecules. Melting the hydrate breaks this structure apart, which requires a large absorption of energy, and results in a large enthalpy of fusion.

5.6. *Thermodynamics of ionic surfactant solutions [36]*

Earl Woolley collaborated with Tom Burchfield from the National Institute for Petroleum and Energy Research in Bartlesville OK, to develop a model for describing the thermodynamic properties of aqueous surfactant solutions. The model assumes a mass action equilibrium involving a single–surfactant aggregate species (micelle) [37,38]. The equilibrium expression is

$$(n\beta)M^{\pm} + nA^{\mp} = M_{n\beta}A_n^{\mp n(1-\beta)} \tag{3}$$

In Eq. (3), $A^{\mp}$ is the monomeric surfactant, $M^{\pm}$ the free counter ion, $M_{n\beta}A_n^{\mp n(1-\beta)}$ the micelle, n the aggregation number, and $n\beta$ the number of counter ions 'bound' to the micelle.

Starting with Eq. (3) and assuming Debye–Hückel expressions for calculating activity coefficients, equations can be derived for calculating as a function of ionic strength, apparent molar volumes, apparent molar heat capacities, and apparent relative molar enthalpies and, hence, enthalpies of dilution.

Earl Woolley and an undergraduate student, Michael Bashford, have made enthalpy of dilution measurements on (surfactant + electrolyte) mixtures using a Tronac isoperibol titration calorimeter [36]. The fit of the experimental results to the model equations for two different surfactants are shown in Fig. 18 and 19. The fit of the model to the experi-

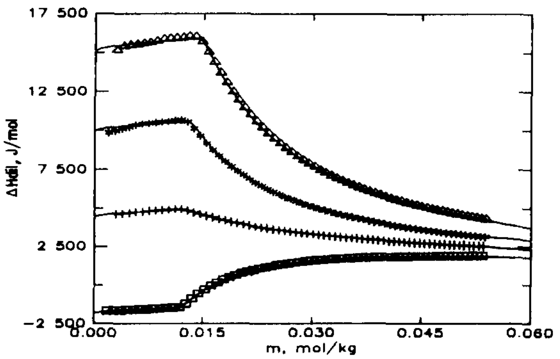


Fig. 18. Enthalpies of dilution of equimolar (dodecyltrimethylammonium bromide + sodium bromide) solutions at the following temperatures: □ – 10°C; + – 25°C; * – 40°C; and △ – 55°C. The solid lines are the fit to the model. Reproduced by permission from Ref. [36].

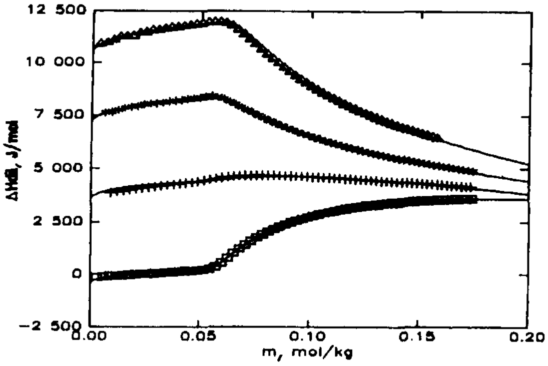


Fig. 19. Enthalpies of dilution of equimolar (decyltrimethylammonium bromide + sodium bromide) solutions at the following temperatures: □ - 10°C; + - 25°C; * - 40°C; and △ - 55°C. The solid lines are the fit to the model. Reproduced by permission from Ref. [36].

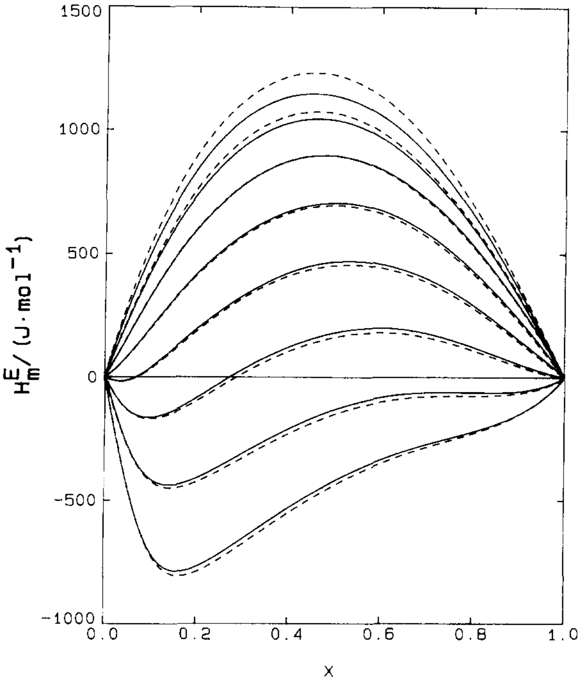


Fig. 20. Excess molar enthalpies H^E_m for $\{xC_2H_5OH + (1-x)H_2O\}$ at temperatures of 298.15, 323.15, 348.15, 373.15, 398.15, 423.15, 448.15, and 473.14 K. The pressures are: ——— - 5; and - - - - 15 MPa. H^E_m increases with increasing temperature so that the bottom curves are at 298.15 K and the top curves are at 473.15 K. Reproduced by permission from Ref. [39].

mental results, including a break at the critical micelle concentration that varies in composition with the size of the micelle, demonstrates that this rather simple equilibrium assumption (Eq. (3)) correlates well with the properties of the surfactant mixtures.

5.7. Excess enthalpies and excess volumes for (ethanol + water) mixtures [39,40]

Bevan Ott, Jim Christensen, and their students made comprehensive measurements of the excess enthalpies H^E_m for (ethanol + water) mixtures over the temperature range from 298.15 to 473.15 K and pressures from 0.4 to 15 MPa [39]. The measurements were made with one of the high-temperature high-pressure flow calorimeters that was constructed with special care to give as accurate results as possible, since this system has been suggested as a test mixture for checking the calibration of flow calorimeters [39].

The results at a series of temperatures and two pressures are shown in Fig. 20. It can be seen that the pressure effect is small, but changes sign and increases in magnitude with increasing temperature. On the other hand, the effect of temperature is large, with negative H^E_m skewed toward low mole fraction of ethanol at 298.15 K, changing to positive H^E_m that are nearly symmetrical with mole fraction at 373.15 K.

The negative H^E_m at low temperatures and the effect of temperature on H^E_m are explained as resulting from a hydrogen bonded complex in the liquid mixture, with the ethyl group of the ethanol surrounded by a hydrogen bonded cage of water molecules as shown schematically in Fig. 21. The structure of this complex is in many ways similar to that of the solid pinacol hexahydrate described earlier, where it was shown that the formation of the hydrate results in a significant lowering in energy [33].

Hydrogen bonds break more readily with increasing temperature. Thus, at higher temperatures, the hydrogen bonded cage breaks down so that less of the complex forms, and H^E_m becomes more positive.

Excess molar volumes V^E_m have also been measured for (ethanol + water) mixtures at the temperatures of 298.15, 323.15, and 348.15 K and pressures of (5 and 15) MPa, by inserting the measuring cell of an Anton–Paar vibrating tube densitometer into the flow line between the exit tube of the calorimeter and the back pressure regulator [40]. The measured excess volumes are shown in Fig. 22. Negative V^E_m, that decrease in

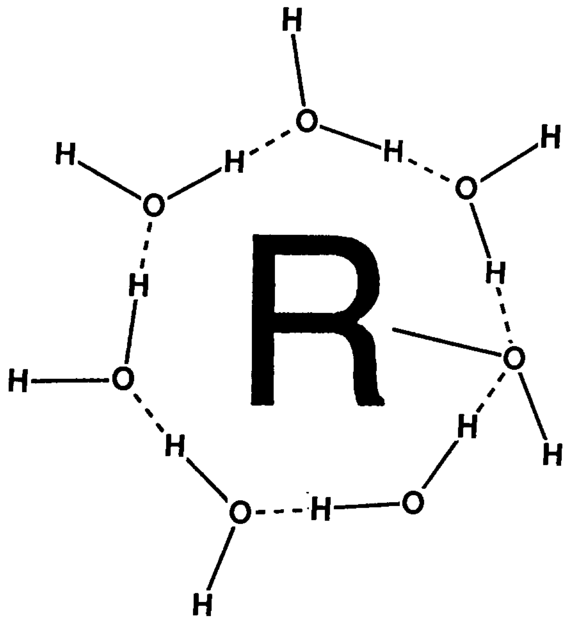


Fig. 21. Schematic representation of the complex in (ethanol + water) mixtures. R represents the ethyl group of the ethanol. It is surrounded by a hydrogen-bonded cage of water molecules.

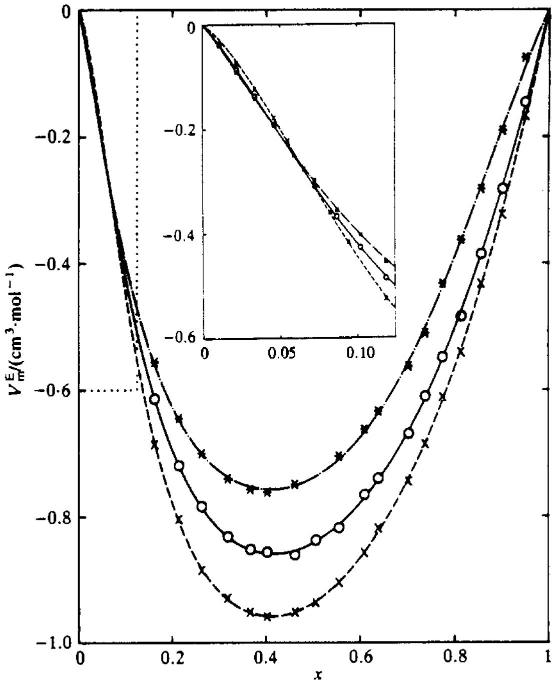


Fig. 22. Comparison of excess molar volumes V_m^E at p = 15 MPa for $\{xC_2H_5OH + (1-x)H_2O\}$. The temperatures are as follows: × - $T = 298.15$ K; ○ - $T = 323.15$ K; and * - $T = 348.15$ K. The insert shows the intersection at low values of × of the three $V_m^E(x)$ curves. Reprinted with permission from Ref. [40].

magnitude with increasing T and p, are as expected if complex formation as described earlier is present.

5.8. *Interaction of* SO_4^{2-} *with* H^+ *and* Na^+ *at high temperatures [41]*

The flow calorimeter can be used to simultaneously measure ΔH and $\log K$ (or ΔG) at high temperatures and pressures for dissociation or association reactions. The procedure is similar to that described earlier, using the titration calorimeter at ambient temperature and pressure. Table 3 summarizes results obtained by John Oscarson, Sue Gillespie, Reed Izatt, and Jim Christensen, along with Phil Brown as a graduate student.

Note that $\log K$ increases and, hence, dissociation decreases with increasing temperature for all three reactions. Thus, H_2SO_4, that is completely dissociated and a strong acid at lower temperatures becomes associated and a weak acid at high temperatures. Likewise, the ionic salt Na_2SO_4 is not completely dissociated at high temperatures.

The reasons can be explained in terms of the thermodynamics of the reactions. $\log K$ is related to $\Delta_r H$ and $\Delta_r S$ by the equation

$$2.303RT \log K = -\Delta_r H + T\Delta_r S \tag{4}$$

As can be seen in Table 3, $\Delta_r H$ and $\Delta_r S$ are positive for all three reactions. The positive values are usually explained as resulting from the release of waters of hydration when a chemical product with lower ionic charge is formed. The $\Delta_r H > 0$ reflects the increase in energy due to this process, while the $\Delta_r S > 0$ results from the increased disorder as waters of hydration are released. The disorder effect is affected more by increasing temperature than is the energy effect so that the $T\Delta_r S$ term increases faster than $\Delta_r H$, and $\log K$ as the difference between the two, increases with increasing T.

5.9. *Phase transitions in langbeinites [42]*

The langbeinites are a family of compounds with the general formula $A_2B_2(SO_4)_3$. They are isomor-

Table 3

Equilibrium constant K, $\Delta_r H$ and $\Delta_r S$ for reactions of H^+ and Na^+ with SO_4^{2-} at temperatures T and pressures p as determined from high-temperature high-pressure flow calorimetric measurements

Reaction	T/°C	p/MPa	log K	$\Delta_r H$/(kJ mol^{-1})	$\Delta_r S$/(J K^{-1}mol^{-1})
$H^+ + SO_4^{2-} = HSO_4^-$	150	2.31	3.56	57.36	204
	175	2.24	3.98	64.97	221
	200	2.31	4.41	75.05	243
	250	10.3	5.31	105.03	303
	300	11.0	6.44	150.98	387
	320	12.8	6.94	174.42	427
$H^+ + HSO_4^- = H_2SO_4$	150	2.31	−1.05	19.62	26
	175	2.24	−0.91	21.63	31
	200	2.31	−0.77	24.78	38
	250	10.3	−0.41	47.80	83
	300	11.0	0.23	109.55	196
	320	12.8	0.62	148.43	262
$Na^+ + SO_4^{2-} - = NaSO_4^-$	150	2.31	0.95	24.68	77
	175	2.24	1.15	32.80	95
	200	2.31	1.38	42.06	115
	250	10.3	1.93	64.12	160
	300	11.0	2.60	91.09	209
	320	12.8	2.90	103.28	230

phous with the naturally occuring mineral, $K_2Mg_2(SO_4)_3$, named Langbeinite. They have a cubic structure at high temperatures, but some transform to either ferroelastic or ferroelectric low-temperature phases. The change in structure usually occurs in one of two ways: type I langbeinites change from cubic to monoclinic to triclinic to orthorhombic as the temperature is lowered, while type II change directly from cubic to orthorhombic.

Julie Boerio-Goates and her graduate students have used a cryogenic calorimeter to measure the heat capacity of several of these langbeinites to low temperatures and study the phase transitions, which have proven to be more complicated than a simple first order phase transition. Graduate students Johanne Artman and Brian Woodfield have studied the original langbeinite $K_2Mg_2(SO_4)_3$ [42]. They obtained the heat capacity vs. temperature curve shown in Fig. 23. Transitions are evident in the temperature region from 50 to 70 K. Fig. 24 is an enlargement of this temperature region of the heat capacity curve. At least three different peaks are evident, but none looks like a strongly first-order transition predicted by theory, and the values obtained are sensitive to the method used to make the measurements. Heating over small temperature intervals, 0.5–2 K, is required to obtain the detail. When this is not done, the transition can be missed completely. Robie et al. [43] reported measurements on this system at about the same time, using heating increments of 2.6 to 5 K, but did not find the transitions.

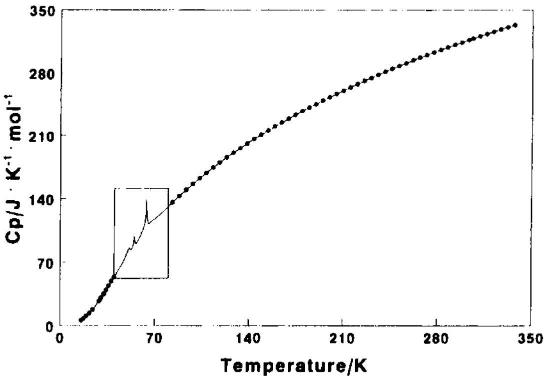


Fig. 23. The heat capacity of $K_2Mg_2(SO_4)_3$ as a function of temperature. For clarity, experimental points have been omitted in the transition region from 45 to 80 K that is shown in more detail in Fig. 24. Reproduced by permission of Ref. [42].

Recently, a graduate student, Hongjie Cao, and Julie Boerio-Goates have used the calorimeter to study $Tl_2Cd_2(SO_4)_3$. In contrast to the transitions in $K_2Mg_2(SO_4)_3$, they did find three sharp first-order

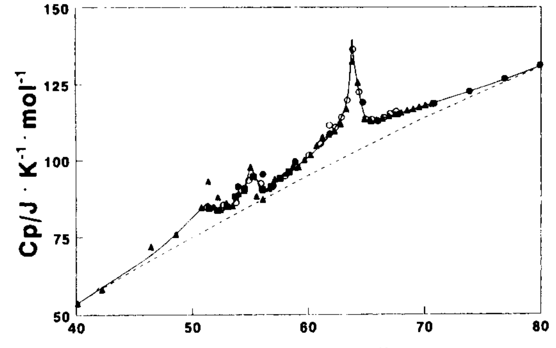


Fig. 24. An expanded view of the experimental heat capacities in the temperature region of the transitions. The different symbols represent measurements made during different experimental runs. Reproduced by permission from Ref. [44].

transitions at 96.0, 123.0, and 129.9 K in $Tl_2Cd_2(SO_4)_3$ [44].

5.10. Kinetics of drug decomposition [45]

The development of heat conduction calorimeters having a detection limit of ±0.1 μW provided a method for measuring very small heat effects. Lee Hansen, Ed Lewis, and Delbert Eatough, in collaboration with colleagues from outside BYU, used a heat conduction calorimeter to measure the rate of decomposition of drugs by following the heat of the reaction. Such information is useful, since slow rates of decomposition at room temperature can be detected and studied, and reaction rates as low as a few percent per year are significant in determining how long drugs can be stored.

Lovastatin, a drug marketed as a cholesterol-lowering agent, was chosen as an example for study. The rate of decomposition of Lovastatin is extremely sensitive to trace impurities and surface properties and hence, different lots have different decomposition rates.

Table 4 compares the effects of atmospheric composition and temperature on the rate of heat production in Lovastatin [45]. In the table, q is the rate of heat production and D_0 the amount of the drug present in the sample at $t = 0$. The samples were sealed in glass ampules to prevent atmospheric contamination.

Table 4
Effect of atmosphere and temperature on the rate of decomposition of Lovastatin as determined from heat conduction calorimetry

Atmosphere	T/°C	$(q/D_0)/(\mu W\ g^{-1})$
N_2	25	−0.1±0.1
O_2	25	0.9±0.1
N_2	50	1.1±0.3
O_2	50	22.8±1.1

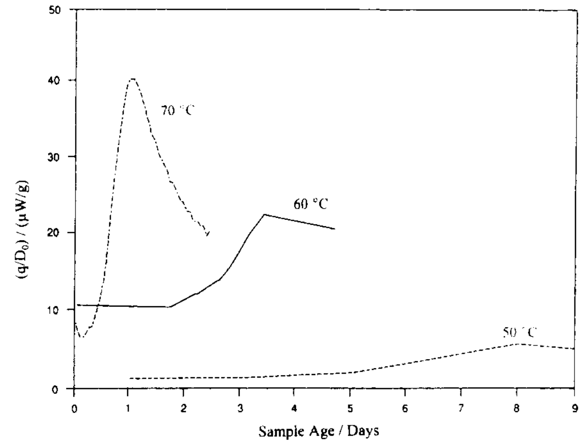


Fig. 25. The effect of temperature on the decomposition by autoxidation of a given sample of Lovastatin. The lines simply connect the data points collected. Reproduced by permission from Ref. [45].

It is obvious from the results that decomposition is due to reaction with oxygen. Table 4 demonstrates that temperature has a major effect on the rate of decomposition. Fig. 25 shows the effect of temperature and time on the rate of decomposition. The initial rapid increase in rate indicates that the decomposition is autocatalytic. The decrease in rate at longer times results from depletion of the reactive portion of the solid.

Fig. 26 compares the rate of decomposition of two different samples of Lovastatin. Such differences in rate can be used to test samples and determine how long a lot can be stored without serious decomposition.

5.11. Molecular-dynamics modeling of excess enthalpies [46]

Bill Tolley, a graduate student working with John Oscarson and Reed Izatt, has measured the excess

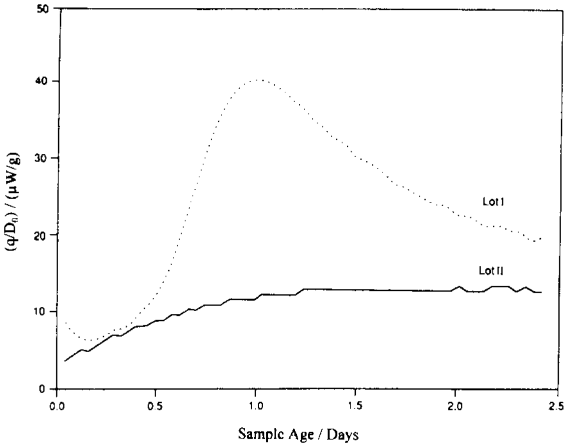


Fig. 26. Calorimetric determination of the rate of decomposition at 70°C of two different lots of Lovastatin. Reproduced by permission from Ref. [45].

molar enthalpies H_m^E for mixtures of neopentane $[C(CH_3)_4]$ with CO_2. The measurements were made at two temperatures, (310 and 313.15) K, that are slightly above the critical temperature of CO_2 (304.19 K), and at three pressures (6.29, 8.36, and 10.44) MPa. Two of these pressures are well above the critical pressure of CO_2 (7.38 MPa), while the third is below. The critical temperature and pressure of neopentane are 433.8 K and 3.20 MPa, so that the measurements were made between the two critical temperatures, and (fluid + fluid) phase equilibria are possible, especially at $p = 6.29$ MPa.

This system was chosen for study because it is an interesting one to use in testing methods for predicting H_m^E. It was of special interest in testing predictions from molecular-dynamics simulations because the neopentane molecule is spherical and can be represented by a spherical potential. The CO_2 molecule is ellipsoidial, but not far from spherical, and it would be interesting to see what type of potential is required to correctly represent the properties of this molecule.

A graduate student, Neil Giles, working with Richard Rowley, a chemical engineering professor at BYU, made the molecular-dynamics calculations. Neopentane was modeled with a spherical Leonard–Jones potential. CO_2 was modeled, both as a spherical Leonard–Jones fluid and as a linear, two-site Leonard–Jones fluid.

The comparisons between the experimental and calculated H_m^E for $\{xC(CH_3)_4 + (1-x)CO_2\}$ at the two temperatures and three pressures are shown in Fig. 27. H_m^E changes significantly with pressure and temperature, and yet, the molecular-dynamics simulation does a good job in predicting H_m^E at all the pressures and temperatures. The prediction using the two-site potential for CO_2 is a marked improvement over the prediction assuming a spherical potential. Of special interest is to note how well the simulation predicts the (fluid + fluid) phase equilibria that is present at $p = 6.29$ MPa, since phase equilibria predictions are often a more exacting test of predictive methods than are energy (or enthalpy) predictions.

5.12. Plant calorimetry [47,48]

Lee Hansen and colleagues from the University of California at Davis have used a heat conduction DSC to study the rates of metabolism of plants. For example, Fig. 28 compares the rate of heat production in the DSC (in the dark without photosynthesis) as a function of temperature, of samples of orange and apple leaf segments. Assuming that the rate of heat production is a measure of the metabolic rate, it is apparent that orange cells thrive at a higher temperature than apple cells, a result that is not too startling from knowing that orange trees grow in warmer climates than do apple trees. The difference in the effect of temperature, however, is interesting. Fig. 28[47] demonstrates that the metabolism of the orange leaf has a much more abrupt high-temperature cut-off than does the apple leaf. Thus apple cells are more tolerant to temperature change and can thrive over a wider range of climatic conditions.

By assuming that the Arrhenius equation can be used to represent the effect of temperature on the metabolic rate, energies of activation can be calculated from the effect of temperatures on the rate of heat production in the calorimeter. Table 5 compares E_A/R, the energy of activation divided by R, the gas constant, for several different kinds of plants. The correlation of energy of activation with climate shows that plants that grow in warm climates have higher activation energies than do similar plants that grow in colder climates. The conclusion that can be drawn is that the lower activation energy in the colder, more variable, climate allows for faster growth across a wider range of temperatures.

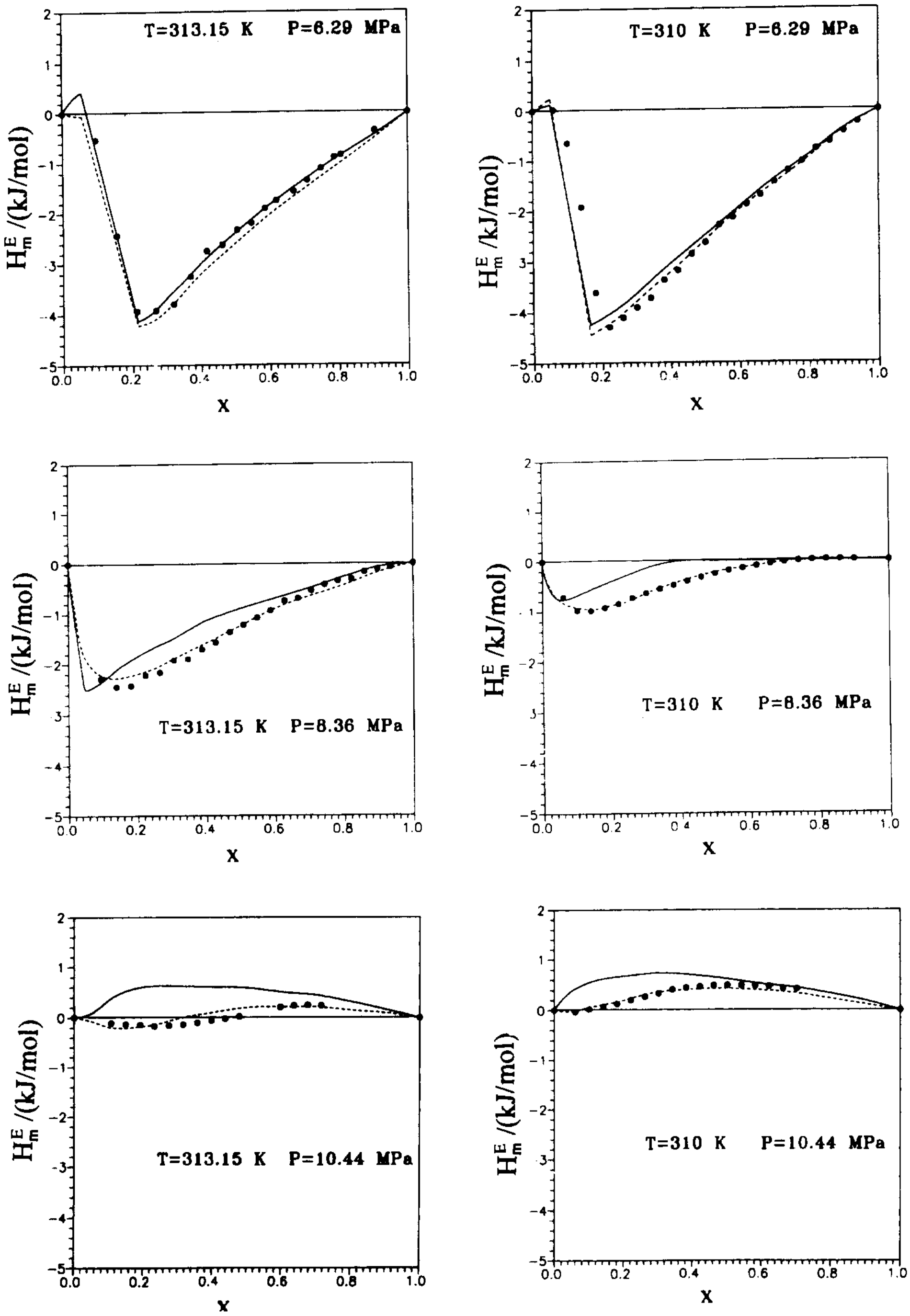


Fig. 27. Comparison of experimental and predicted H^E_m for $\{xC(CH_3)_4 + (1-x)CO_2\}$ at two temperatures and three pressures. The representations are as follows: • • • – experimental; ——— – molecular-dynamics simulation assuming a spherical Leonard–Jones potential for CO_2; and - - - - – molecular-dynamics simulation assuming a two site Leonard–Jones potential.

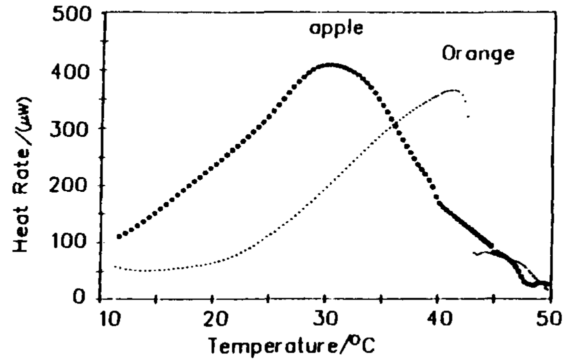


Fig. 28. Metabolic heat rates of (• • •) apple and (· · ·) orange leaf segments as a function of temperature. Reproduced by permission from Ref. [47].

Table 5
Energies of activation for different types of plant cells, illustrating the effect of climate on the metabolic rate

Organism	$(E_A/R)/K$
Coast redwood	8.3
Sierra redwood	5.0
Southern black spruce	8.4
Northern black spruce	7.1
Southern magnolia	7.3
Northern magnolia	5.5
Tomato {(12–32)°C}	6.6

As another example, Fig. 29 [48] compares the metabolic rates of tomato cells and barley root tips as a function of temperature. The two rates are similar up to ~26°C, but tomato tolerates higher temperatures, up to ~32°C, before stress becomes apparent.

5.13. Heat capacity and entropy of sucrose [49]

Julie Boerio-Goates is making some 'sweet' measurements in her cryogenic calorimeter. She is measuring the heat capacity to low temperatures of sugars. Fig. 30 shows $C_{p,m}/R$ for crystalline sucrose as a function of temperature obtained by a graduate student, Robert Putnam. Sucrose appears well behaved with no phase transitions or anomalies. A third law integration of $C^0_{p,m}/T$ vs. T gave a value for S^0_m (sucrose, cr, 298.15 K) of 392.4 J K^{-1} mol^{-1}. This value differs significantly from that obtained many years ago by Parks et al. [50], who reported a value of 350.4 J K^{-1} mol^{-1}. The difference is an unacceptable 32.4 J K^{-1} mol^{-1}.

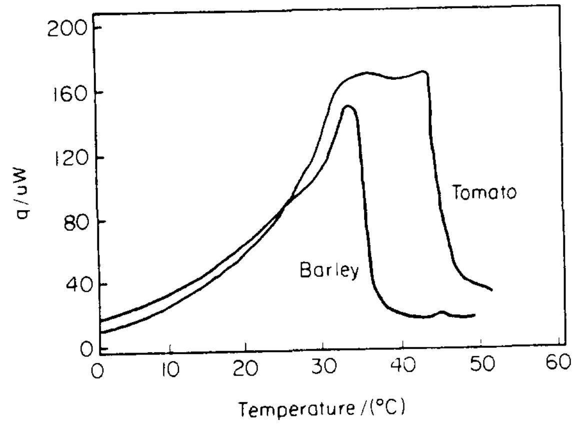


Fig. 29. Metabolic heat rates (q) of tomato cells and barley root tips as a function of temperature. Reproduced by permission from Ref. [48].

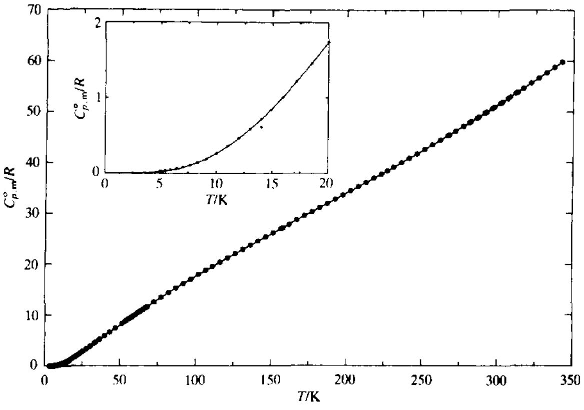


Fig. 30. Graph of $C^0_{p,m}/R$ of crystalline sucrose as a function of temperature; • – experimental data points. Reprinted by permission from Ref. [49].

Parks, Kelley, and Huffman were known for the high quality of their work, even in those early days, and it was difficult to justify the difference. Several possibilities were considered as the source of error. Table 6 compares the calculation by Putman and Boerio-Goates [49] and Parks et al. [50] of ΔS^0_m, the entropy change over two temperature intervals.

Most of the measured difference between the two sets of measurements is above 90 K. However, a comparison of $C^o_{p,m}$ for the two sets of measurements in the temperature range from 90 to 298.15 K shows

Table 6
Comparison of the entropy change for sucrose from $T = 0\,\mathrm{K}$ to $T = 90\,\mathrm{K}$ and from $T = 90\,\mathrm{K}$ to $T = 298.15\,\mathrm{K}$ as reported by Refs. [49] and [50]

	$\Delta_0^{90}S^0_\mathrm{m}/(\mathrm{J\,K^{-1}\,mol^{-1}})$	$\Delta_{90}^{298.15}S^0_\mathrm{m}/(\mathrm{J\,K^{-1}\,mol^{-1}})$
Putnam and Boerio-Goates	95.4	297.0
Parks et al.	92.3	268.0

only small differences. A re-integration of the Parks, Kelley and Huffman $C^0_{\mathrm{p,m}}/T$ data gives a value of $\Delta_{90}^{298.15}S^0_\mathrm{m}$ of 296.9 J $\mathrm{K^{-1}}$ instead of the reported 268.0 J $\mathrm{K^{-1}\,mol^{-1}}$. The new value agrees well with the 297.0 J $\mathrm{K^{-1}\,mol^{-1}}$ value obtained by Putnam and Boerio-Goates [49]. Evidently, the difference between the two sets of measurements resulted simply from an error in the integration of the earlier work.

The new value for S^0_m (sucrose, cr, 298.15 K) leads to revised values for $\Delta_\mathrm{f}G^0_\mathrm{m}$ (sucrose, cr, 298.15 K) of $-(1557.6\pm4.0)$ KJ $\mathrm{mol^{-1}}$ and $\Delta_\mathrm{f}G^0_\mathrm{m}$ (sucrose, aq, 298.15 K) of $-(1564.7\pm4.0)$ kJ $\mathrm{mol^{-1}}$.

5.14. Excess enthalpies for (ethane + ethene) mixtures [51]

Dottie Sipowska, Bevan Ott, and Phil Brown, along with an undergraduate student, Jason Moore, have assisted Mirek Gruszkiewicz, also a graduate student, in measuring the excess molar enthalpies H^E_m for (ethane + ethene) mixtures, using one of the high-pressure high-temperature flow calorimeters. The experimental measurements were made over the 273.15–363.15 K temperature range and the 5–15 MPa pressure range. The critical temperatures and pressures are 4.91 MPa and 305.50 K for ethane and 5.04 MPa and 282.34 K for ethene. Thus, measurements were made at a temperature (273.15 K) where both components are liquid, a temperature (298.15 K) where the ethane is liquid and the ethene a supercritical fluid, and at three temperatures (323.15, 348.15, and 363.15 K) where both components are supercritical fluids.

Fig. 31 compares H^E_m as a function of pressure at $T = 273.15\,\mathrm{K}$ for $\{x\mathrm{C_2H_6} + (1-x)\mathrm{C_2H_4}\}$. The small positive H^E_m are typical of what is obtained when nonpolar liquid hydrocarbons are mixed, although the effect of pressure is larger than usual because the liquid components are at a temperature near their critical temperatures.

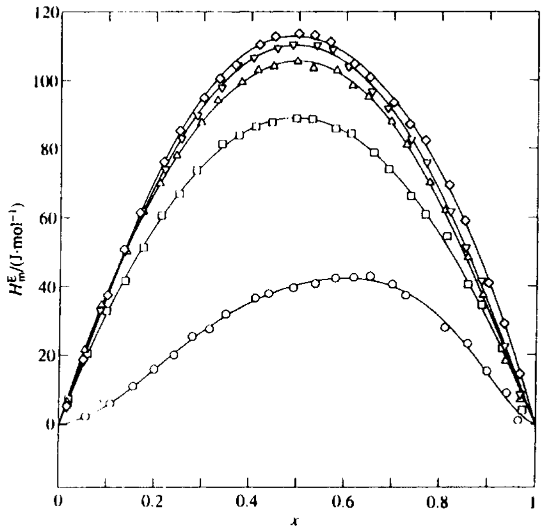


Fig. 31. Excess molar enthalpies H^E_m for $\{x\mathrm{C_2H_6} + (1-x)\mathrm{C_2H_4}\}$ at $T = 273.15\mathrm{K}$. The pressures are as follows: ○ – 5 MPa; □ – 7.5 MPa; △ – 10 MPa; ▽ – 12.5 MPa; ◇ – 15 MPa. Reproduced by permission from Ref. [51].

Fig. 32 compares H^E_m as a function of pressure at $T = 298.15\,\mathrm{K}$ where the ethane is liquid and the ethene a supercritical fluid. At $p = 5\,\mathrm{MPa}$, the supercritical ethene is behaving gas-like while the ethane is still liquid, and H^E_m results principally from the mixing of a gas and a liquid. The gas-like behavior of the ethene can be seen by referring to Fig. 33, which compares the densities of ethane and ethene as a function of pressure and temperature. At $T = 298.15\,\mathrm{K}$ and $p = 5\,\mathrm{MPa}$, ethene has a low density characteristic of a gas, and ethane a higher density characteristic of a liquid.

Mixing a gas and a liquid results in the ‘S’-shaped $H^\mathrm{E}_\mathrm{m}(x)$ curve shown in Fig. 32. (There is evidence that (fluid + fluid) phase equilibrium occurs at $T = 298.15\,\mathrm{K}$ and $p = 5\,\mathrm{MPa}$, and that a short segment of the steep curve around $x = 0.7$ is linear.) Large positive H^E_m are obtained at low x where liquid

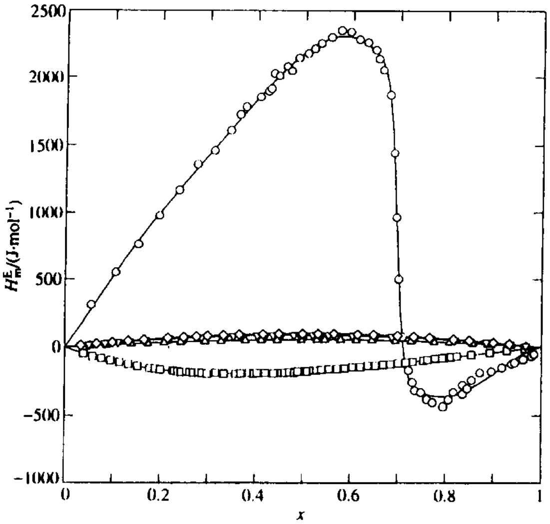


Fig. 32. Excess molar enthalpies H^E_m for $\{xC_2H_6 + (1-x)C_2H_4\}$ at $T = 298.15$K. The pressures are as follows: ○ – 5 MPa; □ – 7.5 MPa; △ – 10 MPa; ▽ – 12.5 MPa; and ◇ – 15 MPa. The values at the three higher pressures increase regularly with pressure, but the effect is small and it is difficult to see the change with the scale used in the figure. Reproduced by permission from Ref. [51].

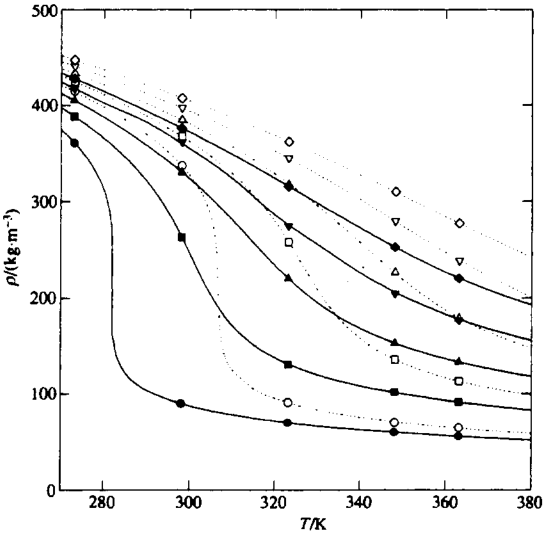


Fig. 33. Change in densities ρ for ethene (solid lines and solid symbols) and ethane (dotted lines and open symbols) as a function of temperature. The symbol shapes, which are plotted at the temperatures at which the measurements were made, designate the different pressures as follows: ○ – 5 MPa; □ – 7.5 MPa; △ – 10 MPa; ▽ – 12.5 MPa; and ◇ – 15 MPa. Reproduced by permission from Ref. [51].

ethane is vaporizing into gaseous ethene, while large negative H^E_m are obtained at high x where gaseous ethene is condensing into liquid ethane. The vaporization and condensation effects are reduced as the pressure increases, since the ethane and ethene become closer in density, and at $p = (10, 12.5, \text{ and } 15)$ MPa, H^E_m similar to those for mixing two liquid hydrocarbons are obtained.

Fig. 34 compares H^E_m as a function of pressure at three temperatures – 323.15, 348.15 and 363.15 K. The effect of pressure on the mixing of these two supercritical fluids can be understood by comparing the densities shown in Fig. 33. For example, at $T = 323.15$ K and $p = 5$ MPa, both the ethane and ethene have low gas-like densities, and a small H^E_m is obtained that is typical of mixing non-polar gases at this pressure. At $p = 7.5$ MPa, the ethene still has a gas-like density while the density of the ethane has increased significantly until it is behaving more liquid-like. The comparatively large positive H^E_m obtained at this pressure and temperature can be thought of as resulting from the evaporation of this liquid-like ethane into the gas-like ethene. At pressures of 10, 12.5, and 15 MPa, both the ethane and ethene have liquid-like densities, and small positive H^E_m are obtained that are similar to those for mixing liquid hydrocarbons, such as those shown earlier at $T = 273.15$ K.

6. Summary

Calorimetry is indeed a versatile tool for studying a wide variety of chemical systems and processes. We have seen that it can be used to study energy and free energy effects in chemical reactions; thermal effects in solution over a wide range of pressure, temperature, and composition conditions, including measurements with supercritical fluids, thermal properties at low temperatures, energy effects in biological processes, and as a method for chemical analysis. And this only represents the beginning of possible applications. The examples given are by no means an exhaustive list of applications of calorimetry at BYU, and BYU is only one of a number of institutions where calorimetric measurements are being made.

But one does not simply pick up a calorimeter and begin making reliable measurements, even though a

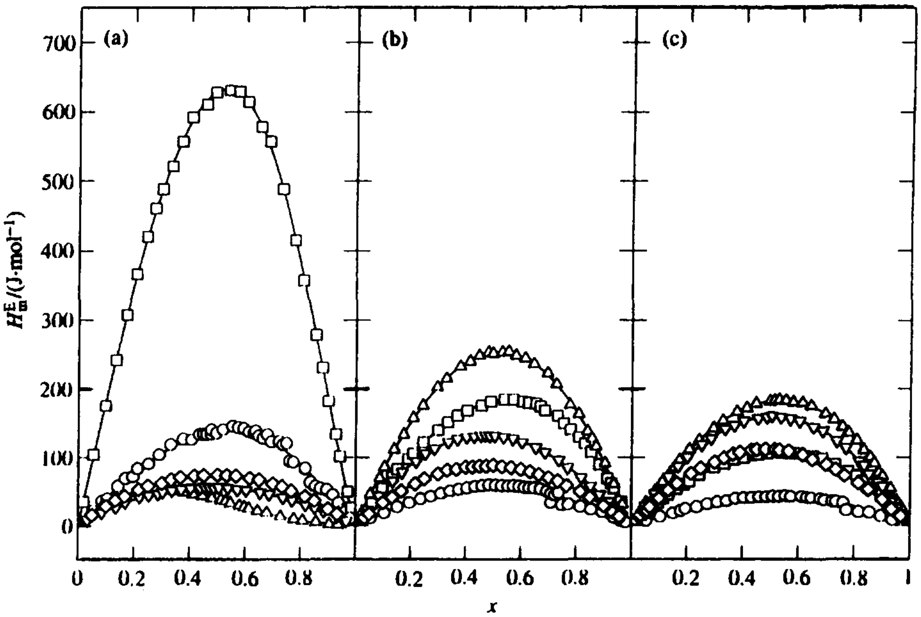


Fig. 34. Excess molar enthalpies H_m^E for $\{xC_2H_6 + (1-x)C_2H_4\}$ at (a) – $T = 323.15$ K; (b) – $T = 348.15$ K; and (c) – $T = 363.15$ K. The pressures are as follows: ○ – 5 MPa; □ – 7.5 MPa; △ – 10 MPa; ▽ – 12.5 MPa; and ◇ – 15 MPa. All results have been plotted on the same scale to compare the magnitude of H_m^E. The results at $p = 5$ MPa and high x are lower than the fitting curves at all three temperatures. This difference is probably due to incomplete mixing as described in [51]. Reproduced by permission from Ref. [51].

number of commercial calorimeters are available. The cold-fusion experiments made over a decade ago are a good example of what can happen when scientists without experience in calorimetry attempt to use the calorimeter and arrive at wrong conclusions. To my knowledge, no established calorimetrist, who attempted to reproduce the cold-fusion experiments, ever reported more heat than could be explained by non-fusion processes, and a number have tried the experiment. Lee Hansen and some of his colleagues have recently published several papers [52,53] to help explain from the point of view of the calorimetrist, what is going on in the calorimeter during this process.

In many ways, the reliable measurement of heat remains as much an art as a science. Making calorimetric measurements is in some ways like playing golf. Golf is a very demanding and skillful game that requires much expertise and experience. A novice may spend much of his time in the rough and out of bounds chasing errant shots. But the shots of the professional are long, true, and a thing of beauty. And so it is with calorimetry. The measurements of the professionals are also beautiful and exciting. Brigham Young University is fortunate to have such a large group of professional calorimetrists making beautiful measurements together. Unfortunately, at BYU and across the world, calorimetrists are maturing together, and with some exceptions, replacements are not being properly groomed. We may wake up one of these days and discover that no one is left to make reliable calorimetric measurements. It will be unfortunate. Much interesting work remains to be done.

The author expresses appreciation to all the faculty, students, post-doctoral fellows, research associates, and visiting scientists who have been involved in calorimetry projects at BYU.

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