

Calorimetry, densitometry and ultrasonics: recent contributions to the thermodynamics of fluids *

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Abstract. This article reviews recent advances in the thermodynamics of fluid nonelectrolytes, pure and mixed. The focus is on high-precision experimental techniques and the following topics are included : vapor-liquid equilibrium studies on dilute solutions, calorimetric techniques for measuring heats of mixing and/or solution as well as heat capacities, densitometry at elevated temperatures and pressures, and speed of sound measurements. Some of the problems encountered in data reduction and data correlation will also be indicated.

INTRODUCTION

The assortment of modern instrumentation accessible to today's experimentalists permits the systematic study of thermodynamic properties of fluids and phase equilibria with ever increasing precision and speed over wide temperature and pressure ranges. An exhaustive description of the present status of research in these areas within the constraints imposed by a conference presentation is clearly impossible, and we have limited our survey to a few topics primarily reflecting our own research interests and limitations of expertise. This approach follows the pattern of our recent reviews (1-11), i.e. critical essays rather than exhaustive presentations of the current literature. To summarize, we will focus on dilute nonelectrolyte solutions (vapor-liquid equilibria, enthalpies of solution etc.), excess enthalpies, excess heat capacities and excess volumes of binary liquid mixtures, and the determination of caloric and PVT properties of liquids, incorporating speed-of-sound measurements, over large temperature and pressure ranges. Aqueous solutions of gases and mixtures containing polar substances are of particular interest. Only a few selected results will be presented and we apologize for the omission of many other equally active topics and important contributions.

DILUTE SOLUTIONS

Current interest in solution thermodynamics has been mainly stimulated by (a) advances in the theory of liquids in general, (b) advances in experimental techniques providing more accurate data in less time, and (c) the need for thermophysical property data and phase equilibrium data in the applied sciences, for instance the chemical and power industry, geology, the gas, oil and coal industry, pollution control, biomedical technology, etc. Focussing now on binary dilute solutions containing a supercritical solute 2 (a gas) dissolved in liquid solvent 1, what are the quantities of interest (1-3, 6, 7, 10) ?

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Isothermal vapor-liquid equilibrium (VLE) measurements in conjunction with the (ϕ, γ) approach (unsymmetric convention) yield the Henry fugacity $H_{2,1}(T, P_{s,1})$ and the corresponding activity coefficient $\gamma'_2(T, P_{s,1}, x_2)$ according to the rigorous relations,

$$H_{2,1}(T, P_{s,1}) = \lim_{x_2 \rightarrow 0} (\phi_2^V y_2 P / x_2) \quad (1)$$

and

$$\ln \gamma'_2(T, P_{s,1}, x_2) = \ln \left(\frac{\phi_2^V y_2 P}{x_2 H_{2,1}(T, P_{s,1})} \right) - \int_{P_{s,1}}^P \frac{V_2^L}{RT} dP. \quad (2)$$

Here, T and P denote experimental temperature and pressure, $P_{s,1}$ is the vapor pressure of the solvent, x_2 and y_2 are the mole fractions of the solute in the liquid phase (superscript L) and vapor phase (superscript V), respectively, ϕ_2^V is the vapor phase fugacity coefficient of the solute, and V_2^L is its partial molar volume in the liquid phase.

This sequential approach is most frequently used at temperatures well below the critical temperature of the solvent $T_{c,1}$ and at low to moderate pressures. We note that from the general definition of the component fugacity coefficient, the limiting behavior of the Henry fugacity as $T \rightarrow T_{c,1}$ and $P_{s,1} \rightarrow P_{c,1}$ (the critical pressure of the solvent) is given by (1-3, 10).

$$\lim_{T \rightarrow T_{c,1}} H_{2,1}(T, P_{s,1}) = P_{c,1} \phi_2^{V\infty}(T_{c,1}, P_{c,1}), \quad (3)$$

where $\phi_2^{V\infty}$ is the fugacity coefficient of the solute at infinite dilution in the vapor phase. Provided that the solute is the more volatile component, Schotte (12) has shown that

$$\lim_{T \rightarrow T_{c,1}} \left[d \ln H_{2,1}(T, P_{s,1}) / dT \right] = -\infty. \quad (4)$$

This behavior has been predicted by Wheeler (13) and Levelt Sengers et al. (14, 15).

Both the temperature and pressure dependences of the quantities introduced above are readily calculated (1-3, 6, 7, 10). For instance, with $\tau \equiv 1/T$.

$$(\partial \ln H_{2,1} / \partial \tau)_P = \Delta H_{2,1}^{\infty} / R, \quad (5)$$

$$(\partial^2 \ln H_{2,1} / \partial \tau^2)_P = -\Delta C_{P,2}^{\infty} / R \tau^2, \quad (6)$$

and

$$(\partial \ln H_{2,1} / \partial P)_T = \tau V_2^{L\infty} / R. \quad (7)$$

Here, $\Delta H_{2,1}^{\infty}$ is the partial molar enthalpy change on solution, $\Delta C_{P,2}^{\infty}$ is the partial molar heat capacity change on solution, and $V_2^{L\infty}$ is the partial molar volume of the dissolved gas at infinite dilution.

Equations (5) and (6) are the basis for comparison of calorimetrically determined enthalpy and heat capacity changes on solution (*direct* methods, (16-25)) with results obtained from van't Hoff analysis of high-precision VLE data of dilute solutions (*indirect* methods, (26-29)). Figure 1a shows results for $H_{2,1}(T, P_{s,1})$ of methane dissolved in water as obtained by Rettich et al. (26), Figure 1b compares the corresponding enthalpies of solution with the direct values reported by Dec and Gill (19, 21, 22) and Olofsson et al. (17) : excellent agreement is observed throughout. Evidently, for such a comparison the fitting equation representing the temperature dependence of the Henry fugacity has to be judiciously selected. Usually, either a Clarke-Glew type expression (31) or a power

series in τ , as suggested by Benson and Krause (32, 33), is used. Since the $H_{2,1}(T, P_{s,1})$ values at different temperatures refer, of course, to different pressures $P_{s,1}(T)$, the enthalpy of solution is given by

$$\Delta H_2^{\infty}(T, P_{s,1}) = R \left[d \ln H_{2,1}(T, P_{s,1}) / d\tau \right] - \tau V_2^{L\infty} (dP_{s,1} / d\tau), \quad (8)$$

with an analogous expression for $\Delta C_{P,2}^{\infty}$ (1-3, 6, 7, 10). The partial molar heat capacity at infinite dilution diverges, as expected, towards positive infinity (24, 25) when the critical point of the solvent is approached from $T < T_{c,1}$. When $T_{c,1}$ is approached from higher temperatures, $C_{P,2}^{\infty}$ tends towards negative infinity.

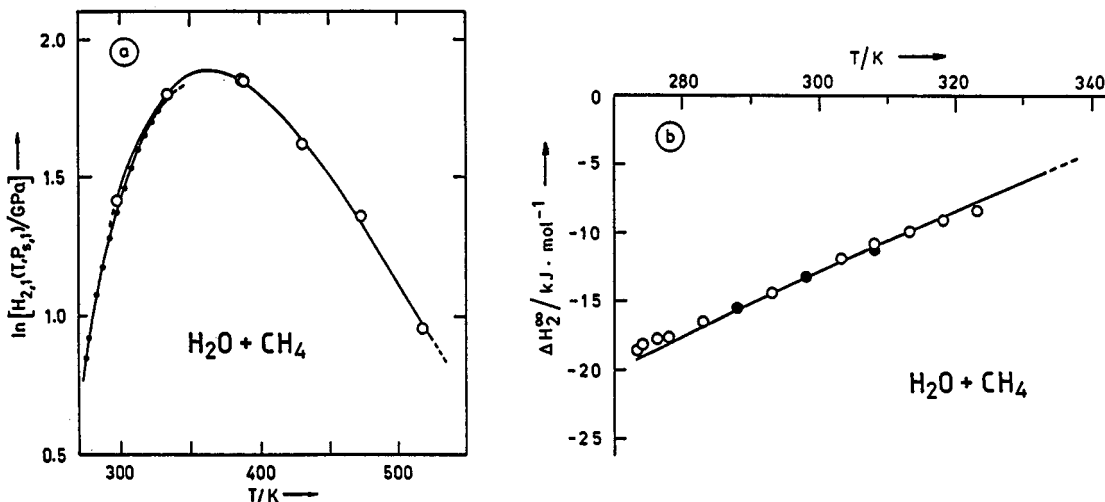


Fig. 1. (a) Plot of $\ln [H_{2,1}(T, P_{s,1})/\text{GPa}]$ against temperature T for methane dissolved in water : ●, Rettich et al. (26) [percentage deviation is ca. $\pm 0.05\%$]; ○, Crovetto et al. (30) [percentage deviation is between 1 and 2%]. (b) Enthalpy of solution of methane in water from 273.15 K to 333.15 K : —, Rettich et al. (26); ○, Naghibi et al. (22); ●, Dec and Gill (19, 21). At this scale, the results of Olofsson et al. (17) cannot be distinguished from those of Refs. (19, 21, 22). Using Rettich's data (26), the extrapolated temperature where $\Delta H_2^{\infty} = 0$ ($T_0 \approx 360$ K) is in excellent agreement with the experimental findings, see Fig. 1a and eqs. (5) and (8).

The effect of pressure on the Henry fugacity is given by eq. (7). However, simplistic application, in the form of the Krichevsky-Kasarnovsky equation, to extract $V_2^{L\infty}$ from high-pressure gas solubility data may yield unreliable results, since Poynting correction and the 'composition effect' embodied in the activity coefficient frequently cancel each other to a significant extent (34, 35). The preferred experimental method for determining $V_2^{L\infty}$ (and V_2^L) is either dilatometry (36, 37) or densitometry (38-41). The latter has proved particularly valuable for investigating V_2^L of dilute solutions in the vicinity of the solvent critical point (41).

MIXTURES

For liquid mixtures, interest generally focusses on excess molar quantities (symmetric convention), such as H^E , C_p^E and V^E , and their dependence on T , P and x . In the past, most experimental calorimetric work was devoted to the determination of excess molar enthalpies H^E , usually at atmospheric pressure. The Picker flow calorimeter for the measurement of "volumetric" heat capacities, i.e. heat capacities per unit volume, C_p/V , was the major step forward towards creation of a large and reliable data base of excess molar heat capacities $C_p^E = (\partial H^E / \partial T)_{P,x}$ for liquid mixtures of nonelectrolytes (42-45). The main asset of this type of instrument is its high sensitivity, permitting the accurate determination of the composition dependence of C_p^E at a given temperature, coupled with easy handling, low substance consumption and speed of an actual experiment. Together with flow calorimeters for measuring H^E and vibrating-tube densitometers for

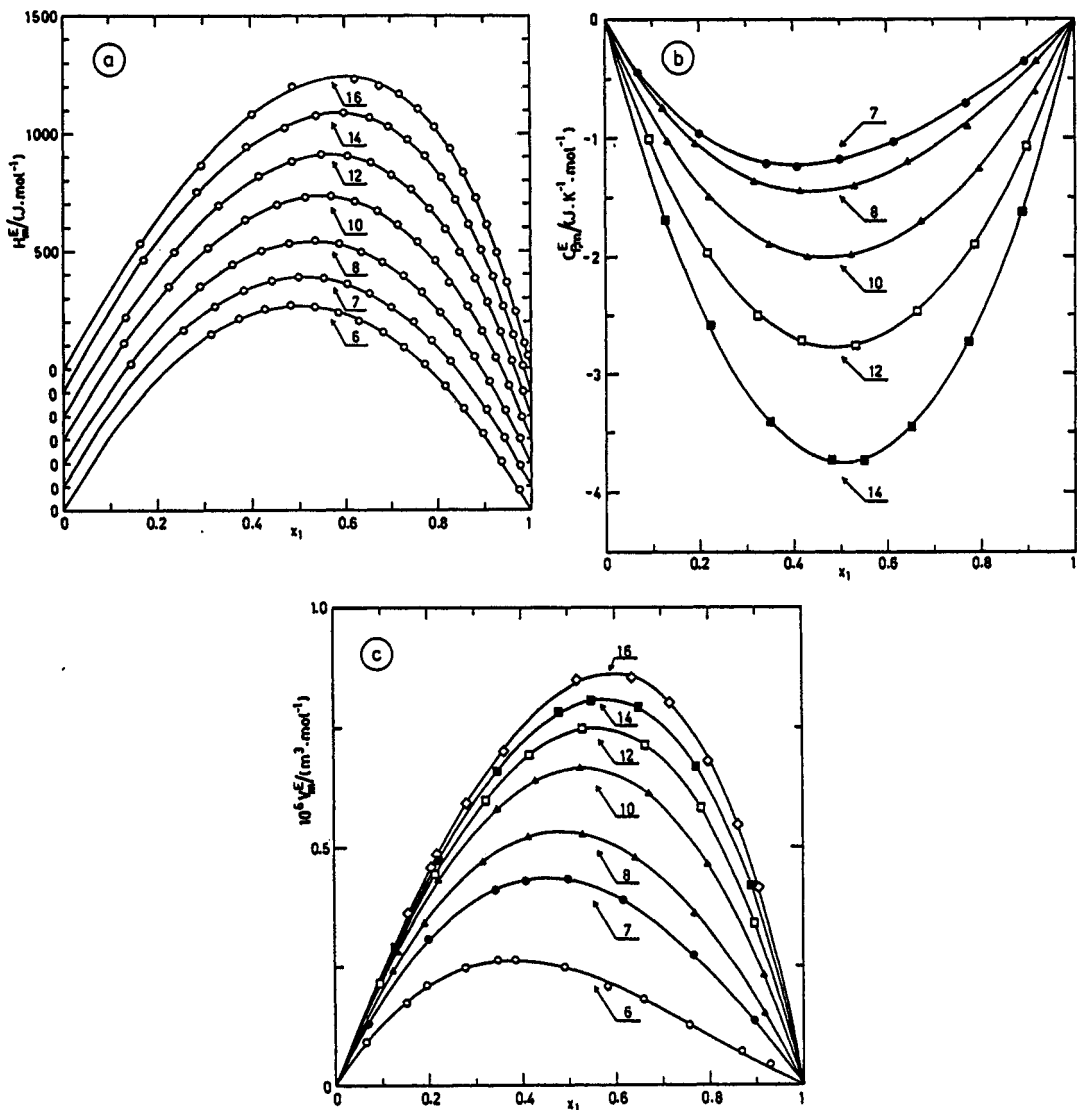


Fig. 2. (a) Excess molar enthalpies of $\{x_1 C_6H_5F + x_2 n-C_{l-1}H_{2l+2}\}$ at 298.15 K and 0.1 MPa.

Circles denote experimental points (52), the numbers are values of the chain length l of the n -alkane.

(b) Excess molar heat capacities of $\{x_1 C_6H_5F + x_2 n-C_{l-1}H_{2l+2}\}$ at 298.15 K and 0.1 MPa.

The experimental results are from Ref. (52), the numbers are values of the chain length l of the n -alkane.

(c) Excess molar volumes of $\{x_1 C_6H_5F + x_2 n-C_{l-1}H_{2l+2}\}$ at 298.15 K and 0.1 MPa. The

experimental results are from Ref. (52), the numbers are values of the chain length l of the n -alkane.

measuring excess molar volumes V_m^E , we now have at hand a group of highly versatile instruments allowing the *systematic* investigation of classes of liquid mixtures within a reasonably short time, see Fig. 2. Some representative articles are listed as Refs. (46-54). A wealth of new information concerning, in particular, the morphology of curves C_p^E vs. x was thereby obtained and has led to exciting new developments (9, 10, 46, 48-50, 53, 55-63). Perhaps one of the most prominent results, the W-shaped curves C_p^E vs. x in binary systems of type (Y + an alkane), where Y denotes a strongly polar substance, is represented by our results (58) for pyridine + an n -alkane shown in Fig. 3.

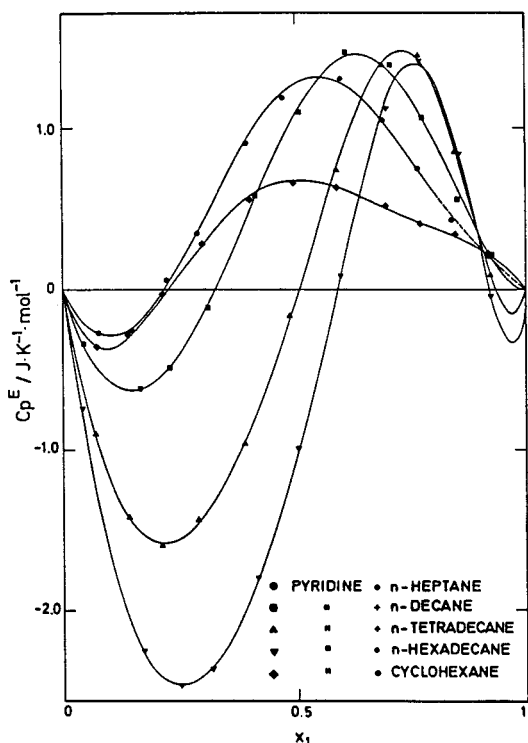


Fig. 3. Excess molar heat capacities of $\{x_1 C_5H_5N + x_2 n-C_{12}H_{24}\}$ and of $\{x_1 C_5H_5N + x_2 C_6H_{12}\}$ at 298.15 K and 0.1 MPa (58).

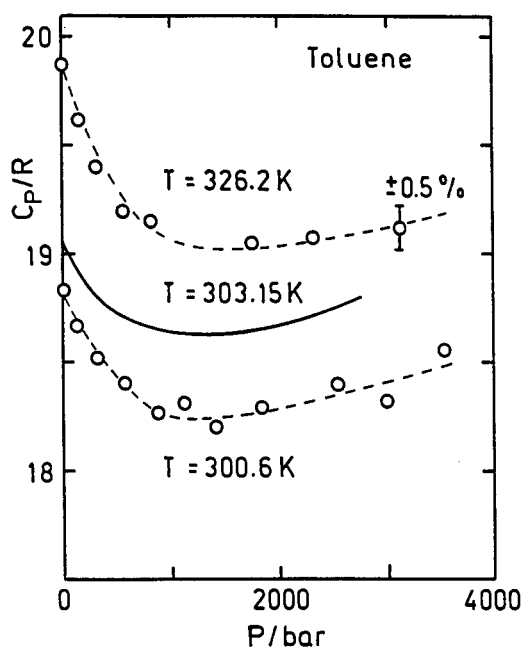


Fig. 4. Pressure dependence of the molar heat capacity C_p of toluene: —, Asenbaum et al. (71) at 303.15 K; ---, direct experimental results of Shulga et al. (72) at 300.6 K and 326.2 K, respectively.

THERMOPHYSICAL PROPERTIES OF LIQUIDS AT ELEVATED TEMPERATURES AND/OR PRESSURES

The data needs of the applied sciences, in particular at elevated temperatures and pressures, have already been indicated. Quantities of interest are, for example, density ρ , heat capacity C_p and heat capacity C_v at constant volume, and various derived quantities, such as isothermal compressibility β_T and isobaric expansivity α_p .

For the measurement of C_p/V of liquids in the temperature range 273–373 K ($P \approx 0.1$ MPa), we currently use a programmable differential scanning calorimeter (Micro DSC, from Setaram) which is based on the Calvet principle. The sample size is about 1 cm^3 , the imprecision amounts to about $\pm 0.01\%$ (64). Combining our results with data on density, expansivity and ultrasonic speed, both C_v and β_T (indirect method, see Ref. (65)) may be obtained from

$$C_p/C_v = \beta_T/\beta_s = \kappa, \quad (9a)$$

$$\kappa = 1 + T M \alpha_p^2 u_0^2 / C_p, \quad (9b)$$

where u_0 is the speed of ultrasound at low frequency (negligible dispersion) and $\beta_s = 1/(\rho u_0^2)$ is the isentropic compressibility.

In the range 300–570 K and for pressures $P \leq 30$ MPa we are using a modified C80 calorimeter from Setaram. Here the cell volume is about 8 cm^3 , the imprecision is about $\pm 0.1\%$. First results on the heat capacity of concentrated salt solutions have already been reported in Refs. (66, 67).

An alternative to the direct experimental route to high-pressure volumetric data and $C_p(T,P)$ is to measure u_0 as a function of P and T , and to combine these results with data on ρ and C_p at ordinary

pressure $P_1 = 0.1$ MPa, i.e. one utilizes the integrated form of eq. (9)

$$\rho(T,P) = \rho(T,P_1) + \int_{P_1}^P u_0^{-2} dP + TM \int_{P_1}^P \alpha_p^2 C_p^{-1} dP, \quad (10)$$

together with the exact thermodynamic relation

$$(\partial C_p / \partial P)_T = -TV \left[\alpha_p^2 + (\partial \alpha_p / \partial T)_p \right] \quad (11)$$

and a suitable integration algorithm (68-70). The 303.15 K isotherm of C_p vs. P of toluene obtained in this way is shown in Fig. 4 (71), together with two directly determined isotherms at 300.6 K and 326.2 K, respectively (72). Note the shallow minimum at about 125 MPa, which agrees with the negative value of $(\partial \alpha_p / \partial T)_p$ observed for toluene at pressure $P \geq 65$ MPa. (see eq. (11)). Qualitatively similar pressure dependences of C_p are now known for several relatively simple liquids.

We conclude this review by presenting an automated *pressure-controlled scanning calorimeter* (11, 73-79) operating at pressures up to 500 MPa and in the temperature range 300 K to 570 K. This novel instrument was built in close collaboration with the Institute of Physical Chemistry of the Academy of Sciences in Warsaw ; it is shown schematically in Fig. 5. Isobaric expansivity $\alpha_p(T,P)$ can be measured in such a calorimeter by either a stepwise method or by continuous (linear) pressure scanning. In the latter case

$$\alpha_p = - \dot{Q} / (v \dot{T} \dot{P}), \quad (12)$$

where \dot{Q} is the thermal power generated or absorbed by the pressure change (under isothermal conditions), \dot{P} is the rate of pressure change, and v is the volume of substance contained in the calorimetric vessel. The rate of linear pressure variation is typically 20 kPa.s^{-1} , but can be as low as 5 kPa.s^{-1} . Results obtained so far for α_p of *n*-hexane for pressures up to 350 MPa (11, 78, 79) are in excellent agreement with the literature data (80, 81). This apparatus can also be used to measure the isothermal compressibility.

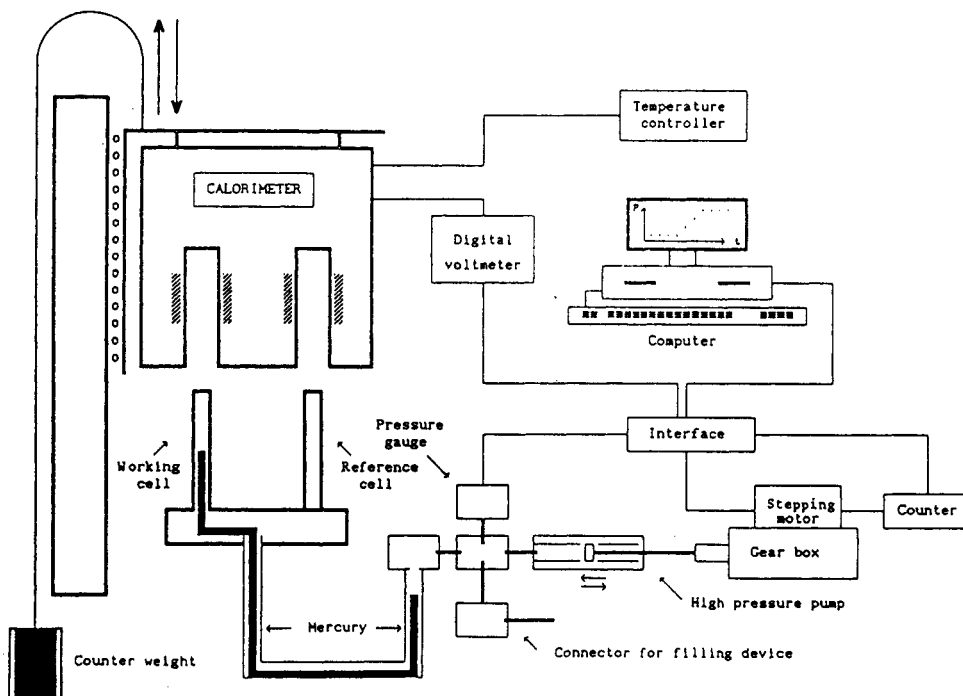


Fig. 5. Schematic diagram of the automated pressure controlled scanning calorimeter. Working and reference cells are kept at a fixed position and are connected to the pressure controlling device. The thermal detector is a C80 calorimeter (from Setaram). It is inverted on a special stand so that it can be moved up and down over the calorimeter cells by means of a counterweight.

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