

Heat Capacity of Hydrofluoric Acid and (Hydrofluoric Acid + 2-Methylpropane) by Temperature-Pulse Calorimetry

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Heat capacities of anhydrous liquid hydrofluoric acid and of HF saturated with 2-methylpropane are reported. The heat capacity of slightly compressed liquid HF is (2.66 and 2.80) $\text{J}\cdot\text{g}^{-1}\cdot\text{K}^{-1}$ at (25.1 and 45.9) $^{\circ}\text{C}$, respectively. The heat capacity of liquid HF slightly compressed and saturated at 24 $^{\circ}\text{C}$ with 2-methylpropane (3.7 mass %) is 2.58 $\text{J}\cdot\text{g}^{-1}\cdot\text{K}^{-1}$ at 24.3 $^{\circ}\text{C}$. Accuracy is within 2%. These are the first available data for the heat capacity of liquid HF above its normal boiling point. A temperature-pulse calorimeter is described.

Introduction

Heat capacities of anhydrous hydrofluoric acid and of HF saturated with 2-methylpropane are needed in the design of HF alkylation equipment used in the manufacture of high-octane gasolines. Only two sets of original data have been published in the literature (Dahmlos and Jung, 1933; Hu et al., 1953); they do not extend above the normal boiling point of HF (19.6 $^{\circ}\text{C}$), and the values disagree by up to 44%.

Because of the toxicity, volatility, and corrosivity of anhydrous liquid HF, it is not only hazardous to handle but also hostile to most materials of construction, including glass and stainless steel. To obtain the required heat capacities with the least possible manipulation of HF, we built a rugged and simple temperature-pulse calorimeter, based on a design by Wilding et al. (1991), using corrosion-resistant Monel 400 alloy (International Nickel Company), an alloy of copper and nickel. The heat capacity is obtained by measuring the retention time of a temperature pulse as it travels along a packed tube through which the test fluid flows. The velocity of the temperature pulse depends on the ratio of the volumetric heat capacity of the fluid to that of the packed tube. The method offers the advantages of rapid data acquisition and ease of interpretation.

Experimental Section

Chemicals. Hydrofluoric acid (0.9999 mass fraction) was from Matheson; 2-methylpropane (0.990 mol fraction) was from Phillips. Methanol and toluene used for heat capacity calibrations were Certified A.C.S. grade from Fisher. All chemicals were used as supplied.

Apparatus: Principle of Operation. The temperature-pulse calorimeter determines the heat capacity of a fluid by measuring the retention time for a temperature pulse carried by the fluid as it flows through a packed tube. The velocity of the temperature pulse depends on the ratio of the volumetric heat capacity of the fluid to that of the packed tube. The instrument operates according to principles described by Sagara et al. (1970); however, Sagara used the method to determine the heat capacity of the stationary solid phase from the known heat capacity of the fluid phase.

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The temperature-pulse calorimeter is applicable to both liquids and gases, and the instrument is fast and easy to operate. The density of the test fluid must be known, relatively large liquid samples are required (200 mL), and results are not as accurate as those obtained by adiabatic calorimetry. On the other hand, the temperature-pulse calorimeter offers several advantages over other means of obtaining fluid heat capacities: The primary measurement is of retention time—there is no need to measure temperature change or electric power. Heat leak does not directly affect the accuracy; it only reduces the size of the temperature pulse. The pressure is easily altered and controlled, so volatile liquids present no experimental difficulty. Heat effects due either to chemical reaction or to pressure drop on compressible fluids do not affect the heat capacity measurement directly; however, the measured heat capacity does correspond to the average composition and density of the sample between inlet and outlet.

According to Wilding et al. (1991), the retention time of a temperature pulse carried through a packed tube by a flowing fluid is given by

$$ft = \rho V^{\circ} + \frac{C_{pc}}{C_{pf}} m_c \quad (1)$$

where f is the mass flow rate per unit time, t is the retention time of the temperature pulse, ρ is the density of the test fluid at the measurement temperature and pressure, V° is the void volume of the packed tube (the space between particles), C_{pc} is the heat capacity per unit mass of the tube and packing, C_{pf} is the heat capacity per unit mass of the test fluid, and m_c is the mass of the tube and packing. Equation 1 may be derived by considering energy balance for both the liquid and solid and neglecting axial and radial heat dispersion.

The first term on the right-hand side of eq 1 gives the retention time for a temperature pulse in a hypothetical packed tube for which there is no heat transfer between the fluid and the thermal mass of the tube or packing. In such a case, a temperature pulse moves at the velocity of the fluid. The second term then gives the increase in retention time due to heat transfer to the tube and packing. This term contains the ratio of the heat capacity of the packed tube to that of the test fluid. For a given packed

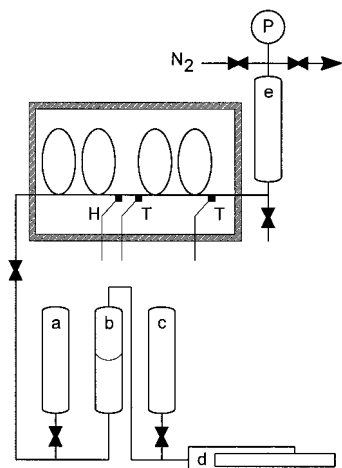


Figure 1. Temperature-pulse calorimeter and fluid-handling apparatus: (H) heater; (T) thermocouple; (a) sample vessel; (b) displacement vessel; (c) 2-methylpropane vessel; (d) pump; (e) receiver.

tube, the smaller the heat capacity of the test fluid, the longer the temperature pulse is retained in the packed tube.

Apparatus: Construction and Operation. Figure 1 is a schematic of the temperature-pulse calorimeter and the apparatus used to pump the fluids through the calorimeter and to control the pressure. The test fluid, either HF or HF saturated with 2-methylpropane, was transferred from vessel a to vessel b, and the Ruska piston-displacement pump d was filled with 2-methylpropane from vessel c. Because HF is more dense than and nearly immiscible with 2-methylpropane, the 2-methylpropane from the pump displaced the test fluid from vessel b into the calorimeter. In this way we avoided exposing the sample pump to corrosive HF. Noncorrosive test fluids were pumped directly. The test fluid exited the calorimeter into a receiver vessel e; the pressure was maintained by nitrogen flowing from a two-stage regulator over the receiver vessel.

The primary element of the temperature-pulse calorimeter used here is a 3.2 mm diameter Monel alloy tube, 198 cm long with wall thickness of 0.51 mm, packed with 25.8 g of Monel alloy filings sized 0.1 to 0.3 mm diameter. The tube was packed to 3 cm from each end; the packing was retained with glass wool plugs. (The glass wool may have dissolved during measurements on HF; however, no change in temperature pulse retention times, to indicate loss of packing, was observed.) The packed tube was formed into a coil of diameter 20 cm.

A thermocouple was formed 15 cm from the inlet end of the packed tube by silver-soldering a 0.6 mm diameter chromel alloy wire to the tube; a second thermocouple was formed in the same way 10 cm upstream of the outlet end. The junctions thus formed had a sensitivity of $23 \mu\text{V/K}$ at room temperature. The two chromel alloy wires were connected to a Hewlett-Packard 3396A chromatographic integrator, via a terminal strip that formed chromel alloy-copper junctions. The terminal strip was wrapped with polymer foam insulation to maintain the chromel alloy-copper junctions at the same temperature.

A heater made from 5 cm of insulated 0.5 mm diameter Nichrome wire was tightly wrapped one and one-half times around the tube, 11 cm from the inlet end, 4 cm upstream of the first thermocouple. It was connected with 1 mm diameter stranded copper wire through a computer-controlled relay to an autotransformer power supply.

The mass of tube and packing was 100.38 g. The calculated mass of tube and packing between the thermocouples was 88.41 g. The calculated void volume of the packed tube between the thermocouples, based on the tubing inside diameter and an estimate of the Monel alloy density, was 3.73 mL.

Heat loss from the tube must be kept small to allow the temperature pulse to be easily detected at the outlet of the packed tube. We placed a 26 cm square of 2.5 cm thick Styrofoam insulation material between each coil of the tube and on each side of the coil. The squares were notched so that the coil was approximately centered within the block formed by the stack of Styrofoam insulation squares. The layers of foam, sandwiching the coil, were then pressed firmly together, and the edges of the stack were covered with adhesive-backed heavy aluminum foil, which held the assembly together. The experimental temperature was obtained from a quartz-crystal thermometer inserted through the insulation approximately to the center of the calorimeter coil. A temperature equilibration coil of length 180 cm was added upstream of the calorimeter, and the whole assembly was placed in a constant-temperature air bath.

Temperature pulses were injected into the flowing fluid by pulsing the heater for 20 ms at about 7 V ac; peaks were recorded by the chromatographic integrator as the temperature pulse passed each thermocouple. The temperature rise registered by the first thermocouple was about 3 K, and the peak width was about 0.3 min. As the temperature pulse traverses the packed tube, it becomes weaker because of heat loss to the surroundings, and it becomes broader because of thermal diffusivity and the finite heat-transfer coefficient between the fluid and solid. At the second thermocouple, the peaks had weakened to about 0.3 K and broadened to between 0.6 and 2.0 min. The temperature pulse retention time, or the time elapsed between the initial and final peak, was from 3.2 to 7.5 min, depending on the fluid heat capacity. At a nominal flow rate of 3 mL/min, the relative standard deviation of temperature pulse retention times for water was 1.1%, and the average absolute error in calculated values of C_{pt} was 2.6%. When the flow rate was increased to 4 mL/min, the relative standard deviation of temperature pulse retention times fell to 0.16% and the average absolute error in C_{pt} decreased to 0.45%. All results reported here were taken at 4.086 mL/min. In experimental runs involving HF or HF mixtures, the number of replicate temperature pulse retention time determinations was limited by the volume of the displacement vessel (150 mL). For this reason, and because a flow rate of 4 mL/min gave satisfactory results, we did not try a faster flow rate.

Data Analysis. The void volume and mass of the tube and packing are best determined by calibration with fluids of known heat capacity. Rearranging eq 1 gives

$$\frac{ft}{\rho} = V^{\circ} + \frac{C_{pc} m_c}{C_{pt} \rho} \quad (2)$$

which may be used to calibrate a temperature-pulse calorimeter at a given temperature; a plot of ft/ρ against $C_{pc}/(C_{pt}\rho)$ has a slope equal to the effective mass of the tube and packing, m_c , and an intercept equal to the effective packed tube void volume, V° .

Adding another term to eq 2 allows us to operate over a range of temperatures by accounting for the effect of temperature on C_{pc} :

$$\frac{ft}{\rho} = V^{\circ} + \frac{m_c}{C_{p_i}\rho} [C_{p_c} + c(\theta - 25)] \quad (3)$$

Equation 3 may be used with temperature pulse retention data on fluids of known heat capacity to calibrate the temperature-pulse calorimeter by linear regression, using ft/ρ and $1/(C_{p_i}\rho)$ as dependent and independent variables respectively, C_{p_c} at 25 °C and the temperature θ as known parameters, and V° , m_c , and c as adjustable parameters.

Solving eq 3 for C_{p_i} , the heat capacities of other fluids can be found from f , t , ρ , C_{p_c} , θ , and the adjustable parameters:

$$C_{p_i} = \frac{m_c [C_{p_c} + c(\theta - 25)]}{ft - V^{\circ}\rho} \quad (4)$$

Calibration and Accuracy. Experimental temperatures and pressures were determined to within 0.1 K and 14 kPa, respectively. We calibrated the temperature-pulse calorimeter against distilled water, methanol, and toluene, including 40 points between (14.0 and 27.1) °C and 29 points between (45.2 and 46.4) °C. We used the heat capacity of water obtained by regression of data given by Lemmon et al. (1998):

$$C_p / (\text{J} \cdot \text{g}^{-1} \cdot \text{K}^{-1}) = 150.9194 - 0.295861(T/K) + 2.25106 \times 10^{-4}(T/K)^2 - 3.25031 \times 10^{-4}(T/K)^{-1} + 2.70933 \times 10^6(T/K)^{-2}$$

Heat capacities of methanol and toluene were computed from the DIPPR correlations (Daubert and Danner, 1994). The heat capacity of the tube and packing was estimated from heat capacities for nickel and copper (Gray, 1972) (Monel alloy is 67% Ni and 30% Cu, by mass). We used $C_{p_c} = 0.426 \text{ J} \cdot \text{g}^{-1} \cdot \text{K}^{-1}$, which needs not be accurate because of the adjustable coefficient m_c in eq 3.

Fitting the 69 calibration points using eq 3 gave an effective tube and packing mass of 90.39 g (standard deviation 0.22) and effective packed tube void volume of 4.06 mL (standard deviation 0.13). These values are close to those calculated from measurements taken during construction (88.41 g, 3.73 mL) but differ for various reasons including uncertainties in the tube dimensions and in the packing density and heat capacity, uneven particle distribution in the packing, and channeling in the fluid flow.

Temperature pulse retention times were repeatable to within 0.9% or better. Figure 2 shows the percent difference between heat capacities calculated from eq 4 and the reference values for the 69 calibration points vs the reference heat capacity values for the three calibration fluids. The average absolute difference was 0.45%.

Combination of all experimental parameters and their measured or estimated uncertainties in a Monte Carlo error analysis (Hammersley and Handscomb, 1965) leads to an expected standard deviation in C_{p_i} of $0.033 \text{ J} \cdot \text{g}^{-1} \cdot \text{K}^{-1}$, or about 1.3%. The error in C_{p_i} was most sensitive to uncertainty in the temperature-pulse retention time.

Results and Conclusions

The temperature-pulse calorimetric method is both rapid and accurate, and data analysis requires only simple calculations. The method is advantageous for obtaining heat capacities of volatile or corrosive fluids, which are difficult to handle by conventional calorimetric methods.

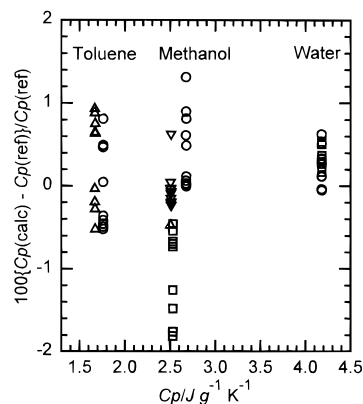


Figure 2. Percent difference between heat capacity calculated from eq 4 and reference heat capacity for the three fluids used to calibrate the temperature-pulse calorimeter, at four temperatures: (Δ) 15 °C; (▽) 20 °C; (□) 25 °C; (○) 45 °C.

Table 1. Heat Capacity of Anhydrous Liquid HF and of HF + 2-Methylpropane

fluid	$\theta/^\circ\text{C}$	P/kPa	$C_p / (\text{J} \cdot \text{g}^{-1} \cdot \text{K}^{-1})$	sd	n
HF	25.1	650	2.658 ^b	0.005	3
HF	45.9	800	2.801	0.006	3
HF + 2-methylpropane ^a	24.3	740	2.577	0.018	3

^a HF saturated with 2-methylpropane at 24 °C (Butler et al. (1946) report solubility of 3.7 mass %). ^b Expected standard deviation of C_p is $0.033 \text{ J} \cdot \text{g}^{-1} \cdot \text{K}^{-1}$. The number of replicate determinations is given under n .

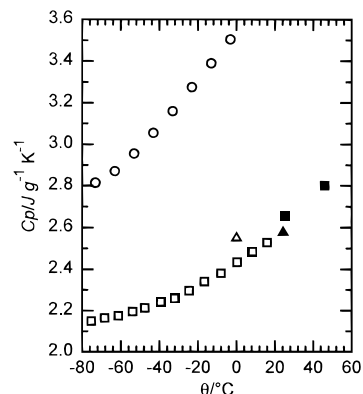


Figure 3. Heat capacity of anhydrous HF: (■) HF, this work; (▲) HF + 2-methylpropane, this work; (○) Dahmlos and Jung, 1933; (□) Hu et al., 1953; (Δ) Du Pont, 1990.

Heat capacities of anhydrous liquid hydrofluoric acid (HF) and of HF saturated at room temperature with 2-methylpropane are given in Table 1. Given that the solubility of 2-methylpropane in HF at 24 °C is 3.7 mass % (Butler et al., 1946), the heat capacity of HF saturated at 24 °C with 2-methylpropane is about 2% less than the “ideal” value calculated by linear combination of the heat capacities of the pure materials.

Figure 3 shows heat capacities obtained in this work compared with the data of Dahmlos and Jung (1933), Hu et al. (1953), and Du Pont (1990). The heat capacity of HF at 25.1 °C and 650 kPa obtained in this work is only 70% of the previously accepted value upon which acid coolers for HF alkylation units have been designed (Phillips, 1946). Therefore, acid coolers in new or revamped HF alkylation units can be built significantly smaller, with corresponding savings in capital expense.

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