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Extension of the Enthalpy of Sublimation for Adipic Acid to Temperatures below 80 °C

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The enthalpy of sublimation for adipic acid is available from several literature sources (Chemical Rubber Co. *Handbook of Chemistry and Physics*, 66th ed.; Chemical Rubber Publishing: Boca Raton, FL, 1985−1986. Configurational Thermal Vacuum Stability Test Method Development, TR-427-001; Lyndon B. Johnson Space Center, White Sands Test Facility, January 3, 1989. Afeedy, H. Y.; Liebman, J. F.; Stein, S. E. *NIST Chemistry WebBook, NIST Standard Reference Database No. 69*; NIST: Gaithersburg, MD, November 1998) for temperatures of ≥80 °C. Those references generally cite the work of Davies and Thomas (Davies, M.; Thomas, G. *Trans. Faraday Soc.* **1960**, *56*, 185−192) on the lattice energy of dicarboxylic acids. Measurements made with a 15 MHz temperature-controlled quartz crystal microbalance demonstrate that the enthalpy of sublimation, (129 ± 1.0) kJ·mol^{-1}, for adipic acid is constant in the range of 25 to 80 °C.

Introduction

The accumulation of molecular deposits on optically sensitive surfaces of spacecraft such as spacecraft radiators and observation ports is a concern for spacecraft with long orbital lifetimes. The selection of materials that will perform well in the vacuum of space, generally referred to as low-outgassing materials, requires that the deposition rate of volatile condensable materials be measured. One of the most common methods for measuring molecular deposition, American Society for Testing and Materials Method E-1559[5] measures volatile condensable materials with one or more quartz crystal microbalances. This instrument measures the rate of condensation of volatile condensable materials on an oscillating quartz crystal. The difference in oscillation, the beat frequency, between a reference crystal and the crystal on which the volatile condensable materials are deposited is used to calculate the deposition rate. The calculation utilizes a vendor-supplied conversion factor that converts the measure change in frequency with time to a deposition rate reported as g·cm^{-2}·s^{-1}.

Calibration of the microbalance is commonly done by calculating the enthalpy of sublimation for organic acids from the condensation or deposition rates measured with the microbalance. On the basis of calibration measurements made at the Lyndon B. Johnson Space Center Outgassing Facility, the temperature range for the enthalpy of sublimation for adipic acid can be extended below 80 °C to 25 °C.

Experimental Section

Adipic acid was placed in an aluminum weighing pan and heated to fuse the acid into a smooth and relatively uniform surface. Two samples were prepared in this manner. The first sample with a surface area of 27.30 cm^2 was prepared during July 1996, and a second sample with a surface area of 20.43 cm^2 was prepared for measurements made during June 1999. For each set of measurements, one of the samples was placed in an effusion cell constructed to the dimensions in the American Society for Testing and Materials E-1559 test method.[5] The effusion cell was then installed in a vacuum chamber, containing a single temperature-controlled quartz crystal microbalance (America Society for Testing and Materials E-1559, Method B), which could be evacuated to a pressure of 1.3 × 10^{-5} Pa. The temperature-controlled quartz crystal microbalance was mounted along the axis of the effusion cell orifice, and the plane of the deposition surface (crystal) is perpendicular or normal to the orifice axis.

Table 1. Adipic Acid Deposition Rates at Different Effusion Cell Temperatures

effusion cell temp (°C)	measurement 1 × 10^{-9} (g·cm^{-2}·s^{-1})	SD 1 × 10^{-11} (±g·cm^{-2}·s^{-1})	minimum measurement duration (h)	year/no. of measurements
25	0.007	0.101	4.0	1996/3
29	0.017	0.215	3.96	1996/4
37	0.058		2.5	1996/1
41	0.103	0.977	2.8	1996/5
46	0.170	1.55	7.0	1996/4
50	0.233	0.565	4.6	1996/2
56	0.563	1.84	4.2	1996/2
25	0.005	0.028	3.85	1999/3
30	0.015	0.085	3.3	1999/6
37	0.038	0.247	3.2	1999/5
44	0.164	0.152	1.3	1999/3
48	0.255	0.46	3.95	1999/5
51	0.318	1.70	2.5	1999/2
57	0.793	6.85	3.0	1999/8
66	2.72	3.53	3.98	1999/2

The temperature of the oscillating quartz crystal pair was held at (−41.7 ± 0.1) °C for the July 1996 measurement, and the deposition surface for the June 1999 measurements was (−42.2 ± 0.1) °C. Two different 15 MHz temperature-controlled quartz crystal microbalances were used for the measurements, and the coldest minimum temperature differed slightly between the two instruments. This may be due to minor differences in the effectiveness of the Peltier device, a subcomponent of the temperature-

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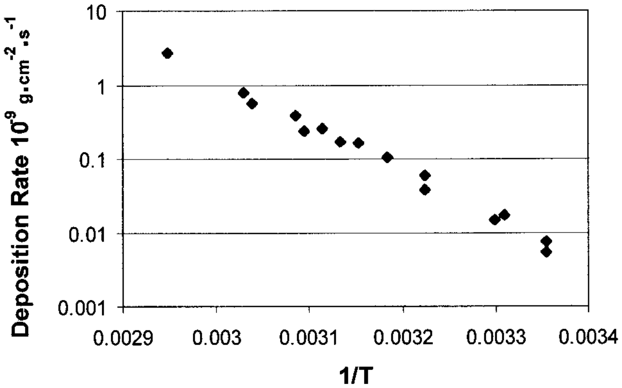

Figure 1. Adipic acid deposition measurements at effusion cell temperatures of 25 °C to 60 °C. Deposition surface temperature was −41.7 °C to −42.2 °C.

controlled quartz crystal microbalance, used to cool the oscillating quartz crystals. The effusion cell, containing the sample, was maintained at ±0.5 °C of the source temperature during the measurements.

The frequency output from the temperature-controlled quartz crystal microbalance, the temperature of the temperature-controlled quartz crystal microbalance crystal pair, and the effusion cell temperature were electronically recorded during each measurement period. The rate of deposition on the microbalance crystal was calculated from the change in frequency with time.

The measured deposition rates were then used, along with the sample surface area and a view factor, to calculate the outgassing rates for the sample. The view factor, 176 cm^2, was calculated according to American Society for Testing and Materials Method E-1559 for the "line-of-sight" path of the molecules emitted from the effusion cell to the temperature-controlled quartz crystal microbalance. The view factor is a complex factor that modifies the observed deposition rate to account for the orientation of the deposition surface in relation to the source of the deposited material, the Clausing factor of the effusion cell orifice, and the contribution of source to the microbalance's "field-of-view".

The recorded frequency data were plotted, and data with a regression coefficient of 0.989 or better, for a given measurement period, were considered to be a valid deposition measurement. From the slope of the frequency data, the deposition rates were calculated for each of the selected periods. Multiple deposition rates, recorded at the effusion cell temperatures listed in Table 1, were averaged together to arrive at the deposition rates presented in Table 1. Deposition rates for temperatures below 25 °C, not reported here, were scattered with increasingly poor results obtained as the deposition rate approached the chamber background deposition rate of 4×10^{-14} $g \cdot cm^{-2} \cdot s^{-1}$.

The measured deposition rates are plotted in Figure 1, and the linear regression for the data from 66 °C to 25 °C was found to have a regression coefficient of 0.99491.

Table 2. Predicted Deposition Rates

T (°C)	calcd rate 1×10^{-9} ($g \cdot cm^{-2} \cdot s^{-1}$)	enthalpy of sublimation ($-kJ \cdot mol^{-1}$)	difference from 80 °C enthalpy of sublimation[3] ($kJ \cdot mol^{-1}$)
25	0.007	121.01	−7.99
30	0.015	121.01	−7.99
40	0.073	121.02	−7.98
50	0.309	121.02	−7.98
60	1.19	121.00	−8.00

Table 2 contains the predicted deposition rates, based on a linear regression analysis of the measured deposition rates, and the calculated enthalpy of sublimation. The enthalpy of sublimation was calculated using the van't Hoff relation[6] and the predicted deposition rates at the selected temperatures in the temperature range of the actual mass deposition measurements. The almost constant error of 8 $kJ \cdot mol^{-1}$ in the calculated enthalpy of sublimation maybe due to a re-evaporation of a minor portion of the deposited material. Measurements made with multiple quartz crystal microbalances, viewing a common outgassing source, often measure as much as a decade difference in the deposition rates when one of the microbalances is cooled to cryogenic temperatures and the other microbalances are operated at warmer temperatures. The same flux of material reaches the deposition surface of all the microbalances, but a portion of the flux either does not stick to the warmer deposition surface or may deposit and then re-evaporate from the deposition surface.

Summary

The deposition or condensation rates measured for adipic acid, over the temperature range of 66 °C to 25 °C, can be used to accurately calculate the enthalpy of sublimation for this organic acid. The calculated enthalpy of sublimation is 121 $kJ \cdot mol^{-1}$ or 8.0 $kJ \cdot mol^{-1}$ less than the literature value of 129 $kJ \cdot mol^{-1}$ for the acid, at temperatures of ≥80 °C. The almost constant error in the predicted enthalpy value may represent a constant but minor re-evaporation of the deposited material from the deposition surface.

The temperature-controlled quartz crystal microbalance deposition measurements reported here support the use of the accepted heat of sublimation to temperatures as low as 25 °C.

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