

SO₂ ON IO: A THERMODYNAMIC PERSPECTIVE

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The presence of condensed SO₂ on Io mandates a finite abundance of SO₂ vapor which must be present, regardless of plume activity. Currently, even the order of magnitude of the ambient SO₂ pressure is unknown. However, a number of models indicate that the pressure may be near saturation much of the time. Among the models that suggest atmospheric pressure does not approach saturation is that of Matson and Nash, [1983], who base their model in part on the argument that Io's surface must have a very high porosity, and in part on the argument that the particulate material in Io's volcanic plumes has a very fine grain size. This implies that a significant amount of cold, particulate, surface area is likely to be in diffusive contact with an SO₂ atmosphere that probably at least approaches saturation locally.

These conditions indicate that adsorption of SO₂ may be important SO₂ adsorbate. We have measured the adsorption of SO₂ on particulate sulphur, and examined the equilibrium between adsorbed SO₂, SO₂ vapor, and SO₂ ice based upon our measurements and simple thermodynamic considerations.

Measurements of SO₂ adsorption on particulate sulphur at conditions near those of Io were made on a Numinco Model MIC 103 00R Surface-Area Pore-Volume Analyzer. Adsorption data were gathered at 178K, 193K and 225K. These are higher than surface temperatures on Io, which peak around 130K. The SO₂ vapor pressure (1 to 10³Pa) also exceeds Io surface pressures. The adsorptive behavior of the system must be extrapolated to Io conditions.

The most rigorous extrapolation method of which we are aware is one presented by Anderson et al. [1967]. They showed that it is possible to compute adsorption isotherms for temperatures below those covered in adsorption measurements via the equation

$$\ln \left[\frac{(P^a/P^i)_2}{(P^a/P^i)_1} \right] = \frac{(\Delta H_{va} - \Delta H_{vi})(T_2 - T_1)}{RT_1T_2} \quad (1)$$

Where P^a and Pⁱ are the vapor pressures over the adsorbed phase and the solid phase, respectively. The subscript 1 refers to state variables at condition 1, where data are available, and 2 refers to state variables at condition 2 for which we would like to calculate the relative vapor pressure. ΔH_{va} is the change in partial molar enthalpy in going from the vapor to the adsorbed phase, and ΔH_{vi} is the same quantity for the vapor to ice phase change.

In order to use Eq.(1), we must know ΔH_{vi}(T) and, from the data, we must find ΔH_{va}(T). ΔH_{va} is found by solving the Clausius-Clapeyron equation at points of constant adsorptive coverage. Since the data are not at constant adsorptive coverage we must fit a curve to the data and read equilibrium pressures at constant adsorptive coverage from that.

We are then able to extrapolate our adsorption isotherms to lower temperatures via Eq.(1). In all cases, our isotherms agree with the data to better than a factor of 2.5; the average precision of the data is ±50%.

At a fixed temperature, the equilibrium vapor pressure over adsorbed SO₂ may be thought of as an extensive property of the system; it increases as the mass of SO₂ in the system increases. The equilibrium vapor pressure over ice however is intensive; it does not matter how much SO₂ is in the solid phase, the vapor pressure depends only on temperature. That means that at a fixed temperature, there is a maximum adsorptive coverage, which occurs at the point at which the equilibrium

vapor pressure over the adsorbed phase is equal to the vapor pressure over ice. Thereafter, any additional SO₂ present in the system must exist as ice.

We should now be able to calculate the maximum adsorptive coverage in terms of volume of SO₂ per unit mass of sulphur, although we consider this an intermediate data product. We would really like to know the maximum coverage of SO₂ in terms of number density *per unit surface area* of sulphur (i.e. the monolayer coverage). We need to represent our results in this way because the specific surface area of S on Io is unconstrained, but the upper limit on the number density of the coverage, which is more closely related to the chemical potential, must be the same in the laboratory as on Io.

Fortunately, adsorption measurements provide concurrent measurements of specific surface area through application of BET theory [Brunauer et al., 1938]. We calculate BET surface areas, assuming the size of the adsorbed SO₂ molecule is ~ 30Å². We use the mean specific surface area of ~ 5 × 10⁻³ m² g⁻¹ indicated in our analysis to calculate maximum coverage for sulphur at Io conditions.

This relationship is shown in Figure 1, along with the data. Each of the isotherms is truncated against the vapor pressure curve for SO₂ ice (solid line). A very simple expression can be written to describe the maximum amount of adsorbed SO₂ per square meter of sulphur, at any temperature.

$$\text{Max } \rho_a = \exp(aT-b) \quad (2)$$

where $a = 0.1673 \text{ K}^{-1}$, and $b = 33.89$, and ρ_a is the density of adsorbed SO₂ in terms of g SO₂ m⁻²S. If the maximum surface temperature on Io is around 130 K, the maximum abundance of adsorbed SO₂ on Io is around 5 × 10⁻⁶ g SO₂ m⁻² S. At disk average temperatures of 90 K, the maximum adsorbed SO₂ capacity cannot be more than 8.6 × 10⁻⁹ g SO₂ m⁻² S. If more SO₂ is present in the system at these temperatures, it will exist as ice.

To understand why our results constitute a new perspective, we must examine the previous estimates of SO₂ adsorption on Io.

Unpublished adsorption measurements of SO₂ on S obtained by Fanale and Laue, at warmer, higher pressure, conditions suggested that up to a monolayer of SO₂ could be adsorbed onto S at low relative pressures. It was more or less accepted that at lower pressures and temperatures characteristic of Io, the adsorptive coverage should be about the same, around a monolayer [e.g. Fanale et al., 1982]. Let us examine how many monolayers our current analysis indicates. The upper limit of adsorptive coverage is around 5 × 10⁻⁶ g SO₂ m⁻² sulphur at 130K (Fig. 1). This mass represents around 4.7 × 10¹⁶ molecules per square meter. If we assume that each adsorbed molecule occupies 30Å², the maximum number of adsorbed SO₂ molecules occupies no more than 1.4 × 10⁻² m². Thus ~ 1.4 × 10⁻² is the maximum number of adsorbed monolayers, well over an order of magnitude less than previously believed. Nash [1983] calculated that 0.5 monolayers of adsorbed SO₂ would be required to create the 30% 4-μm absorption. We argue that the maximum adsorbed SO₂ coverage must be significantly less than 0.5 monolayers, making spectroscopic detection of adsorbed SO₂ highly problematic.

The question of how important the adsorbed phase on Io is, now becomes largely a question of what the adsorbent is.

We selected sulphur as our adsorbent because it is clear that sulphur allotropes constitute a significant fraction of Io's surface. To the extent that elemental sulphur dominates the Ionian surface, we have excellent confidence in our results. However, the Na and K in the magnetosphere require the presence of other phases on the surface.

The importance of the adsorbed phase in suppling the magnetosphere, and in diurnal exchange of SO_2 with the atmosphere, depends on the abundance and adsorptive capacity of other surface materials, as well as on the specific surface area of the sulphur on the Io surface. Nash [1986], in experiments on vacuum sublimation of solid sulphur, identified a very fluffy form which results from preferential sublimation of ring sulphur (S_8) over polymeric sulphur. Such a filamentary residue might be expected to have a very high surface area, and hence render the surface adsorbed phase a significant sink by mass, although monolayer coverage would remain very small.

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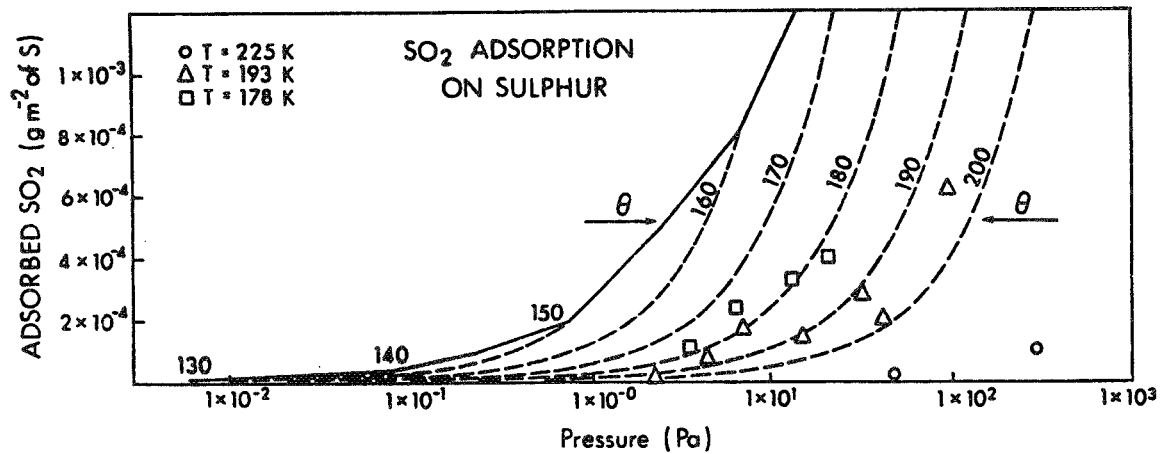


Fig. 1 - The pressure temperature field tangential to that of Io. The isotherms are found from Eq. (1) (dashed lines) and each is truncated at the vapor pressure over SO_2 ice (solid line). Coverage corresponding to one monolayer is indicated by the arrows (θ). On Io, ($T < 130\text{K}$), adsorption is limited to a fraction of a monolayer by equilibration with ice.