

Standard Molar Entropy of Solid Aluminum Oxide

Comments to Tandy Grubbs - wgrubbs@stetson.edu

Goals: Heat capacity data for Al_2O_3 over the temperature range 15 K to 300 K is analyzed to obtain the standard molar entropy of this substance.

Prerequisites: A basic knowledge of entropy and related thermodynamic principles.

Resources you will need: This exercise should be carried out within a quantitative analysis software environment that is capable of fitting a polynomial function of arbitrary order to an x-y data set. You will also be graphing the data along with the fitted function.

Background:

Standard molar entropy (S_m°) is one of the most useful types of thermodynamic data for a substance. But how does one measure this property? Unfortunately, there is no instrument that directly measures entropy. Instead, values are determined indirectly through the measurement of constant pressure heat capacities (C_p).

To understand how this works, we start with the Clausius Inequality

$$dS \geq \frac{dq}{T}, \quad (1)$$

where the equality in equation (1) only applies to a reversible process. The slow heating of a substance at constant pressure so that the sample is always in quasi-static thermal equilibrium with the surroundings is approximately reversible. In such a case, equation (1) becomes

$$dS = \frac{C_p dT}{T}, \quad (2)$$

where we have rewritten the differential heat transfer in terms of the constant pressure heat capacity times the differential temperature change.

Imagine slowly heating a pure solid substance at constant pressure from absolute zero up to some arbitrary temperature, T . Integration of equation (2) over the full temperature range will yield the absolute entropy of the substance relative to absolute zero,

$$S_T = S_{T=0} + \int_0^T \frac{C_p}{T} dT. \quad (3)$$

The 3rd Law of Thermodynamics defines entropy to be zero for any pure crystalline solid at absolute zero, so the term $S_{T=0}$ can be dropped from equation (3).

Whenever a substance in thermal equilibrium with its surroundings undergoes a phase transition at constant pressure, the corresponding entropy change given by

$$\Delta S_{\text{trans}} = \frac{\Delta H_{\text{trans}}}{T}. \quad (4)$$

If any phase transitions occur as we are heating a substance from absolute zero, each will contribute to the

overall absolute entropy of the substance. A refinement of equation (3) that accounts for melting and vaporization is given by

$$S_T = \int_0^{T_{fus}} \frac{C_p(s)}{T} dT + \frac{\Delta H_{fus}}{T_{fus}} + \int_{T_{fus}}^{T_{vap}} \frac{C_p(l)}{T} dT + \frac{\Delta H_{vap}}{T_{vap}} + \int_{T_{vap}}^T \frac{C_p(g)}{T} dT. \quad (5)$$

Equation (5) provides a means of determining the standard molar entropy of most substances. The terms corresponding to heating the solid, liquid, and gas phases, described by the 1st, 3rd, and 5th terms on the right-hand-side of equation (5), respectively, can be evaluated experimentally by measuring the heat capacity of the three phases over the appropriate temperature ranges, plotting these data as C_p/T versus T , and measuring the area under the curve.

The laboratory measurement of heat capacities is normally accomplished through the use of a constant pressure calorimeter that can be operated over a wide temperature range (nearly down to absolute zero). While these calorimeters are often custom designed, one can use a commercial instrument called a Differential Scanning Calorimeter (DSC). This device contains two sample compartments; a substance that has a well characterized heat capacity (a known) is placed in one compartment and the unknown is placed in the other. Starting at the low temperature limit, the known and unknown samples are heated using separate electrical heaters. Since the two samples likely have different heat capacities, more (or less) heat may be required by one sample in comparison to the other to achieve the same final temperature. The instrument measures this differential electrical heat at several points over the full temperature range. This 'differential heat curve' is subsequently analyzed to determine the heat capacity of the unknown substance over the same temperature range. Any phase transitions that occur as the sample is heated will yield peaks in the differential heat curve. The area under the peak is directly proportional to ΔH for the corresponding phase transition. In this fashion, each of the terms on the right-hand-side of equation (5) can be measured piecemeal.

Designing a calorimeter that can measure heat capacities near absolute zero is problematic. A typical commercial DSC used in conjunction with a Helium cold-cycle refrigerator might have a low temperature limit of 15 Kelvin. Consequently, the entropy contribution for heating the sample from $T = 0$ to 15 K has to be accounted for in some other fashion. Theoretical arguments have shown that the heat capacities of most substances at low temperatures are well described by the expression

$$C_p = aT^3, \quad (6)$$

where a is an empirical constant. Using equation (6) to describe the heat capacity of a substance at low temperatures is known as the 'Debye extrapolation.' If the constant a is known for a substance, then the absolute entropy at low temperatures is given by

$$S_{T_{low}} = \int_0^{T_{low}} \frac{aT^3}{T} dT = \frac{aT_{low}^3}{3}. \quad (7)$$

In this exercise, you will determine the standard molar entropy of solid aluminum oxide (Al_2O_3) by analyzing a set of $C_{p,m}$ versus T data and also applying the Debye extrapolation.

Experimental Data:

Click on the following link and save the x - y data to an appropriate folder. The data was obtained from Furukawa, G.T., Douglas, T.B., McCoskey, R.E., and Ginnings, D.C. *Journal of Research of the National Bureau of Standards*, **57**, 67-82 (1956). The first column of numbers is temperature in degrees Kelvin and the second column of numbers is standard $C_{p,m}$ in units of $\text{J}/(\text{K mol})$. The data ranges from 15 K up to 300 K.

[C_{p,m} versus T for Al₂O₃](#)

Exercise:

1. Import the data into an appropriate quantitative analysis software package. Using only the lowest temperature heat capacity value, calculate a value for the empirical constant a in equation (6). Then, determine the Debye extrapolation contribution to the molar entropy from equation (7).
2. Following the appropriate protocol for your software environment, fit the entire $C_{p,m}$ versus T data set to a polynomial function. Plot the fitted function along with the original data. Make sure the polynomial function is of sufficiently high order to yield a good fit over the full data range. Did you end up using a 2nd, 3rd ... 5th degree polynomial?
3. Once you have obtained a reasonable fit to the heat capacity data, calculate the 'non-Debye' contribution to the standard molar entropy by dividing your polynomial function, $P(T)$, by T and integrating the result from the low temperature limit up to 298 K.
4. The standard molar entropy of Al_2O_3 is obtained by adding the Debye extrapolation contribution, calculated in step (1), to the result obtained in step (3). In your opinion, does the Debye extrapolation contribute significantly to the overall value of the standard molar entropy of Al_2O_3 .
5. Consult the NIST Chemistry WebBook (<http://webbook.nist.gov/chemistry/>) and find the literature value for the standard molar entropy of Al_2O_3 . Report the percent difference.

Suggestions for improving this web site are welcome. You are also encouraged to submit your own data-driven exercise to this web archive. All inquiries should be directed to the curator: Tandy Grubbs, Department of Chemistry, Unit 8271, Stetson University, DeLand, FL 32720.

wgrubbs@stetson.edu

