

HEAT CAPACITY OF MINERALS: A HANDS-ON INTRODUCTION TO CHEMICAL THERMODYNAMICS

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INTRODUCTION

Minerals are inorganic chemical compounds with a wide range of physical and chemical properties. Geologists frequently measure and observe properties such as hardness, specific gravity, color, etc. Unfortunately, students usually view these properties simply as tools for identifying unknown mineral specimens. One of the objectives of this exercise is to make students aware of the fact that minerals have many additional properties that can be measured, and that all of the physical and chemical properties of minerals have important applications beyond that of simple mineral identification.

ROCKS AS CHEMICAL SYSTEMS

In order to understand fully many geological processes, the rocks and the minerals of which they are composed must be viewed as complex chemical systems. As with any natural system, minerals and rocks tend toward the lowest possible energy configuration. In order to assess whether or not certain minerals are stable, or if the various minerals in the rock are in equilibrium, one needs to know how much energy exists in the system, and how it is partitioned amongst the various phases.

The energy in a system that is available for driving chemical reactions is referred to as the **Gibbs Free Energy (GFE)**. For any chemical reaction, the reactants and the products are in equilibrium (i.e., they all are stable and exist in the system) if the GFE of the reactants is equal to that of the products. For example:



$$\begin{aligned} \text{at equilibrium: } (G_{\text{calcite}} + G_{\text{qtz}}) &= (G_{\text{wooll}} + G_{\text{CO}_2}) \\ \text{or: } \Delta G &= (G_{\text{reactants}} - G_{\text{products}}) = 0 \end{aligned}$$

If the free energy of the reactants and products are not equal, the reaction will proceed to the assemblage with the lowest total energy.

Being able to assess chemical equilibrium and phase stability is extremely important in many fields of geoscience. In order to do this, a number of fundamental properties of the chemical system, and of the phases in the system, must be known. Obviously, the temperature (T) and pressure (P) of the system are two of the most important variables. In order to evaluate the GFE of a system, two additional variables must also be known -- the **enthalpy (H)** or thermal energy content of the system, and the **entropy (S)** or degree of disorder of the system. The relationship between the free energy, enthalpy, and entropy of a chemical reaction is given by:

$$\Delta G = \Delta H - T\Delta S$$

Today we will examine the **enthalpy** of chemical systems.

HEAT AND THERMAL ENERGY

Energy exists in many forms - electrical, thermal, and mechanical. Energy can be transformed from one form to another but it cannot be created or destroyed; energy is always conserved. Heat is thermal energy that passes from a substance at high temperature to a substance at a lower temperature.

The enthalpy, or total thermal energy content, of a system (or phase) is largely a function of temperature; the higher the temperature of a substance, the more thermal energy it possesses. In addition, the thermal energy of a substance is also a function of the amount of substance. In other words, enthalpy is an **extensive** variable -- it depends upon the amount (or extent) of matter involved.

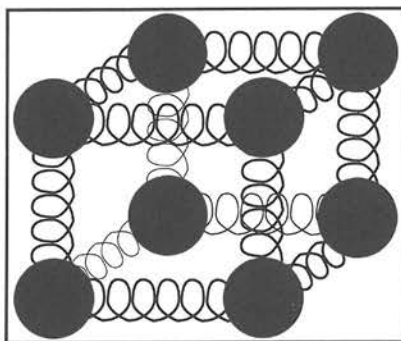
Enthalpy, however, is not simply a function of temperature and mass. For example, if you were to take 100 g of water and 100 g of quartz and heat both to 50° C, they would not contain the same amount of thermal energy. This is because different materials have different capacities for storing thermal energy. This capacity for storing thermal energy is referred to as the **heat capacity** (C_p) of the substance. The relationship between enthalpy (H), temperature (T), and heat capacity (C_p) is given by:

$$\Delta H = C_p * \Delta T$$

or, in words: the total thermal energy content of a substance changes directly as a function of changes in the temperature of the system, times the heat capacity of the material (at constant pressure).

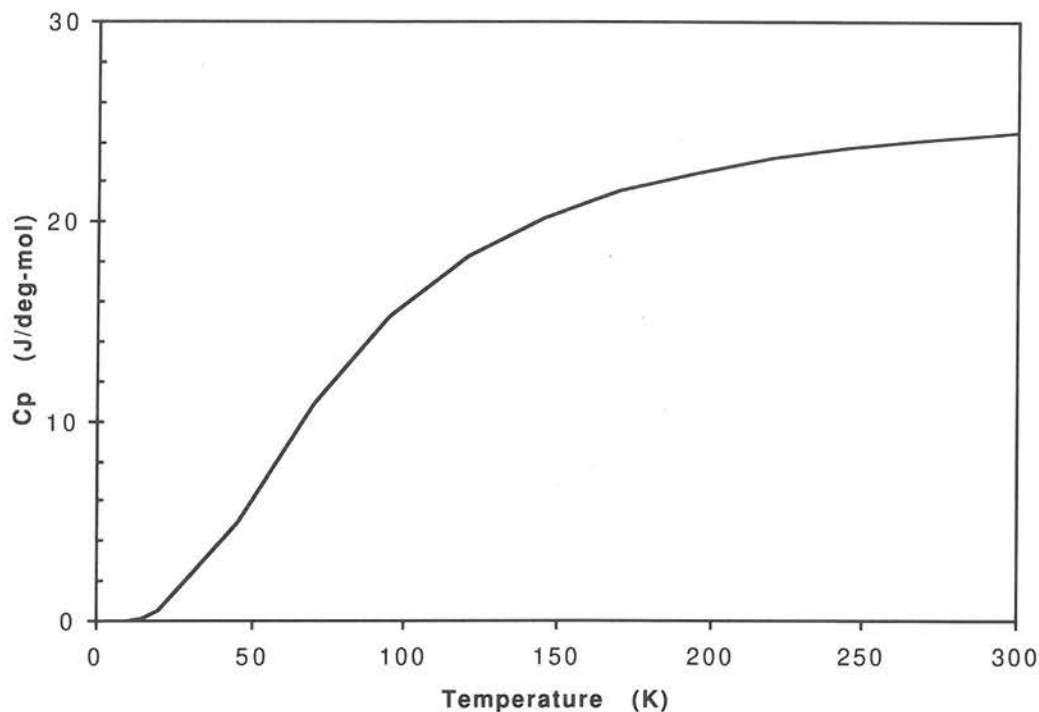
Heat Capacities of Minerals

Minerals are crystalline solids. On an atomic level, each atom in a crystal structure resides in an equilibrium position known as a *lattice site*. At any temperature above absolute zero, atoms have kinetic energy; that is, they don't just sit in a lattice site, they move about, "bouncing" off of adjacent atoms. To a first approximation, individual atoms in a crystal lattice can be considered to be 3-D harmonic oscillators. Imagine that the atoms of a solid vibrate, much as if they were bonded to one another with springs -- as is illustrated in the sketch of a simple cubic lattice cell below.



At absolute zero, the atoms of a perfect solid can not vibrate, thus the heat capacity of the substance, and the total enthalpy are zero. The atoms of a solid can vibrate collectively to progressively greater extents as the temperature is increased; thus, the heat capacity of a substance increases with increasing temperature. For most substances, there is an upper limit to this capacity (see graph on following page), and this limit is commonly attained at temperatures well-below room temperature.

Heat Capacity of Copper vs. Temperature



In the experiment described below, you will measure the heat capacity of a variety of elemental metals and simple polyatomic mineral compounds. You will then be asked to evaluate the precision and accuracy of your data, and to identify some of the factors that influence the heat capacities of crystalline solids.

Units.

The units to be used in the following experiment are:

Mass:	gram (g)
Temperature:	Celsius ($^{\circ}\text{C}$) or kelvin (K); where $^{\circ}\text{C} = \text{K} - 273.15$
Thermal energy:	joule (J); (1 cal = 4.186 J)
Amount of substance:	mole (mol)
Volume:	cubic centimeter (cm^3)
Density:	g / cm^3
Molecular weight:	g / mole

HEAT CAPACITY OF CRYSTALLINE SOLIDS

Part I. Measuring Heat Capacity

By definition, the *heat capacity* * of a substance is the amount of heat needed to raise the temperature of one gram of the material by 1 °C. Thus, the units for heat capacity are:

$$C_p = \text{J} / ^\circ\text{C}\cdot\text{g}$$

Similarly, the *molar heat capacity* of a substance is the ratio of the heat supplied to a mole of substance to its consequent rise in temperature.

$$C_p = \text{J} / ^\circ\text{C}\cdot\text{mol}$$

Relative heat capacities (specific heats*) can be determined by placing two materials, each initially at a different temperature, in contact with each other. Because energy is always conserved, and because heat flows from warmer materials to colder materials, heat will flow between the two materials until the two are in thermal equilibrium. At this point, the thermal energy lost by the initially warmer object must equal the thermal energy gained by the cooler object:

$$(\text{joules lost})_{\text{hot object}} = (\text{joules gained})_{\text{cold object}}$$

Because the change in thermal energy content of each substance is equal to the heat capacity of each object times the change in temperature and the mass of each substance, we get:

$$(C_p \times \text{mass} \times \Delta T)_{\text{hot object}} = (C_p \times \text{mass} \times \Delta T)_{\text{cold object}}$$

In the experiment that you will perform, you will heat various solids (of known mass) in a hot water bath (of known temperature) until the materials come into thermal equilibrium with the hot water. You will then transfer each sample individually into a beaker containing a known mass of water at a known, lower temperature. The highest temperature reached after you have transferred the material into the water is then taken as the temperature at which thermal equilibrium was achieved. Because the heat capacity of water is known, the only unknown in the equation above is the heat capacity of your sample. Rearranging the equation:

$$\frac{C_{p \text{ sample}}}{C_{p \text{ water}}} = \frac{(\text{mass} \times \Delta T)_{\text{water}}}{(\text{mass} \times \Delta T)_{\text{sample}}} = \text{S.H.}_{\text{sample}}$$

Note that the units in the above equation cancel out. The number you end up with is referred to as the “*specific heat*” of the substance (analogous to the *specific gravity* measurements we make with the Jolly balance). You can convert your specific heats into heat capacities by multiplying by the heat capacity of water:

$$C_{p \text{ sample}} = \text{S.H.}_{\text{sample}} \times C_{p \text{ water}} \quad \text{where: } C_{p \text{ water}} = 4.186 \text{ J} / \text{deg}\cdot\text{g}$$

[* - The terminology can be confusing. While “thermal capacity”, “heat capacity”, and “specific heat” are often used interchangeably, for this exercise I will follow the CRC handbook definitions and use “thermal capacity” and “heat capacity” as synonyms (units of J/deg-g); “specific heat” will be used only to refer to the relative heat capacities of substances (unitless).]

Procedure.

1. Work in groups of three in lab. Everyone must record the data and turn in a completed lab exercise and write-up.
2. Make sure you have the necessary supplies:
crystalline solids (provided by instructor)
two Styrofoam cups
a large beaker of boiling water
two thermometers (one 0 to 110 °C thermometer, and one 0 to 50 °C thermometer)
3. Weigh your mineral / metal samples. Record the weights in the tables provided.
4. Suspend the materials in the beaker of boiling water. Record the temperature of the boiling water.
5. Nest together two dry and clean Styrofoam cups. Record the weight of the empty cups. Fill with approximately 50 ml of room temperature water and re-weigh.
6. When your solid sample has reached thermal equilibrium with the boiling water, quickly transfer the sample from the hot water bath to the room temperature water in the Styrofoam cups.
7. Stir and note the maximum temperature reached by the system (water + sample).

PART II. Heat Capacities of Elemental Metals

First the class will measure the heat capacities of six different elemental metals: Al, Si, Fe, Cu, Ag, and Pb. Each group will measure the heat capacities of all six metals. Follow the procedure above and record your data below.

	Metal				Water			
	weight (g)	T initial (°C)	T final (°C)	ΔT (°C)	weight (g)	T initial (°C)	T final (°C)	ΔT (°C)
Al								
Si								
Fe								
Cu								
Ag								
Pb								

PART II. Heat Capacities of Elemental Metals (cont.)

Calculate the gram and molar heat capacities of your samples using your data, and the data collected by your classmates. Calculate and record the mean heat capacity values, along with the standard deviation of each value.

	Al	Si	Fe	Cu	Ag	Pb
C_p (J/deg-g)						
C_p (J/deg-mol)						
Density (g/cm ³)						
Mol. Weight (g/mol)						

Questions

1. Is the heat capacity of elemental metals primarily a function of the mass of the individual atoms? Construct a graph of the molar heat capacities vs. the molecular weights of the six metals. Is there a positive correlation between molecular weights and molar heat capacities?
2. Is the heat capacity of elemental metals primarily a function of the density of the metal? Construct a graph of the molar heat capacities vs. the densities of the six metals. Is there a positive correlation between densities and molar heat capacities?
3. Is the heat capacity of elemental metals primarily a function of the number of atoms (moles) per unit volume? Construct a graph of the number of atoms per cubic centimeter (moles/cm³) vs. the volume heat capacity (J/deg-cm³) of the elemental metals. Is there a positive correlation between # of atoms and heat capacities? (Note: Calculate the volume heat capacities by multiplying the specific heat capacities of each metal by their densities; you should end up with units of J/deg-cm³).
4. Using the volume heat capacities calculated above, note which of the six metals would be best for storing the most amount of thermal energy per unit volume?
5. Most of the metals have molar heat capacities on the order of 25 J / deg-mol, regardless of density and/or molecular weights! Thus, for most metals (and in fact, for most crystalline solids), the heat capacity of the substance is primarily a function of the total number (moles) of atoms present. The accepted heat capacities of the six metals are (in J / deg-mol): Al - 24.4; Si - 20.0; Fe - 25.1; Cu - 24.4; Ag - 25.4; Pb - 26.4). How do these values compare to the values measured in class? If they differ, discuss possible reasons for the observed discrepancies. What are some of the sources of error in our measurements?
6. Diamond (C) has a molar heat capacity of 6.12 (J / deg-mol). Our results for the metals above suggested that the heat capacity of a substance was primarily a function of the number of atoms (approx. 25 J / deg-mol). Why then does diamond have such a significantly different molar heat capacity? What might explain the unusually low heat capacity of diamond? (Hint: In what way does diamond differ from the metals discussed above?)

PART III. Heat Capacities of Minerals

Most minerals are polyatomic crystalline solids. In detail, the heat capacities of polyatomic solids are a function of many complex factors (e.g. quantum state, mass, nature of bonding, etc.). Fortunately, to a first approximation, the heat capacities of polyatomic solids are essentially just the sums of the heat capacities of the constituent atoms. An empirical list of the atomic contributions to the heat capacities of polyatomic solids was first compiled by Kopp in 1865. A list of the “Kopp parameters” is given below (from Winn (1995) and Berry et al. (1980)):

<u>Atom</u>	<u>Cv (J / deg-mol)*</u>
H	10.5
Be	12.5
B	10.5
C	8.4
N	12.5
O	16.7
F	20.9
Al	14.5
Si	15.9
P	22.7
S	22.7
All heavier elements:	25.9

(*Note: These are values for the heat capacity at constant volume. All previous values were for constant pressure. Fortunately, for most crystalline solids, $C_v \sim C_p$. For the rest of this exercise, you may use the values above to estimate heat capacities of solids at constant pressure.)

Let's run through an example of how the Kopp parameters can be used. For quartz, the heat capacity calculated using the Kopp parameters is:

$$\begin{array}{rcl} C_p \text{ silicon} & + & (2 \times C_p \text{ oxygen}) & = & C_p \text{ qtz} \\ 15.9 & + & 33.4 & = & 48.9 \text{ J / deg-mol} \end{array}$$

The accepted value for quartz is 44.5 J / deg-mol. This is a fairly typical result; usually within 10% of the accepted value.

PART III. Heat Capacities of Minerals (cont.)

First we will measure the heat capacities of six different minerals: three oxides and three sulfides. Each group will select one of the minerals, and will make five separate measurements of the heat capacity of their sample. Follow the procedure you used for the metals and record your data below.

Mineral: _____ Formula: _____

Molecular weight: _____ Density: _____

Trial	Mineral				Water			
	weight (g)	T initial (°C)	T final (°C)	ΔT (°C)	weight (g)	T initial (°C)	T final (°C)	ΔT (°C)
#1								
#2								
#3								
#4								
#5								

Calculate the specific heat (S.H.) and the gram and molar heat capacities of your sample using the data above. Record your results below.

Mineral: _____

Trial #:	S.H.	Cp (J / deg-g)	Cp (J / deg-mol)
1			
2			
3			
4			
5			
Mean			
s.d.			

PART III. Heat Capacities of Minerals (cont.)

Estimate the molar heat capacities of the six minerals using the Kopp parameters. Record these values in the table below. In addition, record the mean heat capacity values for each sample as determined by the class.

	Cp (J / deg-mol)		
	Accepted values	Kopp values	Measured values
galena	49.5		
sphalerite	46.1		
pyrite	62.2		
quartz	44.5		
corundum	79.1		
magnetite	143.5		

Questions

1. Compare the measured molar heat capacity values for these minerals with the predicted values (using the Kopp parameters) and the accepted values. Do the measured values correlate with the predicted / actual values? If not, discuss possible reasons for the discrepancies.
2. Attached is a plot of the volume heat capacity (J / deg-cm³) vs. the # of atoms per cm³ for a variety of elements. (Note that the slope of the “best fit” line corresponds to the average Kopp parameter for heavy elements ~ 25 J / deg-mol). On the basis of this plot, what solid material can store the most thermal energy per **cubic centimeter**?
3. Attached is a graph of heat capacity vs. the density of a variety of elements and minerals. On the basis of this plot, what solid material can store the most thermal energy per **gram**?
4. Considering that (in general) metals can store more thermal energy per cubic centimeter and/or per gram than most other solids, why aren't they commonly used as “heat sinks” in passive solar applications? Try to come up with at least three good reasons! (Hint: Think about how **time** might be an important factor!)
5. If you were to take a 1 m³ rock composed of quartz, and a second 1 m³ rock composed entirely of magnetite, how much thermal energy would you need to add to each to increase their temperature by 100 °C? Show your work.

REFERENCES

- Berry, R.S., Rice, S.A., and Ross, J., (1980), Physical Chemistry, John Wiley & Sons, New York, NY.
Winn, John S., 1995, Physical Chemistry, Harper Collins College Publishers, New York, NY.

