

MASSACHUSETTS INSTITUTE OF TECHNOLOGY
Thermodynamics of Materials

3.00 Fall 2002

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Exam 1: Friday 11 Oct, 2002 (11:05-11:55AM)

SOLUTIONS: _____

This exam is composed of two questions. Please read them carefully and thoughtfully before you answer. The first question consists of a set of conceptual exercises for which a good answer will require a short, carefully worded sentence. The last question requires some analytic work and manipulation of formulas. You will not necessarily need a calculator and notes are not permitted.

Your answers should fit in the space provided in the exam. If you find that the provided space is insufficient, use the back of the previous page and clearly indicate that your answer continues.

You may wish to work out your answer on scratch paper before writing on the exam. Your answers will be graded on their accuracy, physical insight, and clarity. A concise clear answer will get a better score than a longer answer with the same content. You may supplement your answer with a figure, a plot, or equations. Your answers will be graded in their entirety—extraneous or irrelevant equations or remarks may reduce the clarity or accuracy of your answer.

The questions are not necessarily ordered according to their difficulty—it would be prudent to read them all before you start. Finally, each question is not weighted equally in the grading; the weights are given below.

There are six pages in this exam, including this cover page.

Question 1.1: 6400 points possible _____

Question 1.2: 3600 points possible _____

Total: 10000 points possible _____

Exam Question 1.1

Read *carefully* and answer the following questions.

The first five statements are true-or-false type; for these, state your conclusion and thermodynamic reasoning. If you claim that a statement is false, you may state which law or laws of thermodynamics it violates or you may employ a physical counter-example or any other plausible physical reason. You may wish to amend any false statement with a clarifying phrase that makes the statement true.

The last three questions require a thermodynamic prediction or explanation that can be satisfactorily answered with a few short sentences.

1-1-i The internal energy of any material system is constant. True or False?

False. By the first law, it is only necessary for the internal energy is constant for an isolated system.

Common Errors	
Symbol	Error Description
α	Specified that statement applied to a closed system.

1-1-ii The work that is performed by the expansion of a system composed entirely of one mole of ideal gas is numerically equal to the heat that is absorbed by the system. True or False?

False. For example, an ideal gas can absorb heat and do no work if it raises its internal energy by $C_V \Delta T$.

Common Errors	
Symbol	Error Description
α	Assumed or specified that process must be reversible.
β	Assumed or specified that process was only true if system is isolated.

1-1-iii The internal energy of a system and its surroundings is conserved during an irreversible process. True or False?

True. The statement is equivalent to the first law.

Common Errors	
Symbol	Error Description
α	Assumed or specified that statement applied only to reversible processes.

1-1-iv Consider an isolated system comprised of body **A** and body **B** that are in thermal contact (i.e., heat can be transferred between body **A** and body **B**) but no work can be transferred between them.

If heat passes from **A** to **B**, then the temperature of **A** must decrease and the temperature of **B** must increase. True or False?

False. For example, heat can be transferred between two bodies which remain at the same temperature during a phase transformation.

Common Errors	
Symbol	Error Description
α	Equated heat with temperature.
β	Neglected statement regarding no work.
γ	Equated statement with the zeroth law..

- 1-1-v If one mole of monatomic ideal gas increases its temperature by 1°C by a reversible (quasi-static) process, the work *performed* on the gas by its surroundings must be numerically equal to the molar heat capacity at constant volume, $\overline{C_V}$. True or False?

False. Changes in internal energy need not come from work alone. The statement would be true if the system is also adiabatic.

Common Errors	
Symbol	Error Description
α	Concluded that all internal energy changes must derive from work.
β	Confused the expression of $\overline{C_V}\Delta T$ for internal energy state function with a process that is constant volume.

- 1-1-vi Near the end of Arthur C. Clarke's novel, 2010, Jupiter (yes, that big gassy planet) rapidly collapses. How and why would the average temperature of Jupiter change as it rapidly collapses?

As the planet collapses, the gravitational potential must be transformed into another form of energy storage. As the planet is rapidly collapsing, the process is approximately adiabatic and therefore the temperature must rise.

Common Errors	
Symbol	Error Description
α	Assumed that the process was reversible or wrote mathematical statements that imply reversibility.
β	Assumed ideal gas law or ideal gas equation of state must apply.

- 1-1-vii The "heat of dissolution" is the amount of heat absorbed by a system as a material goes into solution. For example, for each mole of crystalline NH_4ClO_4 that is dissolved in water at 25°C , 8000 calories are absorbed by the solvent/solute system. (This material could be used to make an excellent emergency cold-press for athletic injuries.) Given that water expands with increasing temperature at constant pressure, answer the following question for a milligram of NH_4ClO_4 dissolved in a gram of water at 25°C . Consider two systems—one is adiabatic and constant pressure and the other is adiabatic and constant volume; which one would have a lower final temperature after dissolution and why?

The process can be conceptually broken into two steps: first, the heat of dissolution is *extracted*; second the body changes its temperature proportional to the appropriate heat capacity. The hint about cold-press was indicative of the fact that the system will tend to lower its temperature which would tend to extract heat from the environment if it were not adiabatically contained. Because the heat extracted is the same, $q = C_p\Delta T_P = C_V\Delta T_V$, therefore $\Delta T_V/\Delta T_P = C_P/C_V > 1$ where the last inequality follows from the positive thermal expansion for water. Therefore $\Delta T_V > \Delta T_P$ and because the temperature is decreasing generally, the temperature of the constant volume system will be lower.

Common Errors	
Symbol	Error Description
α	Sound reasoning, but based on increasing temperatures or exothermic dissolution.
β	Assumed that the ideal gas law was relevant.

1-1-viii List four different ways that a solid can store internal energy and write one differential expression for a reversible change in internal energy dU for your set of choices.

For example, a solid can be polarized, magnetized, stressed, or increase its temperature.

$$dU = V \vec{E} \cdot d\vec{D} + V \vec{H} \cdot d\vec{B} + V \underline{\sigma} \cdot d\underline{\epsilon} + CdT$$

Exam Question 1.2

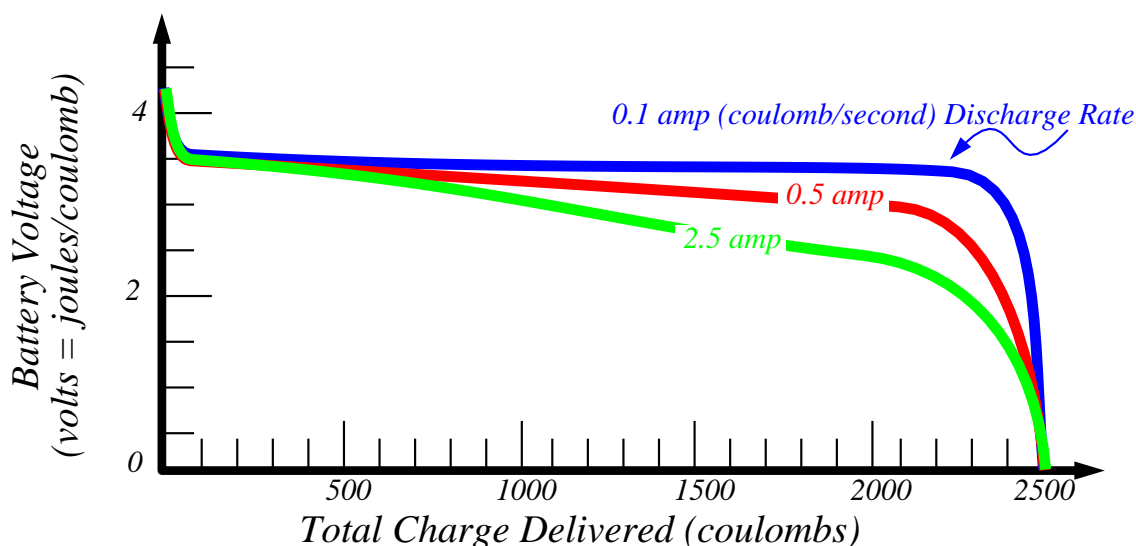


Figure 1: Voltage versus amp-hours delivered for a battery with a fully charged LiFePO_4 cathode/Li anode system composed of a 4 gram cathode. Each curve represents a different battery discharge rate: the top curve is a constant discharge rate of 0.1 coulombs/second, the middle curve is for 0.5 coulombs/second, and the lowest curve is for the most rapid discharge rate of 2.5 coulombs/second.

The data above derive from a recent journal article, “*Electronically Conductive Phosphorolivines as Lithium Storage Devices*” in *Nature Materials* by MIT/DMSE authors S.-Y Chung, J. T. Bloking, and Y.-M. Chiang that was featured in a *New York Times* article last week.

Part A Using concepts from thermodynamics, give an explanation for the observed trend of the voltage versus discharge for different discharge rates. In other words, explain why the curves for 0.1, 0.5, and 2.5 amps differ.

The departure from reversibility increases with discharge rate. (e.g., A rapidly discharging battery generates an enormous amount of heat.) Because the integral is a measure of the work delivered by the battery system, the area under the curve should decrease with discharge rate. This follows from the fact that work is maximized for a reversible process.

Common Errors	
Symbol	Error Description
α	Apparently misunderstood question or gave an irrelevant answer.
β	Didn't use concepts based on thermodynamics.

Part B Consider the effect of battery capacity on the heat of dissolution. In other words, consider the difference in final solvent temperatures between dissolving a charged battery and dissolving an completely discharged battery.

Specifically, consider dissolution of the 4 gram cathode battery system (that was used to obtain the data above) in 500 grams of sulphuric acid. Assume that the sulphuric acid/battery system is adiabatic.

Suppose two batteries, identical except that one is charged and the other is fully discharged, are dissolved adiabatically. Which battery would result in a larger final temperature after dissolution and why?

The additional internal energy of the charged battery must show up as additional heat of dissolution and therefore would result in a higher temperature in an adiabatic process.

Part C Find a numerical estimate of the difference in temperature (between a 4 gram charged cathode system and an identical but uncharged one) if the molar heat capacity of H_2SO_4 is approximately $111 \frac{\text{J}}{\text{K mole}}$; H_2SO_4 has a molecular weight of approximately 98 grams/mole. Please show a symbolic expression as well as a numerical expression—leave your numerical expression in terms of fractions (e.g., $4\pi/(3.1)$ instead of 4.xxxxx).

The energy stored in the (4 gram cathode) battery system can be estimated by visually integrating the limiting slow discharge curve. My estimate is approximately (3.5 volts)(2500 coulombs) joules.

Setting this extra internal energy equal to the heat capacity of the system multiplied by an unknown temperature change (assuming, reasonably, that heat capacity is approximately that of the acid alone)

$$(3.5)(2500)\text{joules} = \frac{(500 \text{ grams})(111 \frac{\text{J}}{\text{K mole}})}{(98 \text{ grams/mole})}$$

$$\Delta T = \frac{98}{111}(3.5)(500)^\circ\text{K}$$

Common Errors	
Symbol	Error Description
α	Used mass of battery system instead of solvent in heat capacity.
β	Couldn't find any expression for the answer.
γ	Didn't realize that extra energy of the charged battery could be inferred or estimated from the data.