

Problem Set PS10

ISSUED: 11/12/02 Due: 11/14/02

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Name _____

Instructions. Complete all questions before class on the due date. You are encouraged to work together. Be sure to struggle with the problem before seeking help. Many of the exercises are very similar to problems in the book. Understanding the solution to these problems will be helpful in completing the assigned exercises.

Mathematical Exercises

1. Let $f(x, y) = 2x^2 - 2xy + y^2$. Write out the total derivative explicitly.
2. Derive the reciprocal rule from the chain rule (Hint: start with $1 = \frac{\partial z}{\partial z}$)
3. Use the chain rule and the reciprocal rule to derive the following

$$\frac{\partial z}{\partial x} = \frac{\frac{\partial z}{\partial y}}{\frac{\partial x}{\partial y}}$$

4. Solve the differential equation

$$\frac{dy}{dx} = \frac{y}{x}$$

by collecting all the x terms on one side of the equation and all the y terms on the other side of the equation and integrating each side of the resulting equation with respect to the appropriate variable.

5. Solve the differential equation

$$\frac{dy}{dx} = (i\omega + \gamma)y,$$

by the same method as the preceding problem.

Exercises

6. Express the working equation for the internal energy of a Redlich-Kwang gas. Then calculate ΔU for an isothermal expansion of this gas from V_1 to V_2 .
7. Express the working equation for the entropy of a Redlich-Kwang gas (see table on page 127 of notes). Then calculate ΔS for an isothermal expansion of this gas from V_1 to V_2 .
8. Using the first law and the fact that the internal energy for an ideal gas is independent of volume to show that for isothermal expansion of an ideal gas

$$dS = \frac{nRdV}{V}$$

and thus

$$\Delta S = \int_{V_1}^{V_2} \frac{nRdV}{V}.$$

Evaluate this integral and then use the ideal gas law to derive an expression for ΔS in terms of pressure.

9. Using the first law show that for constant volume $dS = \frac{C_v dT}{T}$ and thus

$$\Delta S = \int_{T_1}^{T_2} \frac{C_v dT}{T}.$$

For small changes in temperature C_v is constant. Knowing this, determine the change in entropy when 1g of lead at 250K is placed in contact with 1 g of lead at 350K and the total system is isolated (hint: $\Delta S = \Delta S_1 + \Delta S_2$). The specific heat, c_v , for lead is 0.12J/gK. Notice that even though each piece of lead changed temperature by the same amount during the process the entropy change is positive.

10. We know heat capacity is in fact a function of temperature. This function can not really be derived from first principles so one must use an empirical model. A common model for the temperature dependence of heat capacity is the *Maier-Kelley equation*,

$$C_{Pm}(T) = a + bT + c/T^2.$$

Derive an expression for a constant pressure change in molar entropy as a function of temperature starting with

$$\Delta S_m = \int_{T_1}^{T_2} \frac{C_{Pm} dT}{T}.$$

11. Start with a blank sheet of paper and derive every equation in the on page 115 of the notes. Notice that the first working equation is our useful relation.
12. We have discussed several so-called auxiliary functions namely enthalpy, Helmholtz free energy and Gibbs free energy. The goal was to establish functions with various pairs of natural variables. If we consider the case of a piece of matter in an electric field, \mathcal{E} , we can write the Helmholtz free energy as

$$dA = -SdT - PdV - \mathcal{E}dQ$$

where Q is the charge creating the field. What are the (now three) natural variables for this situation? Define a new function \tilde{A} such that the \mathcal{E} becomes a natural variable. Show

$$\mathcal{E} = - \left(\frac{\partial A}{\partial Q} \right)_{T,V}$$

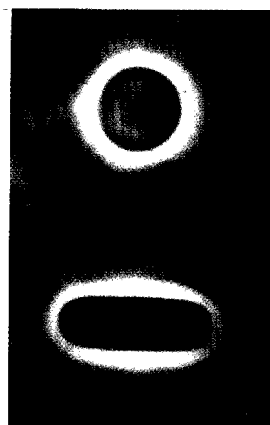
and

$$Q = \left(\frac{\partial \tilde{A}}{\partial \mathcal{E}} \right)_{T,V}.$$

Conceptual Problems

13. We calculated entropy for some examples above and we will do more next semester. As it turns out entropy must be calculated along a reversible path. This seems to limit the usefulness of the concept of entropy since many processes are not reversible. In fact, there is no limitation at all. Explain why this is the case.
14. Julie and Bor Yu are arguing over whether to use Helmholtz free energy (Julie) or Gibbs free energy (Bor Yu) to best describe a particular system. What information would you want regarding the system in order to decide who has the best approach to the problem. Under what conditions would it not matter which free energy is used?
15. Some proponents of creationism state that Darwinian evolution is in conflict with the second law of thermodynamics. Why might they propose this (hint: consider the principle of Clausius)? What are they failing to consider (hint: consider the principle of Clausius)?
16. Read the following update that appeared in *Physics Today* in November of 2001. Write down an expression for Gibbs free energy that one needs to describe this system (dG).

AN OPTICAL STRETCHER, a laser tool for studying the elastic properties of cells, has been developed. When light enters a transparent object with an index of refraction higher than that of the surrounding medium, it gains momentum and therefore exerts a force on the object. A group at the University of Texas at Austin, led by Josef Käs, showed that if a



laser beam is defocused so as to encompass an entire biological cell, the force acts backward where the light enters the cell and forward where it exits the cell. The result is that the cell gets stretched by an amount that depends on the power in the beam. The difference between the front and back forces is the much smaller total scattering force that acts at the cell's center of gravity and tends to push the cell in the direction of the light propagation.

A second divergent laser beam in the opposite direction keeps the cell stationary—and doubles the stretching. The researchers used the technique to study very soft human red blood cells (shown here) and much stiffer mammalian cells that contain a cytoskeleton. The tool might be used to screen cell populations for changes in elasticity due to diseases such as cancer. (An early discussion is J. Guck et al., *Phys. Rev. Lett.* **84**, 5451, 2000. J. Guck et al., *Biophys. J.* **81**, 767, 2001.)

—SGB

17. Consider Robert Frost's famous poem "The road less traveled"

TWO roads diverged in a yellow wood,
And sorry I could not travel both
And be one traveler, long I stood
And looked down one as far as I could
To where it bent in the undergrowth;

Then took the other, as just as fair,
And having perhaps the better claim,
Because it was grassy and wanted wear;
Though as for that the passing there
Had worn them really about the same,

And both that morning equally lay
In leaves no step had trodden black.
Oh, I kept the first for another day!
Yet knowing how way leads on to way,
I doubted if I should ever come back.

I shall be telling this with a sigh
Somewhere ages and ages hence:
Two roads diverged in a wood, and I—
I took the one less traveled by,
And that has made all the difference.

Taking this poem as a metaphor for life, does Robert Frost consider life to be a state function? Explain. Do you consider life to be a state function?

Computer Problems

18. Two fitting functions are commonly used to fit heat capacity data. The first is a series expansion,

$$C_{Pm}(T) = c_0 + c_1T + c_2T^2 + c_3T^3 + \dots$$

and the second is the *Maier-Kelley equation*,

$$C_{Pm}(T) = a + bT + c/T^2.$$

Fit and plot the high temperature graphite heat capacity data (see table below) using the nonlinear fitting function capabilities of MATHEMATICA. Pages 460 and 461 of *Mathematica 3.0 Standard Add-on Packages* (the smaller of the two MATHEMATICA

reference books) explains how to do this.

T (K)	C_{Pm} (J K ⁻¹ mol ⁻¹)
300	8.581
350	10.241
400	11.817
450	13.289
500	14.623
600	16.844
700	18.537
800	19.827
900	20.824
1000	21.610

Data from W.H. Cropper *Mathematica Computer Programs for Physical Chemistry*.

19. Plot the *Maier–Kelley equation*,

$$C_{Pm}(T) = a + bT + c/T^2,$$

for O₂ where $a = 29.86 \text{ J K}^{-1}\text{mol}^{-1}$, $b = 4.184 \times 10^{-3} \text{ J K}^{-2}\text{mol}^{-1}$ and $c = -1.67 \times 10^5 \text{ J K mol}^{-1}$ from $T = 298 \text{ K}$ to $T = 3000 \text{ K}$. What is the total change in heat capacity over this range.

20. Visit the NIST webbook page from the PChem homepage. Click on “NIST Chemistry WebBook” and then on “Thermophysical Properties of Fluid Systems” select water, set the pressure units to bar and the data type to isobaric properties. Press continue. Enter 1 bar for pressure and a temperature range from 280K to 360K in steps of 10K. Play around with changing the y -axis in the resulting plot. Then click the view table button. Select T , C_V and U and record this data into EXCEL (unfortunately you will have to type this data in by hand), Then select T , C_P , and H and record this data into EXCEL. Use EXCEL to verify that

$$C_V = \frac{\partial U}{\partial T} \simeq \frac{\Delta U}{\Delta T}$$

and

$$C_P = \frac{\partial H}{\partial T} \simeq \frac{\Delta H}{\Delta T}.$$

Which of these equations is more correct for this data? Why?

Reflective Questions

21. Please read the following passage regarding the independence of science and moral questions from Richard Feynman’s *The meaning of it all*. Feynman is one of the most famous physicists of all time. He was co-winner of the Nobel prize for his development of quantum electrodynamics—the most advanced version of quantum theory we have to date. Do you think “Should I do this?” questions are fundamentally outside of science? Can science form a foundation for morals and ethics? Do science and ethics progress independently?

And finally I would like to make a little philosophical argument—this I’m not very good at, but I would like to make a little philosophical argument to explain why theoretically I think that science and moral questions are independent. The common human problem, the big question, always is “Should I do this?” It is a question of action. “What should I do? Should I do this?” And how can we answer such a question? We can divide it into two parts. We can say, “If I do this what will happen?” That doesn’t tell me whether I should do this. We still have another part, which is “Well, do I want that to happen?” In other words, the first question—“If I do this what will happen?”—is at least susceptible to scientific investigation; in fact, it is a typical scientific question. It doesn’t mean we know what will happen. Far from it. We never know what is going to happen. The science is very rudimentary. But, at least it is in the realm of science we have a method to deal with it. The method is “Try it and see”—we talked about that - and accumulate the information and so on. And so the question “If I do it what will happen?” is a typically scientific question. But the question “Do I want this to happen”—in the ultimate moment—is not. Well, you say, if I do this, I see that everybody is killed, and, of course, I don’t want that. Well, how do you know you don’t want people killed? You see, at the end you must have some ultimate judgment.

You could take a different example. You could say, for instance, “If I follow this economic policy, I see there is going to be a depression, and, of course, I don’t want a depression.” Wait. You see, only knowing that it is a depression doesn’t tell you that you do not want it. You have then to judge whether the feelings of power you would get from this, whether the importance of the country moving in this direction is better than the cost to the people who are suffering. Or maybe there would be some sufferers and not others. And so there must at the end be some ultimate judgment somewhere along the line as to what is valuable, whether people are valuable, whether life is valuable. Deep in the end—you may follow the argument of what will happen further and further along—but ultimately you have to decide “Yeah, I want that” or “No, I don’t.” And the judgment there is of a different nature. I do not see how by knowing what will happen alone it is possible to know if ultimately you want the last of the things. I believe, therefore, that it is impossible to decide moral questions by scientific technique, and that the two things are independent.

$$df = \left(\frac{\partial f}{\partial x}\right)dx + \left(\frac{\partial f}{\partial y}\right)dy \quad \left(\frac{\partial f}{\partial x}\right) = 2x+2y \quad \left(\frac{\partial f}{\partial y}\right) = 2y+2x$$

$$df = (2x+2y)dx + (2y+2x)dy$$

$$\textcircled{2} \quad 1 = \frac{2z}{2z} = \frac{2z}{2x} \frac{2x}{2z} \Rightarrow \frac{2z}{2x} = \frac{1}{2x}$$

$$\textcircled{3} \quad \frac{2z}{2x} = \frac{2z}{2y} \frac{2y}{2x} = \left(\frac{2z}{2y}\right) \left(\frac{2y}{2x}\right) = \frac{2z}{2x}$$

$$\textcircled{4} \quad \frac{dy}{dx} = \frac{y}{x} \Rightarrow \int \frac{dy}{y} = \int \frac{dx}{x} \Rightarrow \ln y = \ln x + C$$

$$y = Ax \quad A = e^C$$

$$\textcircled{5} \quad \frac{dy}{dx} = (a+bx)y \Rightarrow \int \frac{dy}{y} = \int (a+bx)dx$$

$$\ln y = (a+bx)x + C \quad y = Ae^{(a+bx)x}$$

$$\textcircled{6} \quad dU = C_V dT + \left[T\left(\frac{\partial P}{\partial T}\right)_V - P\right]dV \quad P = \frac{nRT}{V-nb} - \frac{n^2a}{V^2(V-nb)}$$

$$dU = C_V dT + \left[T\left(\frac{nR}{V-nb} + \frac{1}{2} \frac{n^2a}{V^2(V-nb)}\right) - \frac{nRT}{V-nb} + \frac{n^2a}{V^2(V-nb)}\right]dV$$

$$dU = C_V dT + \frac{1}{2} \frac{n^2a}{V^2(V-nb)} dV$$

$$\Delta U = \int_{V_1}^{V_2} \frac{1}{2} \frac{n^2a}{V^2(V-nb)} dV =$$

$$\textcircled{1} \quad ds = \frac{C_V}{T} dT + \left(\frac{\partial P}{\partial T}\right)_V dV$$

$$ds = \frac{C_V}{T} dT + \left[\frac{nR}{V-nb} + \frac{1}{2} \frac{n^2a}{T^2 V(V-nb)}\right]dV$$

$$\Delta S = \int_{V_1}^{V_2} \left(\frac{nR}{V-nb} + \frac{1}{2} \frac{n^2a}{T^2 V(V-nb)}\right) dV$$

$$\textcircled{8} \quad dU = Tds - PdV \quad dU = C_V dT$$

$$C_V dT = Tds - PdV$$

$$0 = Tds - PdV \Rightarrow ds = \frac{PdV}{T}$$

$$ds = \frac{nRT}{V^2} dV \Rightarrow ds = \frac{nR}{V} dV$$

$$\Delta S = \int_{V_1}^{V_2} \frac{nR}{V} dV = nR \ln \frac{V_2}{V_1}$$

$$V_2 = \frac{nRT}{P_2}$$

$$V_1 = \frac{nRT}{P_1}$$

$$\Delta S = nR \ln \frac{nRT}{P_2} \frac{P_1}{nRT}$$

$$\Delta S = nR \ln \frac{P_1}{P_2}$$

$$\textcircled{9} \quad dU = Tds - PdV \quad \text{const } U \quad dU = Tds$$

$$C_V dT = Tds \Rightarrow ds = \frac{C_V dT}{T}$$

$$\Delta S = \int_{T_1}^{T_2} \frac{C_V dT}{T} \quad \text{for const } C_V \quad \Delta S = C_V \ln \frac{T_2}{T_1}$$

$$\Delta S_1 = 0.12 \frac{J}{K} \ln \frac{300}{250} = 2.18 \times 10^{-2} \frac{J}{K}$$

$$\Delta S_2 = 0.12 \frac{J}{K} \ln \frac{300}{350} = -1.84 \times 10^{-2} \frac{J}{K}$$

$$\Delta S = \Delta S_1 + \Delta S_2 = 3.3 \times 10^{-3} \frac{J}{K} > 0 \quad \checkmark$$

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$$\textcircled{10} \quad \Delta S_{\text{tot}} = \int_{T_1}^{T_2} \frac{(a+bT + \frac{c}{T})}{T} dT$$

$$= \int_{T_1}^{T_2} \frac{a}{T} dT + \int_{T_1}^{T_2} b dT + \int_{T_1}^{T_2} \frac{c}{T^2} dT$$

$$\Delta S_{\text{tot}} = a \ln \frac{T_2}{T_1} + b(T_2 - T_1) - C \left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

$\textcircled{11}$ Your derivation

$$\textcircled{12} \quad \vec{A} = A + EQ$$

$$d\vec{A} = -s dT - PdV - E dQ + E dQ + Q dE$$

$$d\vec{A} = -s dT - PdV + Q dE$$

$$d\vec{A} = \left(\frac{\partial \vec{A}}{\partial T}\right)_{V,E} dT + \left(\frac{\partial \vec{A}}{\partial V}\right)_{T,E} dV + \left(\frac{\partial \vec{A}}{\partial E}\right)_{T,V} dE$$

$$Q = \left(\frac{\partial \vec{A}}{\partial E}\right)_{T,V}$$

$$\text{similarly find } A \quad E = -\left(\frac{\partial \vec{A}}{\partial Q}\right)_{T,V}$$

$\textcircled{13}$ Entropy is a state function

$\textcircled{14}$ Is V const or is P const.

if all work is non- PdV

$\textcircled{15}$ Conflict: evolution yields highly ordered systems and says entropy increases

problem: evolution takes place in a non-isolated system.

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$$\textcircled{16} \quad db = -s dT + v dP + \delta dQ + E dQ$$

substitution term electric field term

$\textcircled{17}$ Frost does not consider life to be a state function because the path through it is important for his opinion.

$\textcircled{18}$ -20

see last years PS10 + PS11

30 SHEETS
100 SHEETS
22-142
22-144
22-146
200 SHEETS

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