Problem Set PS10

ISSUED: 11/8/01 **Due: 11/15/01**

Prof. Darin J. Ulness 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 $f(x, y) = x^2 + 2xy + y^2$. 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. Let $f = f(x, y)$. Starting with the total derivative of f, determine the difference between $\frac{df}{dx}$ and $\frac{\partial f}{\partial x}$. What if $f = f(x)$? What if $f = f(x, y, z)$

5. Let's say $f = f(x, y, z)$, but $z = z(x)$. Show that the total derivative of f is

$$df = 2\frac{\partial f}{\partial x}dx + \frac{\partial f}{\partial y}dy$$

Exercises

6. Use the equation of state for internal energy that we obtained on page 103 of the notes to show that the internal energy of an ideal gas is independent of the volume of the gas. Then show that $\triangle U = 0$ for isothermal expansion of an ideal gas.

7. Using the first law and your result from the previous problem show that for isothermal expansion of an ideal gas

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

and thus

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

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

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

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

For small changes in temperature C_v is constant. Knowing this, determine the change in entropy when 1 gram of lead is heated from 298K to 330K. (c_v for lead is 0.12J/gK) Is $\triangle S$ positive or negative? Does this jive with your common sense?

9. 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

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

10. The constant pressure molar heat capacity of tungsten at 1K is $0.00104 \frac{J}{mol \cdot K}$. What is the entropy contribution from 0K to 1K according to the Debye law.

11. We have discussed several so-called auxiliary functions namely enhalpy, 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 a magnetic field, $\mathcal{H}$, we can write the Helmholtz free energy as

$$dA = -SdT - PdV - Md\mathcal{H}$$

where M is the magnetization of the material. What are the (now three) natural variables for this situation? Define a new function $\tilde{A}$ such that the M becomes a natural variable. Show

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

and

$$\mathcal{H} = \left(\frac{\partial \tilde{A}}{\partial M}\right)_{T,V}$$

Conceptual Problems

12. 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.

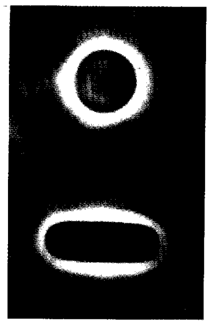
13. Explain the concept of "times arrow" in your own words.

14. What property does each of the laws of thermodynamics deal with?

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)? (By the way, Darwinian evolution is a model founded in the mathematical field of information theory. Statistical mechanics is also founded in the mathematical field of information theory. Thermodynamics must not conflict with statistical mechanics thus if evolution did in fact conflict with the second law then the mathematical field of information theory would be an inconsistent theory because both Darwinism and statistical mechanics are special applications of it).

16. Read the following update that appeared in *Physics Today* in November of 2001. Write down and expression for Gibbs free energy that one need 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

Computer Problems

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

$$C_{Pm}(T) = c_0 + c_1 T + c_2 T^2 + c_3 T^3 + \cdots$$

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.*

18. Plot the *Maier–Kelley equation,*

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

for O_2 where $a = 29.86$ J K^{-1}mol^{-1}, $b = 4.184 \times 10^{-3}$ J K^{-2}mol^{-1} and $c = -1.67 \times 10^5$ J K mol^{-1} from $T = 298$ K to $T = 3000$ K. What is the total change in heat capacity over this range.

Reflective Questions

19. 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.

20. 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?

① $f(x,y) = x^2 + 2xy + y^2$

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

$\boxed{df = (2x+2)dx + (2y+2)dy}$

② $1 = \frac{\partial z}{\partial z} = \frac{\partial z}{\partial x}\frac{\partial x}{\partial z} \Rightarrow \frac{\partial z}{\partial x} = \frac{1}{\frac{\partial x}{\partial z}}$ ✓

③ $\frac{\partial z}{\partial x} = \frac{\partial z}{\partial y}\frac{\partial y}{\partial x} = \left(\frac{\partial z}{\partial y}\right)\left(\frac{1}{\frac{\partial x}{\partial y}}\right) = \frac{\frac{\partial z}{\partial y}}{\frac{\partial x}{\partial y}}$ ✓

④ $f(x,y)$: $df = \left(\frac{\partial f}{\partial x}\right)_y dx + \left(\frac{\partial f}{\partial y}\right)_x dy$

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

$\boxed{\frac{df}{dx} - \frac{\partial f}{\partial x} = \left(\frac{\partial f}{\partial y}\right)_x \frac{dy}{dx}}$

$f(x)$: $df = \frac{\partial f}{\partial x} dx \Rightarrow \frac{df}{dx} = \frac{\partial f}{\partial x} = \frac{df}{dx} - \frac{\partial f}{\partial x} = 0$

$f(x,y,z)$: $df = \frac{\partial f}{\partial x}dx + \frac{\partial f}{\partial y}dy + \frac{\partial f}{\partial z}dz$

$\frac{df}{dx} = \frac{\partial f}{\partial x}\frac{dx}{dx} + \frac{\partial f}{\partial y}\frac{dy}{dx} + \frac{\partial f}{\partial z}\frac{dz}{dx}$

$\frac{df}{dx} - \frac{\partial f}{\partial x} = \frac{\partial f}{\partial y}\frac{dy}{dx} + \frac{\partial f}{\partial z}\frac{dz}{dx}$

⑤ $df = \frac{\partial f}{\partial x}dx + \frac{\partial f}{\partial y}dy + \frac{\partial f}{\partial z}dz$

$\frac{\partial f}{\partial x}\frac{\partial x}{\partial z}dz \quad \frac{\partial x}{\partial z} = \frac{dx}{dz}$ see 2(?)

$df = \frac{\partial f}{\partial x}dx + \frac{\partial f}{\partial y}dy + \frac{\partial f}{\partial x}\frac{dx}{dz}dz$

$df = 2\frac{\partial f}{\partial x}dx + \frac{\partial f}{\partial y}dy$

⑥ $dU = C_v dT + \left(T\left(\frac{\partial P}{\partial T}\right)_V - P\right)dV$

$P = \frac{nRT}{V} \quad \frac{\partial P}{\partial T} = \frac{nR}{V} \Rightarrow T\left(\frac{\partial P}{\partial T}\right)_V - P = T\frac{nR}{V} - \frac{nRT}{V} = 0$

$dU = C_v dT + 0 dV$

$dU = C_v dT$ independent of V

$\Delta U = \int_{T_1}^{T_2} C_v dT$ isothermal expansion $T_1 = T_2 = T$

$\Delta U = \int_T^T C_v dT = 0$ ✓

⑦ $dU = TdS - PdV$ 1st law

$C_v dT = TdS - PdV$ (isothermal)

$0 = TdS - PdV \Rightarrow dS = \frac{PdV}{T} \quad P = \frac{nRT}{V}$

$dS = \frac{nRT}{VT}dV \quad dS = \frac{nRdV}{V}$ ✓

$\Delta S = \int_{V_1}^{V_2} \frac{nRdV}{V} = \boxed{nR\ln\frac{V_2}{V_1}}$ ✓

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

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

⑧ $dU = TdS - PdV$ 1st law

const V: $dU = TdS$

$C_v dT = TdS \Rightarrow dS = \frac{C_v dT}{T}$

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

$\Delta S = 0.12\frac{J}{gK} \cdot 1g \int_{298}^{330}\frac{1}{T}dT = 0.12\frac{J}{K}\ln\frac{330}{298}$

$\Delta S > 0$ makes sense.

⑨ $\Delta S_m = \int_{T_1}^{T_2}\frac{\left(a + bT + \frac{c}{T^2}\right)}{T}dT$

$= \int_{T_1}^{T_2}\frac{a}{T}dT + \int_{T_1}^{T_2} b\,dT + \int_{T_1}^{T_2}\frac{c}{T^3}dT$

$\boxed{\Delta S_m = a\ln\frac{T_2}{T_1} + b(T_2 - T_1) + \frac{c}{3T^2}}$

⑩ $S(1) = \frac{C_P^* T^3}{3} = \frac{0.00104 \cdot 1^3}{3} = 3.46\times10^{-4}\ \frac{J}{K}$

⑪ natural variables T, V, M

$\hat{A} = A + MH \quad d\hat{A} = -SdT - PdV - MdH + MdH + HdM$

$d\hat{A} = -SdT - PdV + HdM$

$\left(\frac{\partial \hat{A}}{\partial H}\right)_{TV} = \left(\frac{\partial}{\partial H}(-SdT - PdV - MdH)\right)_{TV} = -M\frac{dH}{\partial H} = -M$

$M = -\left(\frac{\partial A}{\partial H}\right)_{T,V}$ ✓

$\left(\frac{\partial \hat{A}}{\partial M}\right)_{T,V} = \left(\frac{\partial}{\partial M}(-SdT - PdV + HdM)\right)_{T,V} = H\frac{\partial M}{\partial M} = H$

$H = \left(\frac{\partial \hat{A}}{\partial M}\right)_{T,V}$ ✓

⑫ Entropy is a state function so the path along which one integrates it is unimportant.

⑬ your words

⑭ 0th temperature
1st energy
2nd entropy
3rd entropy

⑮ your words

⑯ $dG = -SdT + VdP + \gamma dA + \mathcal{E}dQ$

Problem 13

In[57]:= << Statistics`nonlinearfit` ← This calls the package that has the nonlinear fit function

In[56]:= data = {{300, 8.581}, {350, 10.241}, {400, 11.817}, {450, 13.289}, {500, 14.623}, {600, 16.844}, {700, 18.537}, {800, 19.927}, {900, 20.824}, {1000, 21.610}};

In[58]:= fitseries = NonlinearFit[data, c0 + c1 T + c2 T^2 + c3 T^3, T, {c0, c1, c2, c3}] ← Fits data to series

Out[58]= $-5.51901 + 0.0582653\,T - 0.0000409722\,T^2 + 9.81017\times10^{-9}\,T^3$

In[62]:= fitMK = NonlinearFit[data, a + b T + c / (T^2), T, {a, b, c}] ← Fits data to Maier-Kelley eqn

Out[62]= $11.5536 - \frac{606058.}{T^2} + 0.0111442\,T$

In[65]:= datplt = ListPlot[data, Prolog -> PointSize[.02], DisplayFunction -> Identity]

Out[65]= -Graphics-

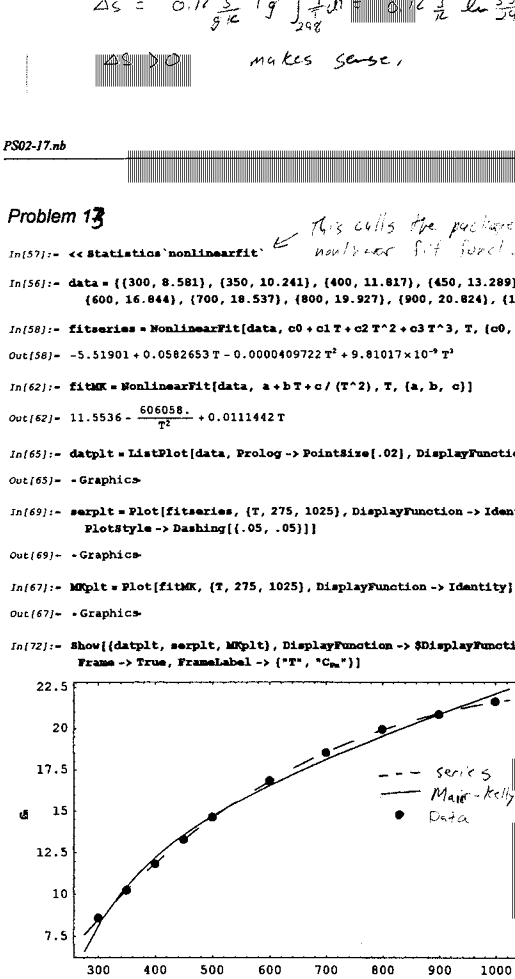
In[69]:= serplt = Plot[fitseries, {T, 275, 1025}, DisplayFunction -> Identity, PlotStyle -> Dashing[{.05, .05}]]

Out[69]= -Graphics-

In[67]:= MKplt = Plot[fitMK, {T, 275, 1025}, DisplayFunction -> Identity]

Out[67]= -Graphics-

In[72]:= Show[{datplt, serplt, MKplt}, DisplayFunction -> $DisplayFunction, Frame -> True, FrameLabel -> {"T", "Cpm"}]



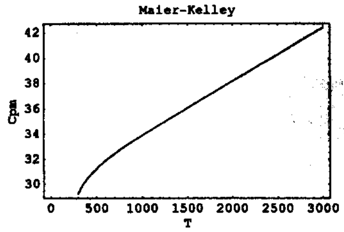
Out[72]= -Graphics-

Problem 11

```
In[1]:= a = 29.86;
        b = 4.184 10^(-3);
        c = -1.67 10^5;

In[8]:= Cpm[T_] := a + b T + c / (T^2)

In[12]:= Plot[Cpm[T], {T, 298, 3000}, Frame -> True, FrameLabel -> {"T", "Cpm"},
          PlotLabel -> "Maier-Kelley"]
```




```
Out[12]= - Graphics -

In[13]:= change = Cpm[3000] - Cpm[298]

Out[13]= 13.1672
```

↳ Total change in heat capacity **13.17 J/K**