

Problem Set PS10
ISSUED: 11/9/00 Due: 11/16/00

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. Let $f(x, y)$ be a function defined by the relation $df = ydx + xdy$. What is $f(x, y)$ (f can be defined to within a constant)?

Exercises

3. Use the equation of state for internal energy that we obtained on page 101 of the notes to show that the internal energy of an ideal gas is independent of the volume of the gas. Then show that $\Delta U = 0$ for isothermal expansion of an ideal gas.
4. 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

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

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

5. 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 1 gram of lead is heated from 298K to 330K. (c_v for lead is 0.12J/gK) Is ΔS positive or negative? Does this jive with your common sense?

6. The constant pressure molar heat capacity of tungsten at 1K is 0.00104. What is the entropy contribution from 0K to 1K according to the Debye law.
7. The constant pressure molar heat capacity of tungsten follows the function

$$C_{Pm}(T) = 1.08T + 0.0346T^3 + 2.84 \times 10^{-8}T^7$$

for the range from 1K to 25K. Note: the units for this equation are mJ/Kmol. Why must we work in these units? How would you convert this equation to J/Kmol units? Plot the heat capacity from 1K to 25K. Calculate the entropy at 25K (don't forget your answer from the previous problem).

8. 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 an insulator in an electric field, E , we can write the Helmholtz free energy as

$$dA = SdT + PdV + EdD$$

where D is the electric displacement of the material. What are the (now three) natural variables for this situation? Define a new function \tilde{A} such that the E becomes a natural variable. This is desirable since we can control E much more easily than we can control D . Show

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

and

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

Conceptual Problems

9. 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.
10. Explain the concept of “times arrow” in your own words.
11. What property does each of the laws of thermodynamics deal with?
12. 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).

Computer Problems

13. 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*.

14. Plot the *Maier–Kelley equation*,

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

for O₂ where $a = 29.86$ J K⁻¹mol⁻¹, $b = 4.184 \times 10^{-3}$ J K⁻²mol⁻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

15. 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 $f(x,y) = x^2 + 2xy + y^2$
 $df = \frac{\partial f}{\partial x} dx + \frac{\partial f}{\partial y} dy$
 $df = (2x+2y)dx + (2x+2y)dy$
 $df = (2x+2y)(dx+dy)$

② $df = ydx + xdy$ so $\frac{\partial f}{\partial x} = y$ $\frac{\partial f}{\partial y} = x$
 so $f = xy + C$

③ $du = cvdT + [T \frac{\partial P}{\partial T} - P] dV$
 $\frac{\partial P}{\partial T} = \frac{\partial}{\partial T} \frac{nRT}{V} = \frac{nR}{V}$
 so $du = cvdT + (\frac{TnR}{V} - \frac{nRT}{V}) dV$
 $du = cvdT \Rightarrow U(T,V) = U(T)$ independent of V
 $\Delta U(T) = U(T_f) - U(T_i)$ but for isothermal expansion
 $T_f = T_i$ so $\Delta U = 0$ ✓

④ $du = dq + PdV$ \rightarrow constant V
 $du = Tds - PdV$ \rightarrow constant V
 $\frac{du}{dT} = \frac{dq}{dT} = \frac{Tds}{dT} \Rightarrow ds = \frac{cvdT}{T}$ ✓
 $\Delta S = \int_{298}^{350} \frac{cvdT}{T} = cv \int_{298}^{350} \frac{dT}{T} = cv \ln T \Big|_{298}^{350}$
 $0.12 \frac{J}{K} \ln \frac{350}{298} = 1.2 \times 10^{-2} \frac{J}{K}$

⑤ $S_m(1K) = \frac{0.00104}{3} = 3.467 \times 10^{-4} \frac{J}{K mol}$

⑥ We must work in $\frac{mJ}{K mol}$ because the coefficients on the RHS are multiplying different powers of T. We could convert the coefficients by multiply by the mJ to J conversion factor raise to the appropriate power such that each term in the sum would have units of $\frac{J}{K mol}$

④ $du = Tds - PdV$
 from problem ③ for isothermal expansion of ideal gas
 $du = 0 = Tds - PdV$
 so $Tds = PdV$
 $ds = \frac{P}{T} dV$ $\rightarrow P = \frac{nRT}{V}$

$ds = \frac{nRT}{TV} dV$
 $ds = \frac{nRdV}{V}$

$\Delta S = \int_{V_i}^{V_f} \frac{nRdV}{V} = nR \ln \frac{V_f}{V_i}$

$\Delta S = nR \ln \frac{\frac{nRT}{P_f}}{\frac{nRT}{P_i}} = -nR \ln \frac{P_f}{P_i}$

⑦ (cont)

```
In(1) := Cpm[T_] := 1.08 T + 0.0346 T^3 + 2.84 10^-8 T^7
In(2) := S(T2, T1) := Integrate(Cpm(T)/T, {T, T1, T2})
In(5) := DS = S(25, 1)
Out(5) := 230.88 <- ΔS from 1K to 25K in mJ/K mol
In(4) := S1 = Cpm[1]/3
Out(4) := 0.371533 <- S from 0 to 1K from Debye's law
In(6) := S25 = DS + S1
Out(6) := 231.251 mJ/K mol
```

$S_m(T=25K) = 0.231 \frac{J}{K mol}$

8 Natural variables T, V, D

$$\tilde{A} \equiv A - ED \rightarrow d\tilde{A} = -SdT - PdV + EdD - DdE - EdD$$

$$d\tilde{A} = -SdT - PdV - DdE$$

$$dA = \left(\frac{\partial A}{\partial T}\right)_{V,D} dT + \left(\frac{\partial A}{\partial V}\right)_{T,D} dV + \left(\frac{\partial A}{\partial D}\right)_{T,V} dD$$

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

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

so $\left(\frac{\partial \tilde{A}}{\partial E}\right)_{T,V} = -D$

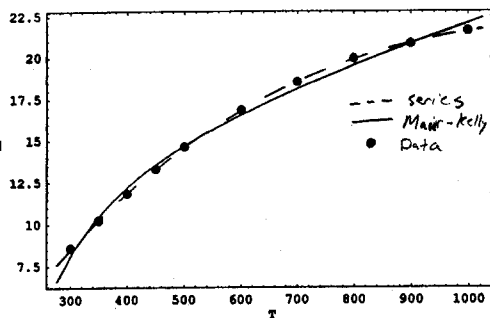
9 entropy is a state function so it does not depend on the path used to calculate it

10 your words

11 0th: Temperature 1st: Energy 2nd + 3rd entropy

Problem 13

```
In[57]:- << Statistics`NonlinearFit
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, a0 + a1 T + a2 T^2 + a3 T^3, T, {a0, a1, a2, a3}]
Out[58]:- 5.51901 + 0.0582653 T - 0.0000409722 T^2 + 9.81017 x 10^-4 T^3
In[62]:- fitMK = NonlinearFit[data, a + b T + c / (T^2), T, {a, b, c}]
Out[62]:- 11.5536 - 606058. / T^2 + 0.0111442 T
In[63]:- dataplt = ListPlot[data, Prolog -> PointSize[.02], DisplayFunction -> Identity]
Out[63]:- 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[{dataplt, serplt, MKplt}, DisplayFunction -> $DisplayFunction,
Frame -> True, FrameLabel -> {"T", "Cp"}]
```



Out[72]:- Graphics

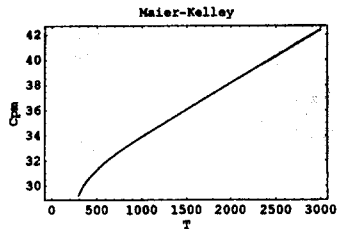
12

The principle of Clausius states that entropy is always increasing yet human life is very organized (not entropic)

The principle of Clausius deals with an isolated system. For open systems, like human life, the entropy of the system may in fact decrease provided it is compensated by an increase in entropy of the environment.

Problem 14

```
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

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In[13]:- change = Cpm[3000] - Cpm[298]
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Out[13]:- 13.1672

Total change in heat capacity

13.17 J/K