Problem Set PS11

Issued: 11/15/01 **Due: 11/29/01**

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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. Solve the differential equation
$$\frac{dy}{dx} = \frac{x}{y}$$
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.

2. Solve the differential equation
$$\frac{dy}{dx} = \frac{y}{x}$$
by the same method as in 1.

3. Solve the differential equation
$$\frac{dy}{dx} = (i\omega + \gamma)y,$$
by the same method as in 1.

Exercises

4. Show that for a reversible process at constant pressure $\triangle H = q$ as we are taught in Freshman Chemistry.

5. Show
$$C_p = \left(\frac{\partial H}{\partial T}\right)_P .$$
You will want to consider dH for a reversible process at constant pressure and identify TdS as heat q.

6. Show the coefficient of thermal expansion,
$$\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P ,$$
for an ideal gas is $\alpha = 1/T$. What does this say about how a gas behaves as one heats it?

7. Show that the isothermal compressibility,

$$\kappa_T = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T,$$

for an ideal gas is $\kappa_T = 1/P$. What does this say about how a gas behaves under pressure?

8. Visit Stephanie Collins' legacy project on Joule-Thomson expansion (Fall 1998). Use what you learn there to show that the Joule-Thomson coefficient is zero for an ideal gas. What does this imply about an ideal gas. Note unfortunately the Joule-Thomson coefficient is given the symbol μ which we will also use as the symbol for chemical potential.

9. 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.

10. Start with the partition function for a container of rigid rods at high temperature. Based on what we did in class for a monatomic gas first guess what the molar internal energy should be. Then calculate the molar internal energy and molar heat capacity (C_{Vm}). Hint you will need the high temperature translational and rotational partition functions. Based on what we did in class for a monatomic gas what should U_m be f

11. Express the working equation for the internal energy of a Redlich-Kwang gas. Then calculate $\triangle U$ for an isothermal expansion of this gas from V_1 to V_2.

12. Derive K_a for the reaction $A + B \rightleftharpoons 2C$ by starting with the condition for equilibrium involving the chemical potentials of the reactants and products.

Conceptual Problems

13. Julie and Bor Yu are arguing over wether 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?

14. Consider a mixture of gas A and gas B where the molecules of both gas A and Gas B tend to attract themselves whereas the dominant interaction between different types of molecules is repulsion. If gas A and gas B are in a container which for time $t < 0$ there is a wall separating the two gases, then at time $t = 0$ the wall is removed; what is the final state of the system at time $t \gg 0$ if

    (a) the minimization of total energy was the sole determinant of a spontaneous change?

    (b) the maximization of entropy was the sole determinant of a spontaneous change?

    Describe what you would really expect the final state of the gas to be.

15. Give "word" definitions of internal energy, enthalpy, free energy and chemical potential.

16. Describe activity in your own words.
17. Discuss the idea of reference states in your own words.
18. Why is chemical equilibrium called a dynamic equilibrium?

Computer Problems

19. 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

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

and

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

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

Reflective Questions

20. Read the following excerpt from an essay entitled "The scientist as rebel" by Freeman Dyson. Freeman Dyson is a famous physicist known for many things but probably most famous for the Dyson series which gives a systematic program for calculations in quantum field theory. Do you agree that science in principle "belongs to everybody who is willing to make the effort to learn it"? Do you agree that science in actual practice "belongs to everybody who is willing to make the effort to learn it"? Do you think that scientists in the public eye are viewed as rebels? Dyson compares the scientist to poets. Do you think scientists have the same type of creativity as poets and other artists? Do you think the public perception of scientists is a one of viewing them as highly creative people?

> There is no such thing as a unique scientific vision, any more than there is a unique poetic vision. Science is a mosaic of partial and conflicting visions. But there is one common element in these visions. The common element is rebellion asgainst the restrictions imposed by locally prevailing culture, Western or Eastern as the case may be. The vision of science is not specifically Western. It is no more Western than it is Arab or Indian or Japanese or Chinese. Arabs and Indians and Japanese and Chinese had a big share in the development of modern science. And two thousand years earlier, the beginnings of ancient science were as much Babylonian and Egyptian as Greek. One of the central facts about science is that it pays no attention to East and West and North and South and black and yellow

and white. It belongs to everybody who is willing to make the effort to learn it. And what is true of science is also true of poetry. Poetry was not invented by Westerners. India has poetry older than Homer. Poetry runs as deep in Arab and Japanese cultures as it does in Russian and English. Just because I quote poems in English, it does not follow that the vision of poetry has to be Western. Poetry and science are gifts to all of humanity.

For the great Arab mathematician and astronomer Omar Khayýam, science was a rebellion against the intellectual constraints of Islam, a rebellion which Khayýam expressed more directly in his incomparable verses:

And this inverted bowl they call the sky,
Whereunder crawling cooped we live and die,
Lift not your hand to it for help, for it
As impotently rolls as you or I

For the first generations of Japanese scientist in the nineteenth century, science was a rebellion against their traditional culture of feudalism. For the great Indian physicists of this century, Raman, Bose and Saha, science was a double rebellion, first against English domination and second against the fatalistic ethic of Hinduism. And in the West too, great scientists from Galileo to Einstein have been rebels. Here is how Einstein himself described the situation:

> When I was in the seventh grade at Luitpold Gymnasium in Munich, I was summoned by my home-room teacher who expressed the wish that I leave the school. To my remark that I had done nothing amiss, he replied only, 'your mere presence spoils the respect of the class for me.'

Einstein was glad to be helpful to the teacher. He followed the teacher's advice and dropped out of school at age fifteen.

From these and many other examples we see that science is not governed by the rules of Western philosophy or Western methodology. Science is an alliance of free spirits in all cultures rebelling against the local tyranny that each culture imposes on its children. In so far as I am a scientist, my vision of the universe is not reductionist or anti-reductionist. I have no use for Westernisms of any kind. Like Loren Eiseley, I feel myself a traveller on a journey that is far longer than the history of nations and philosophies, longer even than the history of our species.

① $\frac{dy}{dx} = \frac{x}{y} \Rightarrow \int y\,dy = x\,dx \Rightarrow \frac{y^2}{2} = \frac{x^2}{2} + c$

② $\frac{dy}{dx} = \frac{y}{x} \Rightarrow \int \frac{dy}{y} = \frac{dx}{x} = \ln y = \ln x + c$

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

③ $\frac{dy}{dx} = (i\omega + \gamma)y \Rightarrow \int \frac{dy}{y} = (i\omega+\gamma)dx$

$\ln y = (i\omega+\gamma)x + c \qquad y = Ae^{(i\omega+\gamma)x}$

④ $dH = TdS + \cancel{VdP}^{\,0} \qquad dH = TdS = dq_{rev}$

$\Delta H = q$ reversible process at const. P.

⑤ from ④ $dH = dq_{rev}$ (Const P)

$dq = C\,dT \rightarrow (dq)_p = C_p\,dT$

so $dH = c_p dT \Rightarrow \left(\frac{dH}{dT}\right)_p = C_p \Rightarrow \left(\frac{\partial H}{\partial T}\right)_p = C_p$

⑥ $V = \frac{nRT}{P}$

$\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p \qquad \alpha = \frac{P}{nRT}\frac{\partial \frac{nRT}{P}}{\partial T} = \frac{\cancel{P}}{\cancel{nR}T}\frac{\cancel{nR}}{\cancel{P}} = \frac{1}{T}$ ✓

at cooler temps the gas expands at a faster rate with temperature than at hotter temps.

⑦ $K_T = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T = \frac{-P}{nRT}\left(\frac{-nRT}{P^2}\right) = \frac{1}{P}$ ✓

A ideal gas compresses under pressure

⑧ $\mu = \frac{\left(T\left(\frac{\partial V}{\partial T}\right) - V\right)}{C_p} = \frac{T\left(\frac{nR}{P}\right) - \frac{nRT}{P}}{C_p} = 0$ ✓

This means there is no temperature change in a JT process for an ideal gas. Most real gases cool upon expansion

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⑨ your derivation

⑩ Oxygen → translation, rotation and vibration.

$q = q_{trans}\, q_{rot}$

$q = \frac{V}{\Lambda^3}\frac{T}{2\theta_r} \qquad Q = q^N$

$U = -\frac{1}{Q}\frac{\partial Q}{\partial \beta} \xrightarrow{\text{mathematica}} U_m = \frac{5}{2}nRT$

$C_{Vm} = \frac{\partial U_m}{\partial T} = \frac{5}{2}nR$

⑪ $dU = c_V dT + \left[T\left(\frac{\partial P}{\partial T}\right)_V - P\right]dV$

R-K gas $\quad P = \frac{nRT}{V-nb} - \frac{n^2a}{\sqrt{T}\,(V-nb)}$

$\left[T\left(\frac{\partial P}{\partial T}\right)_V - P\right] = \frac{3n^2a}{2\sqrt{T}\,(V-nb)}$ mathematica

$dU = C_V dT + \frac{3n^2a}{2\sqrt{T}\,(V-nb)}dV$

Isothermal expansion

$\Delta U = \int_{V_1}^{V_2}\frac{3n^2a}{2\sqrt{T}\,(V-nb)}dV = \frac{3an^2}{2\sqrt{T}}\ln\frac{V_2-nb}{V_1-nb}$

⑫ $\mu_A + \mu_B = 2\mu_C \qquad \mu_i = \mu_i^\ominus + RT\ln a_i$

$\mu_A^\ominus + RT\ln a_A + \mu_B^\ominus + RT\ln a_B = 2\mu_B^\ominus + 2RT\ln a_C$

$\mu_A^\ominus + \mu_B^\ominus - 2\mu_C^\ominus = -RT\ln a_A - RT\ln a_B + RT\ln a_C^2$

$-\Delta\mu^\ominus = RT\ln\underbrace{\frac{a_C^2}{a_A a_B}}_{K_a}$

⑬ see last year's solution

⑭ see last year's solution

⑮ your words, ⑯, ⑰, ⑱ your words

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Temperature (K)	Internal Energy (kJ/mol)	Cv (J/mol*K)	delta U /delta T	Relative % error	Enthalpy (kJ/mol)	Cp (J/mol*K)	delta H /delta T	Relative % error
280	0.51873	75.661			0.52053	75.681		
290	1.2741	75.088	75.537	-0.597965	1.2759	75.423	75.537	-0.114
300	2.0277	74.406	75.36	-1.282155	2.0295	75.315	75.36	-0.045
310	2.7806	73.64	75.29	-2.24063	2.7825	75.29	75.3	-0.01
320	3.5336	72.806	75.3	-3.425542	3.5355	75.314	75.3	0.014
330	4.287	71.923	75.34	-4.750914	4.2888	75.37	75.33	0.04
340	5.0411	71.006	75.41	-6.202293	5.0429	75.453	75.41	0.043
350	5.7961	70.068	75.5	-7.752469	5.798	75.565	75.51	0.055
360	6.5525	69.122	75.64	-9.429704	6.5543	75.706	75.63	0.076

The $C_p = \frac{\Delta H}{\Delta T}$ equation works better for this data because it is constant pressure data.