

Problem Set PS11

ISSUED: 11/21/02 Due: 11/26/02

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.

Exercises

1. Work problems 4.2, 4.15, 4.16 and 4.17 from Laidler, Meiser and Sanctuary.
2. 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.
3. Read the attached pages from R. F. Bruinsma, "Physics of protein-DNA interaction" *Physica A*, **313**, 211, (2002). You can skip section 2.1.2 This is a proceedings article for a summer school on statistical physics, so it is acutally readable.
 - (a) Derive Eq. (2.4).
 - (b) Verify the numbers given for ΔG_0 in the paragraph following equation 7. (Hint: $v \simeq 1$).
 - (c) Explain where the firt line of Eq. (2.8) comes from and then show how one gets to the last line of Eq. (2.8).
 - (d) Verify that F in Eq. (2.8) is on the order of 10^{-2} .
 - (e) How is the $-T\Delta S$ term obtained from the calorimetry and free energy measurements?

Conceptual Problems

4. 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.

5. Why is chemical equilibrium called a dynamic equilibrium?

Reflective Questions

6. 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 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 against 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 Khayyám, science was a rebellion against the intellectual constraints of Islam, a rebellion which Khayyám 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 4.2

I	A	B	Y	Z
	x	3	0	0
C	-2	-2	2	2
E	x-2	1	2	2

$K = 0.1 = \frac{(2)(x)}{(x-2)(1)} \Rightarrow 0.1(x-2) = 4$

$0.1x - 0.2 = 4 \Rightarrow 0.1x = 4.2$

$x = 42 \text{ mol}$

4.15 $\frac{10.0 \text{ g HI}}{127.9 \text{ g/mol}} = 0.0782 \text{ mol HI}$

I	H ₂	I ₂	HI
	0	0	0.0782
C	x	x	-2x
E	x	x	0.0782 - 2x

$K_x = 65.0 = \frac{(0.0782 - 2x)^2}{x^2} \Rightarrow x = 0.007$

$X_{H_2} = \frac{0.007}{0.0782} = 0.009$
 $X_{I_2} = X_{H_2} = 0.009$
 $X_{HI} = 0.80$

4.16 ③ $\Delta G^\circ = -R \ln K = -2.303 \ln 2.14 \times 10^3 = 14.4 \text{ kJ}$

④

I	[D]	[M]	$2.14 \times 10^3 = \frac{(0.1-x)^2}{(x/2)} \Rightarrow x = 0.09$
	0	0.1	
C	$\frac{1}{2}x$	-x	[D] = 0.045 M
E	$\frac{1}{2}x$	0.1-x	[M] = 0.01

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4.17 $K_p = \frac{(0.4)^2(0.2)}{(0.6)^2} = 8.89 \times 10^{-2}$
 $\Delta G^\circ = R(3000) \ln 8.89 \times 10^{-2} = 60.4 \text{ kJ}$

② $N_A + N_B = 2N_C$
 $N_A^\circ + RT \ln a_A + N_B^\circ + RT \ln a_B = 2N_C^\circ + 2RT \ln a_C$
 $N_A^\circ + N_B^\circ - 2N_C^\circ = 2RT \ln a_C - RT \ln a_A - RT \ln a_B$
 $-\Delta \mu^\circ = RT \ln \frac{a_C^2}{a_A a_B}$
 K_x

③ ④ $R + DNA \rightleftharpoons R/DNA$
 $N_R + N_{DNA} = N_{R/DNA}$
 $N_R^\circ + RT \ln [R]V_R + N_{DNA}^\circ + RT \ln [DNA]V_{DNA} = N_{R/DNA}^\circ + RT \ln [R/DNA]V_{R/DNA}$
 $N_R^\circ + N_{DNA}^\circ - N_{R/DNA}^\circ = RT \ln \frac{[R][DNA]V_{R/DNA}}{[R]V_R [DNA]V_{DNA}} - RT \ln [R/DNA]V_{R/DNA}$
 ΔG°

$\Delta G^\circ = RT \ln \frac{[R/DNA]V_{R/DNA}}{[R]V_R [DNA]V_{DNA}}$

$\frac{\Delta G^\circ}{RT} = \ln \left(\frac{[R/DNA]}{[R][DNA]} \right) \left(\frac{V}{V} \right) \quad V = \frac{V_{R/DNA}}{V_{R/DNA}}$

$\frac{-\Delta G^\circ}{RT} = \ln \frac{[R][DNA]V}{[R/DNA]}$

$e^{-\frac{\Delta G^\circ}{RT}} = V \frac{[R][DNA]}{[R/DNA]} \Rightarrow \frac{1}{V} e^{-\frac{\Delta G^\circ}{RT}} = \frac{[R][DNA]}{[R/DNA]}$

b) $\Delta G^\circ = RT \ln K_{eq}$ Note ΔG° is defined as reactants - products

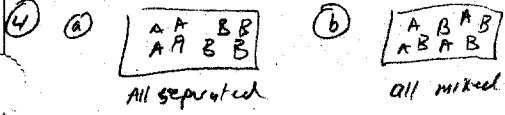
oper $\Delta G^\circ = RT \ln 10^{-10} = -23 \text{ kJ}$
 non op $\Delta G^\circ = RT \ln 10^{-4} = -9.2 \text{ kJ}$

c) $F = \frac{[R]}{[R] + [R/DNA]}$ [R] divided by total [R]
 $F = \frac{\frac{[DNA]}{[R/DNA]} [R]}{\frac{[DNA]}{[R/DNA]} [R] + [R/DNA]} = \frac{[R] \frac{[DNA]}{[R/DNA]} - K_{eq}}{\frac{[R] \frac{[DNA]}{[R/DNA]} + [R/DNA] \frac{[DNA]}{[R/DNA]}}{K_{eq}}}$

$F = \frac{K_{eq}}{K_{eq} + [DNA]}$

d) $F = \frac{10^{-4}}{10^{-4} + 10^{-2}} \approx \frac{10^{-4}}{10^{-2}} = 10^{-2}$

e) Calorimetry $\Delta H = \Delta Q$ ΔQ is measured
 Then $\Delta G = \Delta H + T\Delta S$
 $T\Delta S = \Delta G - \Delta H$



① Almost all mixed up but somewhat "clumpy"

② Reactants or dissolving products and product are going back to reactants at equilibrium, but there is no net change.

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