**Problem 1: Carbon** - First some definitions and numerical values:
1. Bi-directional exchange = two transports in opposite directions. Net exchange is smaller (or even 0).
2. Gt = gigaton = $10^9$ tons = $10^{12}$ kg
3. Earth radius = 6370 km = $r_e$
4. 70% of the surface of Earth is ocean
5. Mean ocean depth = 3.8 km
6. Atmospheric Mass = $P/g \times \text{Surface Area}$; $P = 10^5$ Pa
7. Molecular Mass of Air = 29 g /mole; Mass of CO$_2$ = $44/29 \times \text{(Mass of Atmosphere)} \times \text{(mixing ratio CO}_2\text{)}$ [see ticket].
8. Concentration of dissolved inorganic carbon in ocean water:
    - $[\text{CO}_2(aq)] = 0.03 \times 10^{-3} \text{ moles / kg}_\text{water}$
    - $[\text{HCO}_3^-] = 2.00 \times 10^{-3} \text{ moles / kg}_\text{water}$
    - $[\text{CO}_3^{2-}] = 0.10 \times 10^{-3} \text{ moles / kg}_\text{water}$
9. Earth's atmosphere is 21% O$_2$; 360 ppmv CO$_2$.

A budget for carbon for the preindustrial holocene is illustrated below (from Jacob, Atmospheric Chemistry). Units are Gt C for reservoir sizes and Gt C yr$^{-1}$ for fluxes.

A. Show that the estimate of 615 Gt for the atmospheric reservoir is consistent with what we understand the preindustrial CO$_2$ mixing ratio to be.
B. Taking the mass of the entire atmosphere as one unit, how many atmospheres of CO$_2$ are tied up in the sediments of Earth's crust (this is mostly limestone, CaCO$_3$ - shells of marine organisms)? Compare this number with CO$_2$ in the atmosphere of Venus. Venus has an atmosphere of nearly 100% CO$_2$ with P$_{\text{surface}} = 90$ bars, g = 9 m/s$^2$, R$_{\text{Venus}} = 6000$ km

C. Compare the mass of the terrestrial biosphere with the mass of O$_2$ in the atmosphere. If the entire biosphere burned, what reduction in O$_2$ would occur? Repeat the calculation assuming complete combustion of the fossil fuel reservoirs, estimated to be ~4000 Gtons C.

D. Current estimates predict a warming of ~3K for doubling CO$_2$. Assuming the climate forcing is proportional to $\sqrt{\text{[CO$_2$]}}$, what fraction of the ocean DIC would be required to be transferred to the atmosphere to produce the Cretaceous climate (~ 10 degrees warmer than today)? 40 degrees warmer (10$^9$ years ago)?

E. Equate the 60 Gt/year annual exchange between biosphere and atmosphere with mass of carbohydrate (C$_6$H$_{12}$O$_6$) per unit area per year, assuming only land areas are involved - i.e. what is the annual thickness of this "mulch", assuming the density is 0.1 g/cc?

Define "lifetime" of a molecule as the number of molecules in a reservoir divided by the total flux out of the reservoir (this equals the bi-directional flux into/out of reservoir at steady-state). For CO$_2$ exchanging with the biosphere, this is 615/60 = 10 years. What is the lifetime of oxygen exchanging with the biosphere?

F. Compare the 60 Gt/year exchange with the annual oscillation of atmospheric CO$_2$ (6 ppmv peak-to-trough) during the northern hemisphere. What does this tell us about the 'lifetime' of carbon fixed in the terrestrial biosphere? In the southern hemisphere, very little annual cycle is observed. Oceans make up much of the surface of this region. Exchange into the oceans, however, is not much smaller than into the terrestrial biosphere. What does this tell us about the lifetime of organic carbon in the surface ocean?

G. What fraction of the 60 Gt/year is due to human metabolism? Assume 5 billion people each consuming 0.5 kg of food (C$_6$H$_{12}$O$_6$) per day. H. What is the power (in Watts) of human metabolism? Assume food contains 4000 kcal/kg, where 1 kcal = 4.185 x 10$^3$ J. Assume our class room has no fresh air exchange during lecture. With 25 of us, estimate how much CO$_2$ will increase during 1 hour.

**Problem 2.** Sinks of atmospheric CO$_2$ deduced from changes in atmospheric O$_2$ [Problem from Jacob, Atmospheric Chemistry]

Measurement of the long-term trend in atmospheric O$_2$ has been used to
determine the fate of fossil fuel CO$_2$ in the atmosphere and the relative importance of uptake by the ocean and by the biosphere. Here is the principle of the method.

We first examine the O$_2$:CO$_2$ stoichiometry of the individual CO$_2$ sources and sinks.

A. The mean stoichiometric composition of fossil fuel burned is CH$_{1.6}$ (1 part carbon for 1.6 parts hydrogen). We view fossil fuel combustion as a stoichiometric reaction where CH$_{1.6}$ is oxidized by O$_2$ to yield CO$_2$ and H$_2$O. Show that 1.4 moles of O$_2$ are consumed per mole of CO$_2$ emitted by fossil fuel combustion.

B. How many moles of O$_2$ are produced per mole of CO$_2$ taken up by the biosphere?

C. Is any O$_2$ produced or consumed when CO$_2$ dissolves into the ocean?

We are now equipped to use the method. Observations from July 1991 to July 1994 (3 years) indicate a 3.2 ppmv increase in atmospheric CO$_2$ and a 8.8 ppmv decrease in atmospheric O$_2$. Global fossil fuel combustion during this period was 6.3x10$^{12}$ kg C yr$^{-1}$.

D. If fossil fuel were the only process affecting CO$_2$ and O$_2$ concentrations during the 1991-1994 period, by how much would these concentrations have changed?

E. From the observed trends of atmospheric CO$_2$ and O$_2$, determine the fraction of CO$_2$ emitted from fossil fuel combustion over the 3-year period that (a) was taken up by the biosphere, (b) dissolved in the oceans, (c) accumulated in the atmosphere.

[Source: Keeling, R.F., et al., Global and hemispheric CO$_2$ sinks deduced from changes in atmospheric O$_2$ concentrations, Nature, 381, 218-221, 1996.]