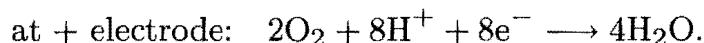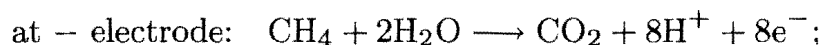Problems 5.5 (*20 marks – (a) to (d) five marks each*). Problem 5.16 (*20 marks*). Problem 5.32 (*20 marks – (a) to (d) five marks each*). Problem 5.17 (*40 marks – (a) to (d) 10 marks each*). Total 100 marks.
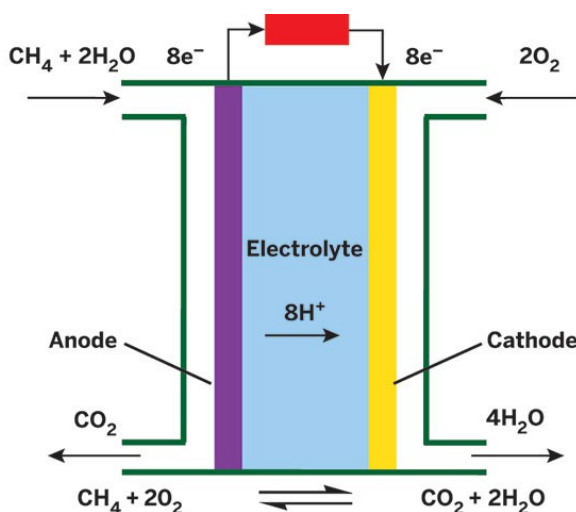
Problem 5.5. Consider a fuel cell that uses methane ("natural gas") as fuel. The reaction is

$$CH_4 + 2O_2 \longrightarrow 2H_2O + CO_2.$$
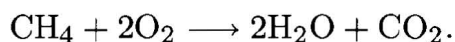
(a) Use the data at the back of this book to determine the values of ΔH and ΔG for this reaction, for one mole of methane. Assume that the reaction takes place at room temperature and atmospheric pressure.

(b) Assuming ideal performance, how much electrical work can you get out of the cell, for each mole of methane fuel?

(c) How much waste heat is produced, for each mole of methane fuel?

(d) The steps of this reaction are

$$at - electrode: \quad CH_4 + 2H_2O \longrightarrow CO_2 + 8H^+ + 8e^-;$$
$$at + electrode: \quad 2O_2 + 8H^+ + 8e^- \longrightarrow 4H_2O.$$

What is the voltage of the cell?

1

Problem 5.16. A formula analogous to that for $C_P - C_V$ relates the isothermal and isentropic compressibilities of a material:

$$\kappa_T = \kappa_S + \frac{TV\beta^2}{C_P}.$$

(Here $\kappa_S = -(1/V)(\partial V/\partial P)_S$ is the reciprocal of the adiabatic bulk modulus considered in Problem 1.39.) Derive this formula. Also check that it is true for an ideal gas.

Problem 5.32. The density of ice is 917 kg/m^3.

(a) Use the Clausius-Clapeyron relation to explain why the slope of the phase boundary between water and ice is negative.

(b) How much pressure would you have to put on an ice cube to make it melt at $-1°C$?

(c) Approximately how deep under a glacier would you have to be before the weight of the ice above gives the pressure you found in part (b)? (Note that the pressure can be greater at some locations, as where the glacier flows over a protruding rock.)

(d) Make a rough estimate of the pressure under the blade of an ice skate, and calculate the melting temperature of ice at this pressure. Some authors have claimed that skaters glide with very little friction because the increased pressure under the blade melts the ice to create a thin layer of water. What do you think of this explanation?

Problem 5.17. The enthalpy and Gibbs free energy, as defined in this section, give special treatment to mechanical (compression-expansion) work, $-P\,dV$. Analogous quantities can be defined for other kinds of work, for instance, magnetic work.[*] Consider the situation shown in Figure 5.7, where a long solenoid (N turns, total length L) surrounds a magnetic specimen (perhaps a paramagnetic solid). If the magnetic field inside the specimen is $\vec{B}$ and its total magnetic moment is $\vec{M}$, then we define an auxilliary field $\vec{\mathcal{H}}$ (often called simply the magnetic field) by the relation

$$\vec{\mathcal{H}} \equiv \frac{1}{\mu_0}\vec{B} - \frac{\vec{M}}{V},$$

where μ_0 is the "permeability of free space," $4\pi\times10^{-7}\,\mathrm{N/A^2}$. Assuming cylindrical symmetry, all vectors must point either left or right, so we can drop the $\vec{}$ symbols and agree that rightward is positive, leftward negative. From Ampere's law, one can also show that when the current in the wire is I, the $\mathcal{H}$ field inside the solenoid is NI/L, whether or not the specimen is present.

(a) Imagine making an infinitesimal change in the current in the wire, resulting in infinitesimal changes in B, M, and $\mathcal{H}$. Use Faraday's law to show that the work required (from the power supply) to accomplish this change is $W_{\text{total}} = V\mathcal{H}\,dB$. (Neglect the resistance of the wire.)

(b) Rewrite the result of part (a) in terms of $\mathcal{H}$ and M, then subtract off the work that would be required even if the specimen were not present. If we define W, the work done on the *system*,[†] to be what's left, show that $W = \mu_0\mathcal{H}\,dM$.

(c) What is the thermodynamic identity for this system? (Include magnetic work but not mechanical work or particle flow.)

(d) How would you define analogues of the enthalpy and Gibbs free energy for a magnetic system? (The Helmholtz free energy is defined in the same way as for a mechanical system.) Derive the thermodynamic identities for each of these quantities, and discuss their interpretations.
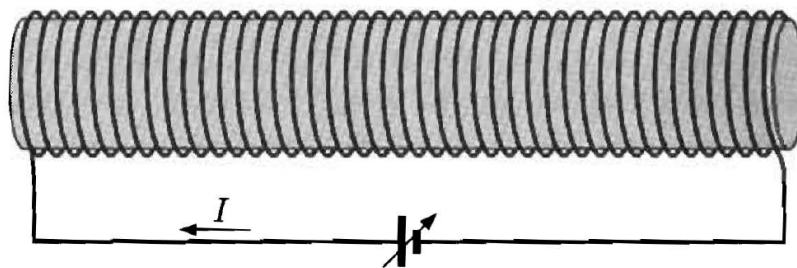

Figure 5.7. A long solenoid, surrounding a magnetic specimen, connected to a power supply that can change the current, performing magnetic work.