## Physics 313 Problem Set 7

## Important concepts from lectures 19-22

**Throttling** is an adiabatic (but not reversible) process where the pressure of a gas or fluid is lowered by passage through a throttling valve. This leads to an increase in volume. Enthalpy is constant in this process. In most gases, the average interaction between the particles is attractive; increasing the volume increases the average potential energy and decreases the kinetic energy, lowering the temperature.

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Helmholtz free energy $F = U - ST$

Gibbs free energy $G = U + PV - ST = H - ST$

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Under constant volume and temperature, the most work a system can do equals to the decrease is its Helmholtz free energy, F.

Under constant pressure and temperature, the most work a system can do equals to the decrease is its Gibbs free energy, G.

The reason why constant temperature is important is because heat is allowed to flow in and out of the system. Whether this makes the work a system can perform larger (heat flows in, helping) or smaller (heat flows out, wasted) depends on whether entropy of the system increases (heat flows in) or decreases (heat must flow out). (Draw yourself a diagram like the one in figure 5.6 if this is confusing.) The free energy automatically takes this into account.

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More thermodynamic identities:

$$dU = T\,dS - P\,dV + \mu dN, \quad \text{U=U(S,V,N)}$$

$$dH = T\,dS + V\,dP + \mu dN, \quad \text{H=H(S,P,N)}$$

$$dF = -S\,dT - P\,dV + \mu dN, \quad \text{F=F(T,V,N)}$$

$$dG = -S\,dT + V\,dP + \mu dN, \quad \text{G=G(T,P,N)}$$

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All sorts of partial derivative formulas can be derived from the above identities, by setting two of the variables constant and varying the third. For example, in G, keep T and N constant and vary P to obtain

$$\frac{\partial G}{\partial P}|_{T,N} = V$$

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Intensive quantities: stay the same when the system is doubled. Examples: T, P, $\rho$, $\mu$

Extensive quantities: double when the system is doubled. Examples: V, N, S, U, H, F, G

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$$\frac{\partial G}{\partial N}|_{T,P} = \mu \qquad \Rightarrow \qquad G = N\mu \quad \text{because both T and P are intensive}$$

## Problem Set

Due at the end of class, Wednesday November $5^{th}$ (late assignments will not be accepted).

**1.** Schroeder 4.22, pg 137.

**2.** **(a)** Schroeder 4.29, pg 140.
**(b)** How much does the entropy change? does the sign of the change make sense?

**3.** Schroeder 4.30, pg 141.

**4.** Consider the oxidation (burning) of glucose:

$$C_6H_{12}O_6 + 6O_2 \longrightarrow 6CO_2 + 6H_2O$$

This is what your body does to get energy out of sugar. Using the tables at the back of the book, calculate the useful work you get out of burning (metabolizing) 1 gram of sugar at room temperature and 1atm of pressure.

In the context of dietary science, it is assumed that one gram of sugar has 4 calories. Do you agree? (Recall that a dietary calorie is 1000 times bigger than an SI kcal.)

[See Schroeder 5.6 and 5.7 for more details on the metabolism of sugar.]

**5.** Schroeder 5.5, pg 155.

**6.** Schroeder 5.11, pg 158.

**7.** An engineer is working on the problem of rusting of bridge support poles under water. The bride foundation is very deep, at 80m. At this depth, the pressure is about 9atm. The temperature of the water varies from 5°C to 17°C. To study the thermodynamics of rusting, the engineer needs to know values of the Gibbs free energy of iron at these different pressures and temperatures, but all she has is the tiny data table at the back of Schroeder. (Her dog ate her handbook of Physics and Chemistry.) Let's see if we can help her.

**(a)** How much does the Gibbs free energy of 1 mole of iron at room temperature change for every 4atm increase in pressure? Explain why you need to assume that iron is basically incompressible.

**(b)** What is the entropy of 1 mole of iron at 1atm and 17°C? 5°C? (assume the heat capacity is independent of temperature, which is quite accurate).

**(c)** You can see from the previous question that while the entropy is not constant, it does not vary much (less than 10% over the range of interest). How much does G increase at fixed pressure when the temperature is decreased by 4°C?

**(d)** Using your answers to parts (a) and (c), make a table of the Gibbs free energy of one mole of iron as a function of temperature and pressure as follows

| | 1atm | 4atm | 9atm |
|---|---|---|---|
| 5°C | | | |
| 9°C | | | |
| 13°C | | | |
| 17°C | | | |

**(e)** BONUS Make the table above more accurate by taking into account the variability of entropy with temperature. Assume that the heat capacity is constant.

Extra practice: On Problem Set 5, Question 4, Part II, you studied the how the chemical potential changes with hight in air under the influence of gravity. If you want another way to look at it, read the discussion in Schroeder at the bottom of page 165, and try problem 5.22. This might be of particular interest to those of you who study the Earth's atmosphere.