

## Problem 1. Energy In Combustion

**Note:** This is one of the few places where one needs to work rather precisely to see the physics point. My rule of thumb is that an Avagadros number times an electron volt is 100 kJ. But, here should use a more accurate evaluation,  $N_A \cdot \text{eV} = 96.5 \text{ kJ}$ . In evaluating the numbers below you should keep to an accuracy of one part in a thousand,  $R = 8.314 \text{ J/K}\cdot\text{mol}$ .

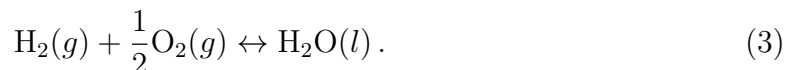
- (a) (Optional) Repeat the argument presented in class for the equation

$$dH = \delta Q_{\text{in}} + V dp \quad (1)$$

where  $H = U + pV$  represents the enthalpy. Enthalpy is particularly useful when the pressure is constant, leading to

$$dH = \delta Q_{\text{in}} \quad (2)$$

- (b) Consider the combustion of Hydrogen gas:



resulting in the formation of liquid water vapor. Tables of enthalpies for reactions are available in many books.

- (i) Look up the enthalpy of the products and reactants at 298 °K and standard pressure<sup>1</sup> in the accompanying data table. Determine the change in enthalpy,  $\Delta H^\circ$ , for each mole of  $\text{H}_2\text{O}$  produced.
- (ii) Consider the reactants as ideal gasses, and treat the liquid product  $\text{H}_2\text{O}$  as having negligible volume compared to the gasses. Calculate the heat released during the combustion and the change in internal energy,  $\Delta U^\circ = U_{\text{final}} - U_{\text{initial}}$ , per mole. (Ans:  $Q_{\text{out}} = 285.8 \text{ kJ}$  and  $\Delta U = -282.1 \text{ kJ}$ )

- (c) Consider the reaction at



at NTP, which is accompanied by a large release of heat. Using the enthalpy data tables, determine the energy of a bond between the two atoms in a  $\text{H}_2$  molecule in eV. (Ans:  $\Delta U = -433.5 \text{ kJ}$  and  $\Delta = 4.48 \text{ eV}$ .)

*Hint:* First use the enthalpy data tables to determine the enthalpy change and heat released during the reaction. Use this to find  $\Delta U$  for the reaction, treating all components as ideal gasses. The energy of a single  $\text{H}_2$  molecule is its kinetic energy (translational and rotational) and its potential (or binding) energies:

$$E_{\text{H}_2} = \text{KE} + \text{PE} = \text{KE} - \Delta \quad (5)$$

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<sup>1</sup>This temperature and pressure is the so-called Normal Temperature and Pressure (NTP) and denoted with a circle, i.e.  $T^\circ$ ,  $p^\circ$  and  $H^\circ$  denote the temperature, pressure, and enthalpy at NTP.

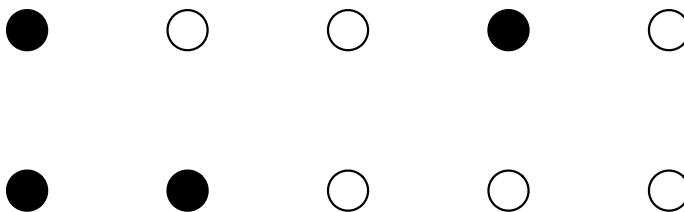
Here  $\text{PE} = -\Delta$  is the binding energy (i.e. the bond energy) of the two atoms. (The negative sign indicates that the energy is lower when the two atoms are bound compared to when they are unbound.  $\Delta$  is a positive value and is what we are trying to find.) The total energy  $U$  is the sum of kinetic and potential energies of the atoms. Use what we know about the kinetic energy of ideal gasses (both the mono-atomic and diatomic cases) to relate  $\Delta U$  for one mol of  $\text{H}_2$  produced to  $\Delta$ .

## Problem 2. Combinatorics and The Stirling Approximation

- (a) Consider one mole of atoms laid out in a row. The atoms can be in two states, a ground state, and an excited state.  $1/3$  of them are in the excited states. Using the Stirling approximation, show that the number of configurations with this number of excited states is approximately

$$\Omega = 10^{1.67 \times 10^{23}} \quad (6)$$

For instance, if the number of atoms is five, and the number of excited atoms (shown by the black circles) is 2, then two possible configurations are shown below.



- (b) Now repeat the calculation, but work with symbols rather than numbers. Assume there are  $N$  atoms laid out in a row. Assume that  $N_1$  of them are in the ground state, and  $N_2$  are in the excited state, with  $N_1 + N_2 = N$ . Show that the log of the number of configurations is

$$\ln \Omega = - \sum_{i=1,2} N_i \ln(N_i/N) \quad (7)$$

$$= N \sum_{i=1,2} -P_i \ln P_i \quad (8)$$

In the last step we have recognized that the  $P_1 = N_1/N$  is the probability that an atom will be in the ground state, and  $P_2 = N_2/N$  is the probability that an atom will be in the excited state.

**Discussion:** The log of the number of configurations  $\ln \Omega$  is known as the entropy of the system<sup>2</sup>. Then entropy per site, i.e.  $\ln \Omega/N$ , is given by

$$\frac{\ln \Omega}{N} = \sum_i -P_i \ln P_i \quad (9)$$

which is known as the Shannon formula for the entropy of a probability distribution. The importance of these things will become clearer as the course progresses.

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<sup>2</sup>Actually  $\ln \Omega$  is the entropy up to a conventional constant. For historical reasons the entropy is defined as  $k_B \ln \Omega$ , with  $k_B$  the Boltzmann constant. Similarly the entropy per site is defined only up to a conventional constant and later in the course we will respect tradition and take  $-k_B \sum_i P_i \ln P_i$  as the entropy per site.