

## Problem 1. Central Limit Theorem and Random Walk

In a random walk, a collegiate drunkard starts at the origin and takes a step of size  $a$ , to the right with probability  $p$  and to the left with probability  $1 - p$ .

- Take  $p = 1/2$ , i.e. equal probability of right and left steps. Determine the probability of the drunkard having position  $X$ , i.e.  $P(X)$ , after three steps. Plot  $P(X)$  where  $X$  can be one of  $X = 0, \pm 1, \pm 2, \pm 3$ . Note how your graph begins to approach a Gaussian after just three steps.
- Now keep  $p$  general. What is the mean and variance in the drunkard's position  $X$  after one step, and after two steps?
- After  $n$  steps (with  $n \gg 1$ ) find his mean position  $\langle X \rangle$ , and the std. deviation in his position  $\sigma_X = \sqrt{\langle \delta X^2 \rangle}$ . Check your result by comparing with the figure below

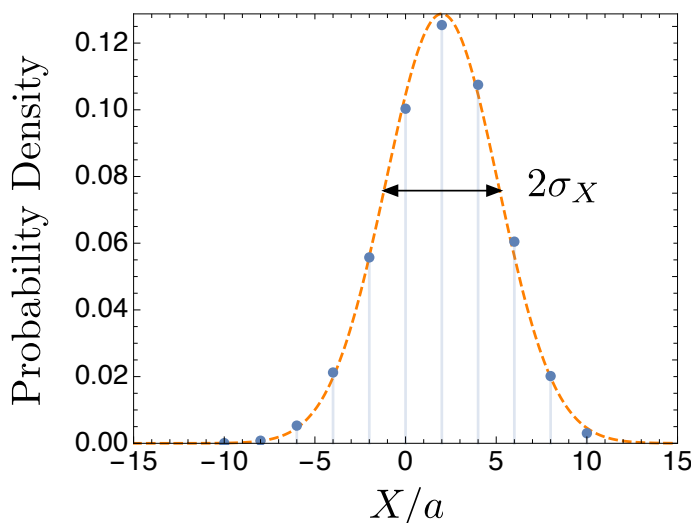


Figure 1: Probability of our drunkard having position  $X$  after  $n = 10$  steps (the blue points). Of course after 10 steps the drunkard will be between  $-10 \dots 10$ , and it is easy to show that he will be only at the even sites, i.e.  $-10, -8, -6, \dots 10$ . For  $p = 0.6$ , I find  $\langle X \rangle = 2.0$ . Twice the std deviation,  $2\sigma_X$ , is shown in the figure and is about six in this case. The orange curve is a gaussian (a.k.a the “bell-shaped” curve) approximation discussed in class and approximately agrees with the points – this is the central limit theorem. Recall that the central limit theorem says that if the number of steps  $n$  is large, the probability of  $X$  (a sum of  $n$  independent events) is approximately  $P(x) dX \propto \exp(-(X - \langle X \rangle)^2 / 2\sigma_X^2)$ . Evidently the gaussian approximation works well already for  $n = 10$ .

Hint:  $X$  is a sum  $N$  independent events  $x_i$  where  $x_i = \pm a$ . Use results from class on the probability distribution of a *sum* of independent events.

- (Optional. Don't turn in) If  $p$  is very nearly  $\frac{1}{2}$ , say  $p = 0.5001$ , determine how many steps it will take before the mean value  $\langle X \rangle$  is definitely different from zero. By

“definitely” I mean that  $\langle X \rangle$  is “more than two sigma” away from zero,  $\langle X \rangle > 2\sigma_X$ . If  $p = \frac{1}{2} + \epsilon$  (with  $\epsilon$  tiny), you should find (approximately) that

$$N_{\text{steps}} \simeq \frac{1}{\epsilon^2} \tag{1}$$

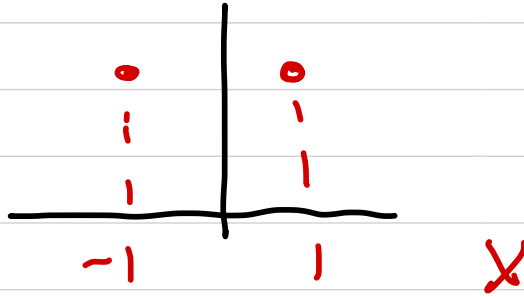
up to corrections of order  $\epsilon$ . Here  $p = \frac{1}{2} + \epsilon$  with  $\epsilon = 0.0001$ , how does the result scale with  $\epsilon$ , e.g. if I where two half  $\epsilon$  how would the number of required steps change?

# Random Walk

After 1 step :

$$P_1 = \frac{1}{2}$$

$$P_{-1} = \frac{1}{2}$$

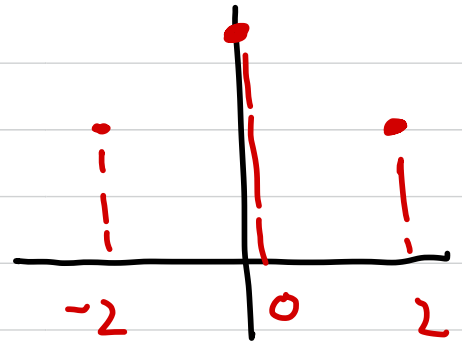


After 2 steps

$$P_2 = \frac{1}{2} \cdot \frac{1}{2} = \frac{1}{4}$$

$$P_0 = \frac{1}{2} \cdot \frac{1}{2} + \frac{1}{2} \cdot \frac{1}{2} = \frac{1}{2}$$

$$P_{-2} = \frac{1}{2} \cdot \frac{1}{2} = \frac{1}{4}$$



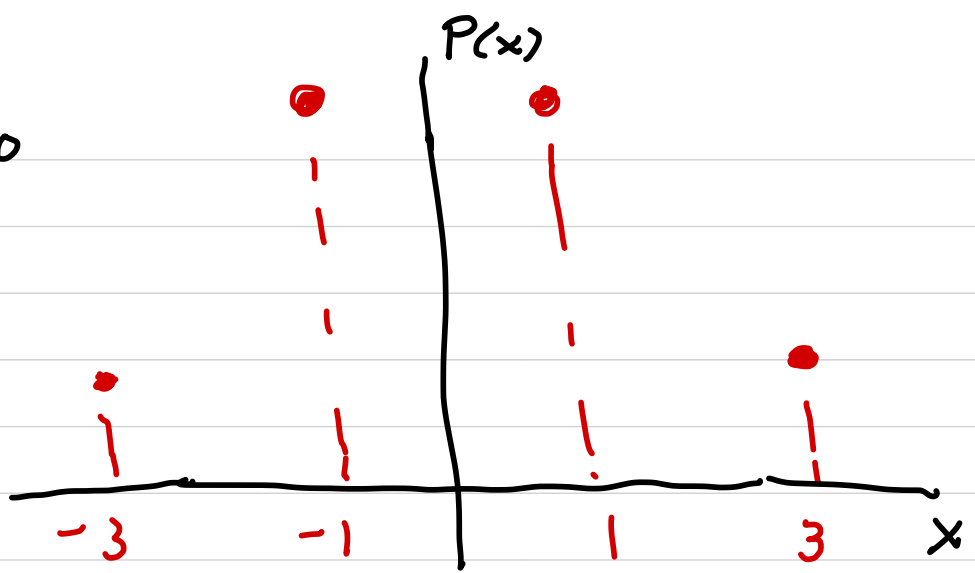
After 3 steps

$$P_3 = \frac{1}{4} \cdot \frac{1}{2} = \frac{1}{8}$$

$$P_1 = \frac{1}{4} \cdot \frac{1}{2} + \frac{1}{2} \cdot \frac{1}{2} = \frac{3}{8}$$

$$P_{-1} = \frac{3}{8}$$

$$P_{-3} = \frac{1}{8}, \text{ So}$$



b) The mean and variance for one step are:

$$\bar{X} = a p - (1-p) a = a(2p-1) = \bar{X}_1$$

$$\overline{X^2} = a^2 p + (1-p) a^2 = a^2 = \delta x^2$$

$$\langle \delta x^2 \rangle = \overline{X^2} - \bar{X}^2 = a^2 - a^2 (2p-1)^2$$

$$= a^2 (1 - (2p)^2 - 2(2p) + 1) = 4a^2 p(1-p)$$

Now the mean and variance add

$$\bar{X}_2 = 2 \bar{X} = 2a(2p-1)$$

$$\langle \delta X_2^2 \rangle = 2 \langle \delta x^2 \rangle = 8a^2 p(1-p)$$

two steps  
are twice  
one step

c) Now for part (c)

$$\bar{X}_N = N a (2p - 1)$$

For  $N=10$   $p=0.6$   $\bar{X}_N = 10 (2 \cdot 0.6 - 1) = 2$

This clearly agrees with the figure which is centered at  $X/a = 2$

Similarly we compute the variance

$$\langle \delta X_N^2 \rangle = 4N a^2 p(1-p) \quad \text{for } N=10 \quad p=0.6$$

we find  $\langle \delta X_N^2 \rangle \approx 9.6$  so  $\sigma \equiv \sqrt{\langle \delta X^2 \rangle} \approx 3.1$

Comparison with the graph gives  $2\sigma \approx 6.2$  which seems about right.

d) The mean is  $Na(1-2p) = \langle X \rangle$ . The standard deviation is  $\sigma_X = \sqrt{N} 2a(p(1-p))^{1/2}$ . Requiring that  $\langle X \rangle > 2\sigma_X$  gives

$$N(1-2p) > 2\sqrt{N} (4p(1-p))^{1/2}$$

Solving for  $N$  we have

$$N > \frac{16 p(1-p)}{(1-2p)^2}$$

So for  $p = 1/2 + \varepsilon$ , we have

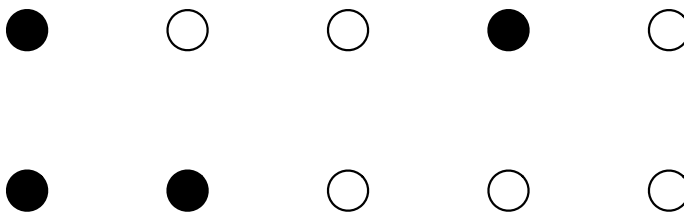
$$N > \frac{16 \cdot \frac{1}{2} (1 - \frac{1}{2})}{(2\varepsilon)^2} \approx \frac{1}{\varepsilon^2}$$

## Problem 2. Combinatorics and The Stirling Approximation

- (a) Consider a chain of  $6 \times 10^{23}$  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

$$\Omega = 10^{1.67 \times 10^{23}} \quad (2)$$

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 work analytically. 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

$$\ln \Omega = - \sum_{i=1,2} N_i \ln(N_i/N) \quad (3)$$

$$= N \sum_{i=1,2} -P_i \ln P_i \quad (4)$$

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. If you get stuck, look in the course notes.

**Discussion:** The log of the number of configurations  $\ln \Omega$  is known as the entropy of the system<sup>1</sup>. Then entropy per site, i.e.  $\ln \Omega/N$ , is given by

$$\frac{\ln \Omega}{N} = \sum_i -P_i \ln P_i \quad (5)$$

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>1</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.

## Combinatorics and Stirling

- The number of selections is

$$N_A C_r = \frac{N_A!}{\left(\frac{1}{3}N_A\right)! \left(\frac{2}{3}N_A\right)!} \quad \text{with } r \equiv \frac{1}{3}N_A$$

- Taking the log

$$\log N_A C_r = \log N_A! - \log \left( \left(\frac{1}{3}N_A\right)! \right) - \log \left( \left(\frac{2}{3}N_A\right)! \right)$$

$$= N_A \log N_A - N_A - \left( \frac{1}{3}N_A \log \left( \frac{1}{3}N_A \right) - \frac{1}{3}N_A \right)$$

$$- \left( \frac{2}{3}N_A \log \left( \frac{2}{3}N_A \right) - \frac{2}{3}N_A \right)$$

$$= -\frac{1}{3}N_A \log(3) + \frac{2}{3}N_A \log\left(\frac{3}{2}\right)$$

$$= \frac{N_A}{3} \log\left(\frac{27}{4}\right) = 0.64 N_A$$

- $S_0$

$$N_A C_r = e^{0.64 N_A} = (e^{\log 10})^{0.64 N_A / \log 10}$$

$$= 10^{0.64 N_A / \log 10} \approx 10^{1.66 \times 10^{23}}$$

## Combinatorics Continued:

$$\Omega = \frac{N!}{N_1! N_2!}$$

So

$$\ln \Omega = \ln N! - \sum_{i=1,2} \ln N_i!$$

Then using sterling  $\ln N! = N \ln N - N$

$$\ln \Omega = N \ln N - \cancel{N} - \sum_i N_i \ln N_i - \cancel{N_i}$$

use  $N = \sum N_i$       use  $N = \sum N_i$

So

$$\ln \Omega = \sum_i N_i (\ln N - \ln N_i)$$

$$\ln \Omega = \sum_i -N_i \ln N_i / N$$

or pulling out  $N$  and with  $p_i = N_i / N$

$$\ln \Omega = N \sum_i -p_i \ln p_i$$



### Problem 3. Parametrizing the EOS

The pressure as a function of temperature and volume,  $p(T, V)$ , or equivalently the volume as a function of temperature and pressure  $V(T, p)$ , is an important physical observable. Recall that its changes are parameterized by the measurables  $\beta_p$  and  $\kappa_T$ . Consider an ideal gas at temperature  $T$  with  $N$  particles

- (a) Explain the physical meaning of the thermal expansion coefficient  $\beta_p$  and isothermal compressibility  $\kappa_T$ , and compute them for an ideal gas.

The first items only involved the EOS,  $p(T, V)$ . The next items also involve the energetics, so the specific heat and adiabatic index play a role. Assume that  $U = c_0 T$  with  $c_0$  a constant

- (b) What is  $c_0$  for a mono-atomic ideal gas? What about a diatomic ideal gas?
- (c) Write down the specific heats  $C_p$  and  $C_v$  for a mono-atomic and diatomic gas and determine  $\gamma$ .
- (d) In class we said that for a general substance (and not necessarily an ideal gas) the specific heats  $C_p$  and  $C_V$  are related by a formula which we will prove in full generality only later:

$$C_p = C_V + \frac{VT\beta_p^2}{\kappa_T}. \quad (6)$$

For an ideal gas (and one mole of substance) we have the following special case of this formula:

$$C_p = C_V + Nk_B. \quad (7)$$

Or

$$C_p^{1\text{ml}} = C_V^{1\text{ml}} + R \quad (8)$$

Show that Eq. (8) follows from Eq. (6) together with the results from parts (a).

- (e) The *adiabatic* compressibility  $\kappa_S$  is defined by<sup>2</sup>

$$\kappa_S \equiv \frac{-1}{V} \left( \frac{\partial V}{\partial p} \right)_{\text{adiab}} \quad (10)$$

This “*adiab*” means that as we change the pressure, the volume and temperature change, so that no heat flows,  $dQ = 0$ . Show for an ideal gas that

$$\kappa_S = \frac{\kappa_T}{\gamma} \quad (11)$$

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<sup>2</sup>The suffix  $S$  means adiabatic,  $dQ = 0$ . We will see that  $dQ$  is related to the change in entropy  $S$ ,  $dS = dQ/T$ . So  $S$  suffix means at fixed entropy.

$$\kappa_S \equiv \frac{-1}{V} \left( \frac{\partial V}{\partial p} \right)_S \equiv \frac{-1}{V} \left( \frac{\partial V}{\partial p} \right)_{\text{adiab}} \quad (9)$$

We will show later that this result is not limited to an ideal gas.

*Hint:* You will need to recall that in an adiabatic change of pressure and volume, we have  $pV^\gamma = \text{const}$  for an ideal gas.

- (f) As discussed in class, the speed of sound is related to the compressibility<sup>3</sup>

$$c_s = \sqrt{\frac{B_S}{\rho}} \quad (12)$$

where the bulk modulus

$$B_S \equiv -V \left( \frac{\partial p}{\partial V} \right)_{adiab} \equiv \frac{1}{\kappa_S} \quad (13)$$

serves as a kind of spring constant for the material, and  $\rho$  is the mass per volume. Air is made of diatomic molecules, primarily (78%) diatomic nitrogen  $N_2$ . Determine the speed of sound of  $N_2$  gas at  $20^\circ C$  treating using only the ideal gas constant  $R$  and the fact that a nitrogen atom consists of 7 protons and 7 neutrons. Compare with the nominal value for the speed of sound in air. You should find favorable agreement.

- (g) The frequency of the tuning note (A440) in the orchestra is 440 Hz. Explain qualitatively why it is the adiabatic compressibility  $\kappa_S$ , and not the isothermal one  $\kappa_T$  which is relevant for the speed of sound, by comparing the time scales of oscillation with a typical time scale for heat conduction.

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<sup>3</sup>I will not derive this. A good derivation at your level is given [here](#). Unfortunately, this derivation uses the symbol  $\kappa$  for  $B_S$ , which for us (and indeed almost everyone) is  $1/\kappa_S$ !

## Parametrizing the EOS

a) For the meaning see lecture. I explained them as well as I could there! Now  $V = NKT/p$

$$\beta_p = \frac{1}{V} \left( \frac{\partial V}{\partial T} \right)_p = \frac{1}{V} \left( \frac{\partial}{\partial T} \right)_p \left( \frac{NKT}{p} \right) = \frac{NK}{p} \frac{1}{V} = \frac{1}{T}$$

$$\kappa_T = -\frac{1}{V} \left( \frac{\partial V}{\partial p} \right)_T = -\frac{1}{V} \left( \frac{\partial}{\partial p} \right)_T \left( \frac{NKT}{p} \right) = \frac{1}{\left( \frac{NKT}{p} \right)} \left( -\frac{NKT}{p^2} \right) = -\frac{1}{p}$$

b) Then

$$U = \frac{3}{2} NKT \quad \text{MAIG}$$

$$U = \frac{5}{2} NKT \quad \text{DAIG}$$

c)  $C_V = \left( \frac{\partial U}{\partial T} \right)_V = \frac{3}{2} NK \quad \text{MAIG}$

$$C_V = \left( \frac{\partial U}{\partial T} \right)_V = \frac{5}{2} NK \quad \text{DAIG}$$

$$C_p = C_V + NK \quad \text{All ideal gasses}$$

$$C_p = \frac{5}{2} NK \quad \text{MAIG}$$

$$C_p = \frac{7}{2} NK \quad \text{DAIG}$$

So

$$\gamma = C_p / C_v = 5/2 / 3/2 = \frac{5}{3} \quad \text{MAI 6}$$

$$\gamma = C_p / C_v = 7/2 / 5/2 = \frac{7}{5} \quad \text{DAI 6}$$

d)

$$C_p = C_v + TV \frac{\beta_p^2}{\kappa_T}$$

Now

$$V = \frac{NKT}{P} \quad \beta_p = \frac{1}{T} \quad \kappa_T = \frac{1}{P}$$

So

$$C_p = C_v + T \left( \frac{NKT}{P} \right) \frac{P}{T^2}$$

$$C_p = C_v + NK$$

e)  $C_p$  is larger than  $C_v$  because for the same change in temperature,  $dT$ , you must add more heat; since some of the thermal energy is being used for mechanical work as the gas expands to keep the pressure constant

Basically in a solid or liquid the coefficient  $\beta_p$  is small. Does a solid expand by much when you heat it? In a gas the system expands a lot when heated.

Compare

$\beta_p \approx 1 \times 10^{-4} \text{ } ^\circ\text{K}^{-1}$  mercury  $\leftarrow$  this is one of the liquids with the largest  $\beta_p$ !

$\beta_p \approx 3 \times 10^{-3} \text{ } ^\circ\text{K}^{-1}$  gas

$\beta_p \text{ gas} \approx 30 \beta_p \text{ mercury}$

f) We have for an adiabatic expansion  $Q=0$

$$pV^\gamma = \text{const}$$

So

$$V^\gamma dp + p\gamma V^{\gamma-1} dV = 0$$

$$dp + \gamma \frac{p}{V} dV = 0$$

So we find

$$-\frac{1}{V} \left( \frac{dV}{dp} \right) = \frac{1}{p\gamma}$$

adiab

We had for an ideal gas we had from (a)

$$\frac{1}{p} = \kappa_T$$

So

$$\kappa_S = \frac{\kappa_T}{\gamma}$$

In air we have

78%  $N_2$

22%  $O_2$  ← We will neglect  $O_2$  and consider  $N_2$  gas.

So

$$C_s = \left( \frac{B_s}{P} \right)^{1/2} = \left( \frac{1}{K_s P} \right)^{1/2} = \left( \frac{\gamma}{K_T P} \right)^{1/2}$$

$$= \left( \frac{\gamma P}{P} \right)^{1/2} = \left( \frac{\gamma N_A K T}{V_P} \right)^{1/2} \quad V_P = m N$$

$$C_s = \left( \frac{\gamma K T}{m} \right)^{1/2}$$

$$\gamma = \frac{7}{5} \leftarrow \text{Diatomic!}$$

$$m = 28 m_p \leftarrow N_2 \text{ has } 28 \text{ nucleons}$$

So

$$C_s = \left( \frac{\gamma N_A K T}{28 N_A m_p} \right)^{1/2}$$

A nucleon is either a proton or a neutron.

$$C_s = \left( \frac{\gamma}{28} \frac{R T}{1g} \right)^{1/2} = \left( \frac{7/5}{28} \frac{8.32 J/K}{0.001kg} 293^\circ K \right)^{1/2}$$

$$C_s = 349 \text{ m/s}$$

For comparison in  $O_2$  gas we have

$$C_s \approx 327 \text{ m/s}$$



## Problem 4. Energy In Combustion

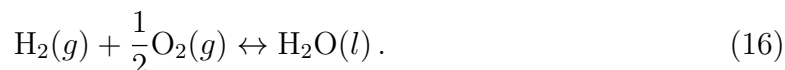
- (a) (Optional, but encouraged) Repeat the argument presented in class for the equation

$$dH = \delta Q_{\text{in}} + V dp \quad (14)$$

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

$$dH = \delta Q_{\text{in}} \quad (15)$$

- (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>4</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 energy,  $\Delta U^\circ = U_{\text{final}} - U_{\text{initial}}$ , per mole.
- (c) Consider the reaction at



at NTP, which is accompanied by a large release of heat. Using the enthalpy data, determine the energy of a bond between the two atoms in a  $\text{H}_2$  molecule in 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 energies:

$$E_{\text{H}_2} = \text{KE} + \text{PE} = \text{KE} - \Delta \quad (18)$$

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  $\Delta$ .

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<sup>4</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.



## Combustion

a) See lecture

b) Looking in the tables  $\Delta_f H$  for  $H_2O$  is  $H_f = -285.8 \text{ kJ}$  per mole, while  $H_2$  and  $O_2$  have  $\Delta_f H = 0$ . So

$$\Delta H = -285.8 \text{ kJ} < 0$$

Now  $\Delta H = Q_{in}$  at constant pressure so

$$Q_{out} = 285.8 \text{ kJ}$$

★ To determine  $\Delta U$  we need the work

$$\Delta U = Q_{in} - W_{out} \quad \text{small}$$

$$= Q_{in} - P_0 (\cancel{V_{H_2O}} - V_{H_2} - V_{1/2 H_2O})$$

Now

$pV = n_m RT$  so  $n_m = 1/2$  for  $O_2$  and thus

$$-W_{out} = \underbrace{RT}_{\text{from } H_2} + \underbrace{\frac{1}{2} RT}_{\text{from } O_2} = \frac{3}{2} RT \approx (1.5) (8.32 \frac{J}{mol \cdot K}) (298 K) = 3.7 \text{ kJ}$$

So

$$\Delta U = Q_{in} - W_{out} = -285.8 \text{ kJ} + 3.7 \text{ kJ}$$

$$\Delta U = -282.1 \text{ kJ}$$

note the work is small compared to heat, here.

c) Then using the data tables

$$\Delta H = -436 \text{ kJ} = Q_{in}$$

this is for 1 mol of  $H_2$

The explanation was given in the tables.

Now

$$\Delta U = Q_{in} - p_0 (V_{H_2} - 2V_{H_2})$$

$$\text{So } pV = n_m RT \text{ so}$$

again this is small

$$-W_{out} = \underbrace{-RT}_{1 \text{ mol } H_2} + \underbrace{2RT}_{2 \text{ mol } H} = RT = 2.47 \text{ kJ}$$

So

$$\Delta U = Q_{in} - W_{out} = -436 \text{ kJ} + 2.5 \text{ kJ} = -433.5 \text{ kJ}$$

Now

$$\circ \quad \Delta U = KE_f + PE_f - (KE_i + PE_i)$$

$$= \underbrace{\frac{5}{2} N_A kT}_{\text{one mole of diatomic gas}} + PE_f - \underbrace{2 \frac{3}{2} N_A kT}_{\text{2 moles of monoatomic gas}}$$

$$= -\frac{1}{2} RT + PE_{\text{final}}$$

$$\text{or } PE_{\text{final}} = \Delta U + \frac{1}{2} RT = -433 \text{ kJ} + 1.2 \text{ kJ} = -432.3 \text{ kJ}$$

This is for one mole of  $H_2$ . Using  $N_A \text{ eV} = 96.5 \text{ kJ}$

$$PE_f = -N_A \Delta = -432.3 \text{ kJ} \quad \Delta = 4.48 \text{ eV}$$