Study guide – thermodynamics (2013 version)

These are mostly concept questions and/or memorizing questions. You have also to be able to solve numerical problems. The assignment of quizzes and exams may differ in a given year for the list below.

Based on the textbook "Physical Chemistry" of T. Engel and P. Reid.

Class 1 - intro

- What is the definition of thermodynamics?
- What are the units of pressure?
- How is pressure defined in mechanics?
- What is an open and closed system?
- What is an extensive and intensive property?
- What is the most basic way to define temperature?
- What is the 0^{th} law of thermodynamics?
- What is Boyles experiment?
- How to measure temperature?
- How does a gas thermometer look like?

Class 2 – gas laws

- How do model systems in thermodynamics look like?
- What are open, closed, isolated model systems?
- What walls may these model systems have?
- An ideal gas is the "fuel" in thermodynamics. We fill the model system (box) with that fuel. What is the definition of an idea gas?
- Illustrate the laws of Boyle, Gay-Lussac, Charles, Avogadro? (Images, equations)
- How to derive the general ideal gas equation?
- Design a simple thought experiment to illustrate one of the gas laws.
- Boyles law does not work for NO2, for example. Why?
- Is it wise to mount a N2 gas cylinder close to a wall heater in a lab? Dangerous? Harmless? Why?
- What assumptions of an idea gas are dropped when considering a real gas?
- What is the difference of an ideal and a real gas?
- What is the van der Waals equation all about?
- What corrections on the ideal gas equation are used to set up the van der Waals equation?
- How to quantify how ideal an ideal gas is?
- What is a compression factor for a gas?
- All gases are idea for zero pressure. Correct? Wrong? Why?

Class 3 – 1^{st} law (heat, work, internal energy, state functions, rev/irreversible)

- Write down the most general version of the 1^{st} law of thermodynamics and briefly discuss it (1-2 sentences).
- Write down a more practical version of the 1^{st} low of thermodynamics.
- What sign definition is used for work and heat?
- How is "heat" defined in thermodynamics?
- Is work done by the system on the surroundings positive or negative?
- Work done reversibly or irreversibly is always identically. Correct/wrong? Why?

- Consider the compression of a gas. The work for a reversible process is larger than the one of a irreversible pathway? Correct/wrong?
- Define a reversible process.
- What is a state function?
- Calculate the maximum work for the compression of an idea gas. Use the general ideal gas equation.
- Consider a temperature change of a system. The amount of heat required to change the temperature is always the same. Correct/wrong? Why?
- What is an exact differential?
- Is work a state function? Yes/no? Why?
- Is dq an exact differential?

Class 4 – applications of 1st law and enthalpy

- The maximum work is associated with a reversible process. Correct/wrong? Why?
- Use a simple example to discuss the difference between a reversible and irreversible process.
- What is the definition of the enthalpy?
- At constant pressure the enthalpy change equals what?
- At constant volume the internal energy change equals the heat put in the system. Correct/wrong? Why?
- The internal energy change and enthalpy change are always identically. Correct/wrong? Why?
- Illustrate a process here the enthalpy change is zero.
- What is the change of internal energy for an ideal gas for a constant temperature process?
- Potassium and water react at constant pressure. Is the enthalpy change larger than the internal energy change? What is your guess? Why?
- Consider a cyclic process. What is the change of the enthalpy?
- When is the enthalpy change smaller than the change of the internal energy?

Class 5 – heat capacity

- What is the definition of the heat capacity?
- What is the idea behind that definition? In other words, spell out/write down in one sentence the definition of the heat capacity.
- Name a practical application that required to know the heat capacity of a system.
- The heat capacity is an extensive property?
- How is the heat capacity measured? (In the simplest case.)
- What is a typical numerical value for the heat capacity of a solid, liquid, or gas?
- Heat capacity at constant volume is related to the enthalpy change. Correct/wrong? Why?
- Would you use a constant volume or constant pressure calorimeter to determine the enthalpy change of a combustion reaction?
- What is the difference of Cp and Cv for an ideal gas.

- Is there a connection of thermodynamics and quantum mechanics when considering the energy density of a system.
- Can you predict the heat capacity if you know the molecular structure of molecules?
- What is more energy efficient an empty or filled refrigerator?
- Would you open the door of your freezer to cool down your house?

Class 6 – Quiz 1 – will cover classes 1-5.

Class 6 – adiabatic gas expansion

- Define adiabatic.
- List examples and/or practical applications of adiabatic gas expansions.
- Compare the general ideal gas equation and the adiabat equation (adiabatic equation).
- Check out the internet and find something interesting about adiabatic expansions.
- How does the temperature change in an adiabatic expansion and adiabatic compression of an ideal gas?
- Plot qualitatively the pressure vs. the volume for an adiabatic and isothermal expansion. Discuss the graph. Distinguish an expansion and compression.
- What about real gases? If you expand a real gas at room temperature does it cool down or heat up?

Class 7 – summary chapter 2 & some more examples

Class 8 - 10 – formal thermodynamics, materials parameters

- What are state functions and path functions? Use a mathematical expression to answer that question.
- Does heat has an exact differential?
- What is an exact differential?
- Calculate the total differential of the function f(V,T) = RT/V
- What is the geometrical interpretation of a partial derivate and a total differential?
- The total differential of P can be written using the expansion coefficient and the compressibility. What are these?
- We have seen before that $\Delta H = q_p$ and $\Delta U = q_v$. Derive these equations from the total differential of U.
- What are the materials parameters in thermodynamics?
- C_p and C_v can be correlated using thermodynamics parameters.
- What is an internal pressure?
- How large is the internal pressure for an ideal gas?
- Write down the total differential of the internal energy.
- How does the total differential of the enthalpy look like?
- The state of a gas is described by P, V, and T. Why is the internal energy, for example, given by a total differential of only two parameters? What about the third parameter?
- Is there any practical application of the total differential procedure?

- What is the difference between C_V and C_P is a general case?

Class 11 & 12 – Joule-Thompson Experiment

- You are stranded on an island and would like to enjoy a cool drink here and then. How would you design the ice machine?
  → http://www.youtube.com/watch?v=JLQ03qCPGzI
- How does a simple model system for the air liquefying machine looks like?
- What is an isenthalpic process?
- Calculate the enthalpy change of a Joule-Thompson experiment.
- You just need to expand H_2 adiabatically and it cools down. Correct?/Wrong?/Why?
- Why is a Joule-Thompson coefficient useful?
- That coefficient is zero for an ideal gas. Correct?/Wrong?/Why?

Class 13

- Chapter 3 summary

Class 14 – Quiz 2 – will cover classes 6-13. Cheat sheet only for midterms.

Class 14 – Thermo chemistry

- What is the purpose of "thermochemistry"?
- What is an exothermic reaction?
- What is an endothermic reaction?
- What is the standard enthalpy of formation?
- When does the enthalpy change equal heat?
- What is the idea of the procedure to obtain the standard enthalpy of formation for a reaction by combusting all reactant and products of that reaction?
- What is the Hess law?
- What is the difference of the "standard enthalpy of a reaction" and "standard enthalpy of formation"?

Class 15 – Temperature dependence of enthalpies, bond energies.

- What is the purpose of Kirchhoff's law?
- Develop Kirchhoff's law.
- Look at examples given in class.
- What is a bond energy/enthalpy?
- What is the difference between a bond energy and bone enthalpy?

Class 16 – Calorimeters quantitative

- Explain how a constant volume calorimeter experiment works.
- How to you calibrate a constant volume calorimeter?

- Why is a constant pressure calorimeter used for liquids and solids?
- Why is the total ΔU and ΔH zero for constant volume and constant pressure calorimeters, respectively?
- How to determine the measuring error in a constant volume experiment? Write down the equation of the error propagation.
- How does a differential scanning calorimeter work?
- What is a latent heat?

Class 17 – First midterm. The midterm will cover classes 1 to 16.

Class 18 – Entropy & 2nd law

- Who is Mr. Entropy?
- What are the 0th and 1st laws of thermodynamics?
- Would a water drop in your hands spontaneously forming an ice cube violate the 1st law?
- What definition of the entropy do you know?
- What is a micro state?
- What is a thermodynamic probability?
- What is Boltzmann's formula?
- Calculate the entropy change for an isothermal expansion of an ideal gas.
- How large is the probability for a spontaneous reversal of the gas expansion?

Class 19 – Carnot cycle, entropy & 2nd law

- Write down the most abstract version of the 2nd law you know.
- Write down a practical version of the 2nd law.
- What is a perpetuum mobile?
- What is a heat engine?
- Calculate the efficiency of a heat engine. Use the simplest approach.
- Describe a Carnot cycle. Sketch the cycle. Name each step.
- Why does the inscribed area in a PV cycle equals the work done by the system on the surroundings?
- Remember the sign definitions for heat and work.
- How was heat defined again? Is there a "cold" in thermodynamics?

Class 20 – Analyzing a Carnot cycle

- Are there any steps with $\Delta U=0$ in the Carnot cycle/ if yes, what steps?
- In what steps of the Carnot cycle is heat transferred? Why? What is the effect of the heat transfer?
- Write the efficiency of that cycle using temperatures only and heats only?
- Remember the equation and interpretation of an isothermal expansion/compression.
- What does the 1st law look like again?

- Definition of heat capacities?

Class 21 – Entropy and Carnot

- Suggest and invention that would violate the 2nd law.
- Why does calculating the efficiency of a heat engine results in the discovery of a new state function (entropy).
- What is the Clausius inequality?
- Calculate the entropy change for a reversible isothermal expansion.
- How to calculate the entropy change of a irreversible process.
- Calculate the entropy change for a reversible and constant volume process.

Class 22 – Entropy and 2nd law

- What versions of the 2nd law do your know.
- Go back and remember how we started the entropy discussion. What different views exist to define or calculate entropy changes?
- What is the connection of the Carnot engine and the entropy?
- How large is the entropy change of the universe for a reversible, isothermal gas expansion?
- What about an irreversible expansion?
- Consider a reversible and irreversible gas expansion. Show that $w_{irr} < w_{rev}$. Next, how large is the entropy change? Compare that entropy change with q_{irr}/T

Class 23 – Quiz 3 – will cover classes 18-22. Cheat sheet only for midterms.

Class 23 – Entropy examples

Class 24 – 3rd law of thermodynamics

- Write a list of all laws in thermodynamics that fits on the backside of a business card.
- There are at least 4 common versions of the 2nd law. How do these look like?
- What is the reference point of the entropy at zero Kelvin?
- Why can we measure absolute entropies but not absolute enthalpies?
- Familiarize yourself with the properties of the entropy. The power point includes a list.
- Why can one not reach exactly zero Kelvin?
- What would be the consequences if we could do? Think about technical applications.

Class 25 – heat pump

- How can you model/describe an air condition in thermodynamics?
- Can you reverse a Carnot process? Why? What would this do?
- Calculate the efficiency of an air condition.
- Look through the concept questions in the power point for class 25.
- What is the difference between a heat pump and heat engine?

Class 26 – Otto (car) cycle

- What is the difference between a Carnot cycle and Otto cycle?
- The efficiency of the Otto cycle depends on the compression ratio. Yes/No? **Why?**
- What is the problem with a large compression ratio?

Class 27 – Chapter summary and examples

Class 28 – Gibbs energy V1

- For a spontaneous reaction in forward direction A → B to occur, $\Delta G > 0$. Correct? Yes/No? Why?
- What is the equilibrium condition when considering the Gibbs energy?
- What is the difference between the Gibbs energy and the Helmholtz energy?
- What is sometimes called the "free energy"?
- Can you synthesize diamonds from graphite at room temperature and ambient pressure? Yes/No? Why?
- Calculate ΔG for the reaction A → B + C.

Class 29 – Second midterm. The midterm will cover classes 18 to 27 (Mr. Gibbs is in the final).

Class 29 – Gibbs energy V2

- Name examples or applications where you would need to consider the Gibbs or Helmholtz energy?
- What is the definition of the Gibbs energy?
- What is the definition of the Helmholtz energy?
- Entropy change for a spontaneous process is positive. Yes/No? Why?
- If this is correct why is the Gibbs energy change for a spontaneous process negative?
- What is the maximum non-expansion work? How to calculate it?
- Just increase the temperature and you can synthesize diamonds. Yes/No? Why?

Class 30 – Gibbs energy V3

- What is the molecular interpretation of the Gibbs equation?
- The entropy of the system decreases. What can you conclude for the surroundings and heat balance? Consider the Gibbs and Helmholtz energy.
- Outline the concept of a H_2/O_2 fuel cell.
- Calculate the efficiency of a fuel cell.
- What is the difference between a H_2/O_2 fuel cell and the electrolysis of water?

Class 31 – Gibbs energy V4, G(P), G(T)

- What is the definition of G, A, H, and U
- Write the differential forms of G, A, H, and U
- Why is that useful?
- Write G as a function of P for a solid.
- Name an application of these equations.

Class 32 – Chemical potential

- Write down the total differential of the Gibbs energy, considering $G = G(T, P, n_i)$
- What is the definition of the chemical potential?
- How would you explain to your younger cousin what the chemical potential is?
- What is the chemical potential for a pure one component system?
- What is the rule for a stable phase using the chemical potential?
- Recall that Gibbs energy follows for 2^{nd} law and the chemical potential is closely related to Gibbs energy. What are the connections here?
- Consider two systems for which $\Delta T > 0$ and $\Delta P > 0$ and $\Delta\mu > 0$. What will happen?
- How is the thermal, mechanical, and material equilibrium defined? In other words, what is the condition for a thermal etc. equilibrium?
- What is the analogy between a mechanical system and thermodynamics in regard of the chemical potential?

Class 33 – Chemical potential and mixtures

- Where is the rule "the stable phase has the smallest chemical potential" coming from?
- Comment on "the chemical potential is a partial molar quantity". What is the concept/idea?
- What is the functional form of the chemical potential for a gas mixture?
- Is mixing a spontaneous process?
- What is the driving force of forming a gas mixture?
- Draw qualitatively the Gibbs energy change when forming a binary gas mixture.
- How does the mixing entropy change when forming a binary mixture?
- How can you decide whether a solution or a physical mixture is formed?

Class 34 – Equilibrium constant

- What is the connection of Gibbs energy and the equilibrium constant?
- Extend of a reaction. What is that?
- Write down the equilibrium condition using the Gibbs energy and the "extend of the reaction".
- How can you calculate the pressure dependence of the equilibrium constant?
- What is the effect of entropy on the equilibrium of a chemical reaction?

Class 35 – Equilibrium constant & van't Hoff Eq.

- Express the standard Gibbs energy change in terms of temperature and equilibrium constant.
- What is a heterogeneous equilibrium?

- What is an entropy driven endothermic reaction?
- Van't Hoff is an extinct variety of whales. Yes/No?
- Gibbs energy change is independent of pressure for solids. Yes/No?
- Why is the concentration of solids not included in the equilibrium constant**?**

Class 36 – van't Hoff Eq. & Ammonia synthesis

- Find a French speaking friend to find out how to pronounce "le Chatelier" correctly.
- Find an example of that principle that was not already discussed in class.
- What is your recommendation for the ammonia synthesis? High P, high T, low P, low T ... Why?

Class 37 – phase diagrams

- Plot the chemical potential as a function of pressure for solids, liquids, and gases.
- Is the Gibbs energy typically increasing or decreasing with pressure? Why?
- In you increase the pressure what happens with the boiling and melting temperatures? Why?
- What is "latent heat"?
- Is heat put in a system always increases the temperature linearly? Yes/No? Why?
- Superheated liquid? What is that?
- Does water ice exists that does not float on liquid water?
- Can you freeze water without changing the temperature? Yes/No? How?
- Supercooled liquid. What is that?
- Pressure cooker. How does it work? What is the idea?
- Why are lakes freezing from the top?
- Ice skating on CO2. Is that possible?
- Dry ice. What is that?

Class 38 – Clausius & Clapeyon eq.

- You get a NSF proposal to review from a colleague showing preliminary data of a new synthesis of a new bombastic compound (super strong). He claims that the superior tensile strength is related to a fipple point (as he calls it) in the phase diagram of this one pot (one component) compound. "Fipple point alloys" develops fast into a new NSF buzzword since the PI has a facebook etc. account. (He got quickly 10 invited talks ...) Would you recommend the $650,000 award?
- Name an application of the Clausius Clapeyon equation.

Class 39 – Raults's law and Henry's law

- How can you verify that a liquid solution behaves ideally?
- Compare Rault's and Dalton's laws.
- What happens if you open a pop can?
- You have a 60 liters volume gas tank at 50 bar pressure. How long can you stay at 50 meters under water? Lung volume may be 5 liters and it will be exchanged every 10 seconds.
- At alpha century they don't have hemoglobin. How could that work? (The natives there also breeze oxygen to keep their exoskeleton functioning. By the way, the *nabradi –gung*

(pronounced λφιυτψγφ) look like lobster. NASA is likely still working on a verification of this hypothesis – Vladimir Ufnikuf from Uni. of Novosibirsk, umpskna came up with this idea.)

- What is the idea of a distillation?

Class xx – rest of liquid thermo will NOT be included in the finals (2013)

Will be continued.