Homework Assignment 9

PHYSICS 314 - THERMODYNAMICS & STATISTICAL PHYSICS (Spring 2018) *Due Friday, April 27th, by noon, Noyce 1135*

I cannot award full credit for work that I am unable to read or follow. For my benefit and for yours, please:

- Write neatly
- Show and EXPLAIN all steps
- o Make diagrams large and clearly-labeled

You are welcome to collaborate with others on this assignment. However, the work you turn in should be your own. Please cite collaborators and outside sources. See the syllabus for details.

Regardless of the number of parts, all homework problems are weighted equally. Regardless of the number of questions, all homework assignments are weighted equally.

1) Calcite and aragonite are two common crystalline forms of calcium carbonate, $CaCO_3$. Use information from the table in the back of Schroeder to answer the following questions.

Based on SCHROEDER 5.28

a) Which of the two forms is the more stable phase at 298 K and 1 bar? Explain.

The more stable phase has a lower Gibbs free energy. Compare the Gibbs free energies of formation per mole from the table in the back of the book.

$$\Delta_f G_{calcite} = -1128.8 \, kJ$$

$$\Delta_f G_{aragonite} = -1127.8 \, kJ$$

The Gibbs free energy per mole of calcite is lower by about $1\,kJ$, and therefore calcite is more stable.

b) At room temperature, what is the pressure at which the other phase becomes more stable? *Hint:* Assume the solids are incompressible.

Use a procedure similar to our class discussion of graphite and diamond. In a plot of Gibbs free energy as a function of pressure, the slope is given by the volume.

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

As in class, assume that the volume of the crystalline solids, and therefore the slope of the plot, is constant. (This is the incompressibility assumption.) Gibbs free energy is then a linear function of pressure, with a slope of volume and some offset.

$$G = VP + offset$$

From part a), calcite has a lower Gibbs free energy at standard conditions. From the table in the back of Schroeder, it also has a greater volume per mole.

$$V_{calcite} = 36.93 \frac{cm^3}{mole}$$

$$V_{aragonite} = 34.15 \frac{cm^3}{mole}$$

Thus, its slope is larger, and its Gibbs free energy increases faster as a function of pressure. Therefore, at some higher pressure, calcite will have a higher Gibbs free energy than (and thus be less stable than) aragonite. The pressure at which the two linear plots cross is where the most stable phase switches to aragonite. Find the intersection.

$$G_{calcite} = G_{aragonite}$$

$$V_{calcite}P + offset_{calcite} = V_{aragonite}P + offset_{aragonite}$$

Solve for pressure.

$$(V_{calcite} - V_{aragonite})P = offset_{aragonite} - offset_{calcite}$$

$$P = \frac{offset_{aragonite} - offset_{calcite}}{V_{calcite} - V_{aragonite}}$$

To make the math slightly easier, measure the pressure *change* from the $1\ bar$ position where the difference in offsets is known from part a).

$$\Delta P = \frac{\Delta_f G_{aragonite}(P = 1 \ bar) - \Delta_f G_{calcite}(P = 1 \ bar)}{V_{calcite} - V_{aragonite}}$$

Plug in the values, using the Gibbs free energies and volumes per mole from above.

$$\Delta P = \frac{(-1127.8 \text{ kJ}) - (-1128.8 \text{ kJ})}{36.93 \text{ cm}^3 - 34.15 \text{ cm}^3}$$
$$\Delta P = \frac{1 \text{ kJ}}{2.78 \text{ cm}^3}$$
$$\Delta P \approx 0.36 \frac{\text{kJ}}{\text{cm}^3}$$

This is a strange unit. Convert to a more standard unit. First convert to joules and meters.

$$\frac{kJ}{cm^3} = \frac{1000 \, J}{(0.01 \, m)^3} = 10^9 \frac{J}{m^3}$$

Rewrite a joule as a newton times a meter. (Energy is force applied over a distance.)

$$10^9 \frac{J}{m^3} = 10^9 \frac{N m}{m^3} = 10^9 \frac{N}{m^2}$$

This is more clearly a unit of pressure. Convert to pascals and then to bar.

$$10^9 \frac{N}{m^2} = 10^9 Pa = 10^9 (10^{-5} bar) = 10^4 bar$$

Plug this more conventional unit into the expression for change in pressure.

$$\Delta P \approx 0.36 \frac{kJ}{cm^3} = 0.36 \times 10^4 \ bar$$

$$\Delta P \approx 3600 \ bar$$

The initial pressure was $1 \, bar$, which is much smaller than the new pressure.

$$\Delta P = P_f - P_i \approx 3600 \ bar - 1 \ bar$$

$$P_f \approx 3.6 \, kbar$$

c) Explain why it would be significantly more difficult to do a similar stability analysis for CO_2 at a temperature between its triple point temperature and its critical point temperature.

At temperatures between its triple point temperature and its critical point temperature, the phase transition of \mathcal{CO}_2 is between a liquid phase and a gas phase. Neither phase, especially the gas phase, can be accurately considered incompressible. The phases are compressible, so volume changes with pressure. Thus, the slope of Gibbs free energy as a function of pressure also changes with pressure.

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

The Gibbs free energy functions would no longer be a straight lines. One would have to know about the compressibility of the fluid phases to find the Gibbs free energies as a function of pressure. These complicated functions are needed to find the intersection where the stability changes.

2) Based on SCHROEDER 5.30

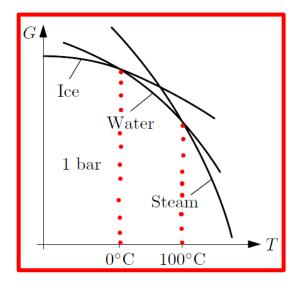
a) Sketch plots of Gibbs free energy as a function of temperature for the three phases of H_2O (ice, water, and steam) at P=1 atm. Plot the three phases on the same axes, including all three phases, not just the most stable phase at each temperature. The sketch should be qualitatively accurate. (I would like more detail here than on HW8 #6.) Label 0° C and 100° C.

As in HW8 #6., the key is that the slope of the plot is given by the opposite of the entropy.

$$\left. \frac{\partial G}{\partial T} \right|_{PN} = -S$$

The entropy is always positive, so the slope is always negative. As in HW8 #6, entropy increases as the substance transitions from a solid to a liquid to a gas. Furthermore, within a given phase, the entropy gets larger with increasing temperature, so the slope becomes increasingly negative. The most stable

phase at a given temperature is the phase with the lowest Gibbs free energy at that temperature. Ice is most stable below 0° C; steam is most stable above 100° C; water is most stable in between.

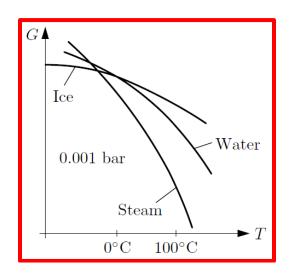


b) Repeat part a), but at $P = 1 \, mbar$. Discuss the differences between this plot and that from part a).

The same general approach holds for the lower pressure plot. However, the plots are shifted. The change in Gibbs free energy with pressure is equal to the volume.

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

With decreasing pressure, all three plots move downwards. However, because steam has a significantly larger volume than the other two phases, its Gibbs free energy will decrease much more quickly. $1\ mbar$ is below the triple point pressure of water ($P\approx 6\ mbar$), so liquid water is at not the most stable state at any state; ice sublimates directly to steam. Thus, the steam plot must be lowered enough the water curve is never the lowest Gibbs free energy for any temperature.



Based on SCHROEDER 5.32

a) Use the Clausius-Clapeyron relation to explain why the slope of the water-ice phase boundary on a P-T phase diagram has the opposite sign of the slope of most liquid-solid phase boundaries.

Begin with the Clausius-Clapeyron in the form of Schroeder equation (5.46), but with the liquid-solid boundary.

$$\frac{dP}{dT} = \frac{S_{liquid} - S_{solid}}{V_{liquid} - V_{solid}}$$

The entropy of the liquid is higher than the entropy of a solid. The liquid is less structured, and thus has a higher multiplicity. This is typical of most substances. Therefore, the numerator is positive.

The volume of ice is *larger* than the volume of water. This is unusual; most substances contract when they freeze. Therefore, the denominator is negative.

The numerator is positive and the denominator is negative, thus the slope of the boundary is negative, unlike most substances. (If you think of the transition in the other direction, liquid to solid, then the numerator is negative and the denominator is positive. What matters is the signs are opposite one another.)

b) The melting point of water is 0° C at atmospheric pressure, and the latent heat of water is $334 \ kJ/kg$. The density of ice is $917 \ kg/m^3$ and the density of water is $1000 \ kg/m^3$. Use these facts to determine approximately by how much and in which direction the pressure must be changed to get ice to melt at just one degree lower, -1° C.

Use the Clausius-Clapeyron equation from Schroeder equation (5.47) to find how pressure changes with temperature.

$$\frac{dP}{dT} = \frac{L}{T\Delta V}$$

The latent heat is in units of energy per mass. Convert the densities to volumes per mass. The mass dependences will cancel. (Alternatively, you could consider the *total* latent heat, rather than the latent heat in energy per mass.)

$$\rho = \frac{m}{V} \to \frac{V}{m} = \frac{1}{\rho}$$

$$\frac{V_{liquid}}{m} = \frac{1}{\rho} = \frac{1}{1000 \ kg/m^3} = 0.001 \frac{m^3}{kg}$$

$$\frac{V_{solid}}{m} = \frac{1}{\rho} = \frac{1}{917 \ kg/m^3} \approx 0.00109 \frac{m^3}{kg}$$

Find the slope at 0° C = 273 K.

$$\frac{dP}{dT} = \frac{334 \ kJ/kg}{273 \ K \left(0.001 \frac{m^3}{kg} - 0.00109 \frac{m^3}{kg}\right)}$$
$$\frac{dP}{dT} \approx -13517 \frac{kJ}{K \ m^3}$$

As in problem 1, convert to more conventional units.

$$\frac{dP}{dT} \approx -13517 \times 10^{3} \left(\frac{J}{m^{3}}\right) \frac{1}{K}$$

$$\frac{dP}{dT} \approx -13517 \times 10^{3} (Pa) \frac{1}{K}$$

$$\frac{dP}{dT} \approx -13517 \times 10^{3} (10^{-5} bar) \frac{1}{K}$$

$$\frac{dP}{dT} \approx -135 \frac{bar}{K}$$

Assuming that this slope is roughly constant over the decrease in one degree, multiply this by the temperature change to find the temperature change.

$$\Delta P \approx \frac{dP}{dT} \Delta T$$

$$\Delta P \approx -135 \frac{bar}{K} (-1K)$$

$$\Delta P \approx 135 bar \approx 133 atm$$

That is a lot of pressure for a single degree difference!

c) What is the pressure z meters below the surface of a glacier with ice of density ρ ?

Consider a thin slice of ice of cross-sectional area A located z meters below the surface. Two forces are acting on the ice. A force downwards from the weight of the ice above.

$$F_{\downarrow} = mg$$

Rewrite the mass as the product of the volume of the ice above the slice, Az, and the density.

$$F_1 = \rho V a = \rho A z a$$

The force from below the slice is the pressure times the area.

$$F_{\uparrow} = PA$$

The ice is not accelerating, so the net force must be zero. Set the forces equal to one another.

$$F_{\uparrow} = F_{\downarrow}$$

$$\rho Azg = PA$$

$$\rho zg = P$$

d) Find the depth in meters below the surface of a glacier at which ice melts at -1° C.

Solve the equation from part c) for depth.

$$\rho zg = P$$

$$z = \frac{P}{\rho g}$$

Plug in values from part b).

$$z \approx \frac{135 \ bar}{917 \ kg/m^3 \ 9.8 \ m/s^2}$$

$$z \approx 0.015 \frac{bar \, m^2 \, s^2}{kg}$$

Convert these units to meters. First change from bar to pascals.

$$z \approx 0.015 \frac{(100\ 000\ Pa)\ m^2\ s^2}{kg}$$

$$z \approx 1500 \frac{Pa \, m^2 \, s^2}{kg}$$

A pascal is a newton per square meter.

$$z \approx 1500 \frac{N/m^2 \ m^2 \ s^2}{kq}$$

$$z \approx 1500 \frac{N s^2}{kg}$$

A newton is a kilogram-meter per second.

$$z \approx 1500 \frac{kg \, m}{s^2} s^2$$

$$z \approx 1500 m$$

4) The Clausius-Clapeyron relation is a differential equation. In principle, it can be solved to find the shape of the entire phase-boundary curve. This can be difficult, though, as the latent heat, L, and the change in volume, ΔV , generally change with pressure and temperature. However, over a reasonably small section of the boundary, the latent heat can be approximated as constant. Also, if the phase transformation is from either a liquid or a solid to a gas, the volume of the initial phase can be ignored because the gas phase is so much larger.

Make all the assumptions mentioned above. Solve the differential equation and find an expression for pressure as a function of temperature. *Hint: In addition to the given variables, your expression will include an unknown constant.*

Based on SCHROEDER 5.35

Start with the Clausius-Clapeyron relation from Schroeder equation (5.47).

$$\frac{dP}{dT} = \frac{L}{T\Delta V}$$

Based on the assumption that we can ignore the volume of the liquid or solid phase, rewrite the change in volume as just the volume of the gas.

$$\Delta V = V_g - V_{initial} \approx V_g$$

Furthermore, in order to be able to solve the differential equation, rewrite the volume using the ideal gas law.

$$\Delta V \approx V_g = \frac{nRT}{P}$$

Substitute this into the differential equation above.

$$\frac{dP}{dT} = \frac{L}{T\left(\frac{nRT}{P}\right)}$$

$$\frac{dP}{dT} = \frac{PL}{nRT^2}$$

In order to solve the differential equation, separate variables. Move all pressure terms to the left and all temperature terms to the right.

$$\frac{1}{P}dP = \frac{L}{nRT^2}dT$$

Integrate both sides. Because it is an indefinite integration, each side will have a constant of integration term, x.

$$\int \frac{1}{P} dP = \int \frac{L}{nRT^2} dT$$

$$\ln P + x_1 = -\frac{L}{nRT} + x_2$$

Now solve for pressure. First combine the constants into a new constant.

$$\ln P = -\frac{L}{nRT} + x_3$$

Now exponentiate both sides.

$$e^{\ln P} = e^{-\frac{L}{nRT} + x_3}$$

$$P = e^{-\frac{L}{nRT} + x_3}$$

Rewrite to bring the constant out front using the rule for sums in exponents.

$$P = e^{x_3} e^{-\frac{L}{nRT}}$$

Just to make it look nicer, create another constant out of the first exponent.

$$P = x_4 e^{-\frac{L}{nRT}}$$

Remember, this only works when the assumptions in the problem hold.

5) Suppose there is a particle in equilibrium with a reservoir at $300 \, K$. The particle has three possible energy states; the particle can either be in state 1 with energy $-0.05 \, eV$, in state 2 with energy $0.00 \, eV$, or in state 3 with energy $+0.05 \, eV$.

Based on SCHROEDER 6.5

a) Calculate the partition function, Z, for this particle.

The partition function Z is the sum of all the Boltzmann factors.

$$Z = \sum_{s} e^{-E(s)/kT}$$

There are three energy states, so there are three factors in the sum.

$$Z = e^{-E(s_1)/kT} + e^{-E(s_2)/kT} + e^{-E(s_3)/kT}$$

Plug in the values. Given the units of energy, it is convenient to use the Boltzmann constant with energy in electron-volts: $k \approx 8.62 \times 10^{-5} \ eV/K$.

$$Z = e^{-\frac{(-0.05 \, eV)}{(8.62 \times 10^{-5} \, eV/K)(300 \, K)}} + e^{-\frac{(0.00 \, eV)}{(8.62 \times 10^{-5} \, eV/K)(300 \, K)}} + e^{-\frac{(+0.05 \, eV)}{(8.62 \times 10^{-5} \, eV/K)(300 \, K)}}$$

$$Z \approx 6.92 + 1.00 + 0.14$$

 $Z \approx 8.06$

b) Calculate the probability of the particle being in each of the three states.

With the partition function calculated, the probabilities can be calculated with the Boltzmann factors.

$$\mathcal{P}(s) = \frac{1}{Z} e^{-E(s)/kT}$$

$$\mathcal{P}(s_1) = \frac{1}{Z} e^{-E(s_1)/kT}$$

$$\mathcal{P}(s_1) \approx \frac{1}{8.06} e^{-\frac{(-0.05 \, eV)}{(8.62 \times 10^{-5} \, eV/K)(300 \, K)}}$$

$$\mathcal{P}(s_1) \approx 0.86$$

$$\mathcal{P}(s_2) = \frac{1}{Z} e^{-E(s_2)/kT}$$

$$\mathcal{P}(s_2) \approx \frac{1}{8.06} e^{-\frac{(0.00 \, eV)}{(8.62 \times 10^{-5} \, eV/K)(300 \, K)}}$$

$$\mathcal{P}(s_2) \approx 0.12$$

$$\mathcal{P}(s_3) = \frac{1}{Z} e^{-E(s_3)/kT}$$

$$\mathcal{P}(s_3) \approx \frac{1}{8.06} e^{-\frac{(+0.05 \, eV)}{(8.62 \times 10^{-5} \, eV/K)(300 \, K)}}$$

$$\mathcal{P}(s_3) \approx 0.02$$

c) Suppose that the energy scale is now shifted so that the ground state is considered $0.00\ eV$. Recalculate part a) and part b) with this new scale.

This changes the energies, shifting them all up by $0.05 \ eV$.

$$E_1 = 0.00 \, eV$$
 $E_2 = 0.05 \, eV$ $E_1 = 0.10 \, eV$

The method is identical with the new values. First find the partition function.

$$Z = e^{-E(s_1)/kT} + e^{-E(s_2)/kT} + e^{-E(s_3)/kT}$$

$$Z = e^{-\frac{(0.00 \text{ eV})}{(8.62 \times 10^{-5} \text{ eV}/K)(300 \text{ K})}} + e^{-\frac{(0.10 \text{ eV})}{(8.62 \times 10^{-5} \text{ eV}/K)(300 \text{ K})}} + e^{-\frac{(0.10 \text{ eV})}{(8.62 \times 10^{-5} \text{ eV}/K)(300 \text{ K})}}$$

$$Z \approx 1 + 0.14 + 0.02$$

Now use this to calculate the probabilities.

$$\mathcal{P}(s_{1}) = \frac{1}{Z} e^{-E(s_{1})/kT}$$

$$\mathcal{P}(s_{1}) \approx \frac{1}{1.17} e^{-\frac{(0.00 \ eV)}{(8.62 \times 10^{-5} \ eV/K)(300 \ K)}}$$

$$\mathcal{P}(s_{1}) \approx 0.86$$

$$\mathcal{P}(s_{2}) = \frac{1}{Z} e^{-E(s_{2})/kT}$$

$$\mathcal{P}(s_{2}) \approx \frac{1}{1.17} e^{-\frac{(0.05 \ eV)}{(8.62 \times 10^{-5} \ eV/K)(300 \ K)}}$$

$$\mathcal{P}(s_{2}) \approx 0.12$$

$$\mathcal{P}(s_{3}) = \frac{1}{Z} e^{-E(s_{3})/kT}$$

$$\mathcal{P}(s_{3}) \approx \frac{1}{1.17} e^{-\frac{(0.10 \ eV)}{(8.62 \times 10^{-5} \ eV/K)(300 \ K)}}$$

$$\mathcal{P}(s_{3}) \approx 0.02$$

d) Comment on the significance of what does and what does not change with the new scale.

The partition function changes. That is acceptable, because it is a calculation tool without a direction physical meaning.

The probabilities do not change. That is expected because the zero of any energy scale is arbitrary. The choice of zero should not affect the outcome (in this case, the probabilities) in the physical world.

6) Consider now energy *levels* made up of n degenerate energy states. Let the multiplicity of the level be equal to the number of degenerate states for that level. Show that the probability of finding an atom in a particular energy level with energy E is given by the expression shown, in which F is the Helmholtz free energy of the level.

$$\mathcal{P}(E) = \frac{1}{Z}e^{-F/kT}$$

Based on SCHROEDER 6.2

Suppose a level has n degenerate states. The probability of the level is the sum of the probabilities of the individual degenerate states.

$$\mathcal{P}(E) = \mathcal{P}(s_1) + \mathcal{P}(s_2) + \dots + \mathcal{P}(s_n)$$

$$\mathcal{P}(E) = \frac{1}{Z}e^{-E(s_1)/kT} + \frac{1}{Z}e^{-E(s_2)/kT} + \dots + \frac{1}{Z}e^{-E(s_n)/kT}$$

This can be simplified because the n energy levels are degenerate, and therefore all have the same energy, E.

$$\mathcal{P}(E) = n \times \frac{1}{Z} e^{-E/kT}$$

Now rewrite n in terms of entropy of the level.

$$S = k \ln n$$

$$\frac{S}{k} = \ln n$$

$$n = e^{S/k}$$

$$\mathcal{P}(E) = e^{S/k} \times \frac{1}{Z} e^{-E/kT}$$

Combine the exponents.

$$\mathcal{P}(E) = \frac{1}{Z} e^{S/k - E/kT}$$

Multiply and divide the first term in the exponent by the temperature.

$$\mathcal{P}(E) = \frac{1}{7}e^{TS/kT - E/kT}$$

$$\mathcal{P}(E) = \frac{1}{Z} e^{\frac{TS - E}{kT}}$$

Factor a negative sign out of the exponent.

$$\mathcal{P}(E) = \frac{1}{Z}e^{-\frac{E-TS}{kT}}$$

Recall the definition of Helmholtz free energy for a level with energy E.

$$F = E - TS$$

$$\mathcal{P}(E) = \frac{1}{Z}e^{-\frac{F}{kT}}$$

7) You have two choices for the reflection problem this week. You may choose to do either Option I or Option II. *I strongly encourage you to do Option I if you are able,* but both options are worth the same number of points.

Option I

Attend the special Squire Lecture Physics seminar on Tuesday, April 24th, at noon.

The speaker is Professor Meredith Hughes from Wesleyan University. The presentation is entitled, "STEM Equity and Inclusion: A Female Astronomer's View". It is an important and often-overlooked topic in the field, and I believe the presentation will be useful for all of us.

After attending the lecture, write a half-page reflection on the presentation.

- Summarize the main points of the presentation.
- Respond to the presentation. If you wish, you could consider some of the following questions.
 - o Was there any information in the presentation that surprised you?
 - What was the most important conclusion that you drew from the presentation?
 - Was there anything in this presentation that reminded you of your or your peers' experiences in STEM fields? There is no need to respond to this potentially personal question if you do not feel comfortable doing so. Feel free to skip this question or to respond in very general terms.
 - Were there any additional related topics that you would have liked to seen discussed?
- Fulfilling the above requirements will earn you a 3.25/4. The rest of the points will be awarded based on the depth and quality of your reflection.

Option II

Read the following material discussing recent topics from class.

Kamerlingh Onnes and the discovery of superconductivity

https://aapt.scitation.org/doi/pdf/10.1119/1.17669

Strange phenomena in matter's flatlands (Nobel Prize in Physics 2016)

https://www.nobelprize.org/nobel_prizes/physics/laureates/2016/popular-physicsprize2016.pdf

Write a short response to the two articles. One paragraph per article is sufficient.

- Summarize the main points of each article in a few sentences.
- For each article, discuss in a few sentences the connections between the science discussed in the article and the material covered in this course.
- Which article did you feel better conveyed the relevant science? Why? (Keep in mind the intended audience of each piece.)
- Fulfilling the above requirements will earn you a 3.25/4. The rest of the points will be awarded based on the depth and quality of your explanations of the connections. (For example, a response that discusses the energy flow of a negative temperature system will earn more points than a response that simply states that negative temperature is something we saw in class.)

NOTICE!!! THE FINAL PROBLEM HAS CHANGED!

- 8) In preparation for the end of the semester, start thinking about questions that could be on the final.
 - a) <u>Create two problems on material from after Test 2 that could be on the final.</u> These problems should be the level of difficulty that could be on a test. They should not be too easy, such as a problem that

- just requires plugging numbers into a formula. They should also not be so difficult that they could not be solved in the amount of time available on a test with many questions.
- b) For each problem, provide a very brief description of **how** the problem could be solved. You do NOT need to solve the problem completely... yet. Just outline the method that could be used to solve the problem.

You will be graded on the appropriateness and originality of your questions and on the outlines of the solutions you provide.

I will provide feedback on your problems, and for the next week's homework, I will ask you to write up full, formal solutions to one problem. For the last homework of the semester, I will have you exchange problems and solve a problem created by one of your classmates. If any of the problems are particularly good, I may use them on the final. Hopefully that is an incentive to write good problems!