Peer Review Rubric for Exam 1 – Fall 2019

BCH 341 - Physical Chemistry with a Biological Focus
Professor Jeff Yarger

September 11-13, 2019

DUE Friday September 13, 2019 by 11:59 PM (UTC-7). Turn in completed peer review (peer grading) of the random 3 exams assigned to each student in ASU Canvas LMS. It is recommended that you submit each peer review as a typeset (no handwriting allowed) <u>single PDF document</u> into the peer review assignment link on ASU Canvas. Please make sure the completed peer review is organized, self-contained and all COMMENTS, text, equations, figures and images are typeset, clear and legible.

<u>Peer Reviewer Identification:</u>

ASU ID #:___I don't think you need my ASU ID #_____
(10-digit number (typically starting with 12xxxxxxxx or 10xxxxxxxx))

<u>OPTIONAL Identification:</u>

Initials: __JLY__ Email: ____yarger@biopchem.education__________

Exam General Instructions
To aid in the anonymous peer review process, you do NOT need to include your full name, just your ASU student ID. There is the option of including your first, middle and last initials, and an email address for contact purposes (which is really helpful).
There are 5 multi-component questions on examination 1 (exam 1). Pick 4 of these problems to work on this examination. Each of the multi-component numbered problems is worth 25 points and you are required to pick 4 of them. Hence, the exam is worth a total of 100 points. If you don't include a number in the space below and provide answers for all 5 questions on the exam, then the first 4 will be graded. You are required to explicitly show all equations, numerical calculations and associated units. All points are associated with explicitly showing all your work and no points are awarded for just determining the correct numerical answer. All assumptions need to be clearly and concisely stated. If thermodynamic parameters are used, the citation, reference or link to where this thermodynamics data came from must be stated. The completed exam should be typeset (no handwriting of equations or numerical values and associated units).

Problem number student **omitted (not graded)**: _____ (1, 2, 3, 4 or 5)

Peer-Review (Peer-Grading) Information
This is a new feature and a trial in ASU Canvas as an additional option for an 'assignment' (exam 1 in Canvas). Details about the peer review (peer grading) process are provided at biopchem.education and this is the rubric to help students provide detailed and accurate comments, suggestions, evaluations, and points/scores.

Peer Review (Peer Grade) Summary:
(1) ___ / 25 pts, (2) ___ / 25 pts, (3) ___ / 25 pts, (4) ___ / 25 pts, (5) ___ / 25 pts: **Total, ____ / 100 pts**
(input an 's' for the question skipped/omitted)

Summary Peer Review Comment: ____
(*optional*)

1. (A) Provide brief molecular interpretations of (i) heat, (ii) temperature and (iii) heat capacity (please limit your answers to 1-2 paragraphs and include associated citations, 10 pts).
(B) Pick a molecular system that you feel best allows you to illustrate the molecular interpretation of heat, temperature and heat capacity. The most common example molecular systems used by textbooks include the kinetic model of gases (pick your favorite common gas molecule, H_2, He, N_2, CO_2, etc) and/or one or more of the various phases of H_2O (ice, water, vapor). Given that this course has a biological focus, you are encouraged to pick an example with biological relevance, i.e., your favorite biological molecule (peptide, protein, nucleic acid, lipid molecule, etc). Points are awarded for creative, insightful and unique molecular examples with clear visual illustrations (plots or graphs are typically very useful as visual illustrations, provide links or citations to any existing material used in your illustrations/examples, 15 pts).

(A) I have done this in video format and uploaded it to YouTube. I don't think summarizing this video transcript or providing the transcript useful. The video can found on the biopchem channel at YouTube and a direct links is provided below:
https://youtu.be/qxRn7GQCpQE

Part (A) is a direct subset of a discussion question asked in Atkin's textbook (Physical Chemistry for the Life Sciences, 2nd Ed.), which was a suggested homework question. The solutions manual that accompanies this textbook (written by C. Trapp and M. Cady) provides an excellent interpretation, which I have provided below:

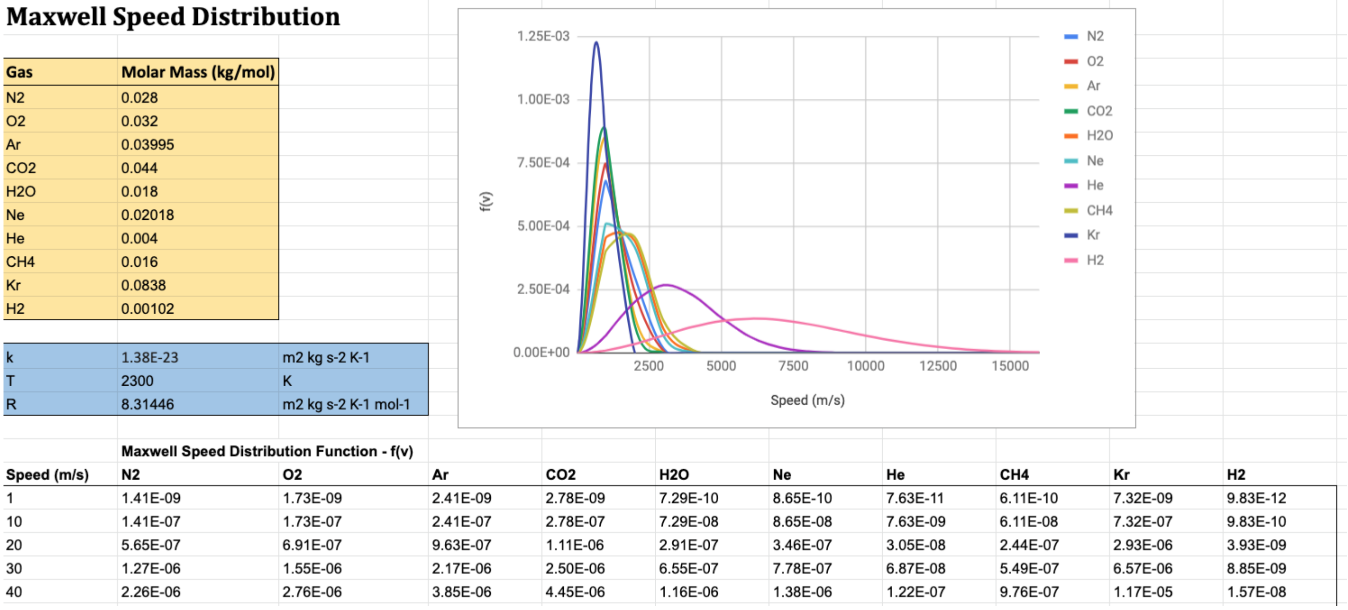
> At the molecular level, work is a transfer of energy that results in orderly, uniform motion of the atoms and molecules in a system as illustrated in text figure 1.5; the motion may even be that of an electrical current. In contrast, **heat** is the mode of transfer of energy that achieves or utilizes random motion of atoms, molecules, and electrons in the surroundings as illustrated in text Figure 1.6. Heat is energy in transit as a result of temperature difference from which for which highly energetic molecules in a region of high temperature either directly carry energy into regions of low temperature during their random meanderings or transfer energy during collisions with lower-energy molecules in a region of lower temperature. Consequently, heat always flows from high temperature to low temperature.
>
> **Temperature**, an intensive property possessed by local regions in thermal equilibrium, is the single parameter that tells us the relative molecular (and/or atomic) populations over the available energy levels of a system. This molecular interpretation is reflected in the Boltzmann distribution,
>
> which reveals that temperature T alone determines the distribution of particles over available energy levels.
>
> $$\frac{N_2}{N_1}=e^{-(E_2-E_1)/kT}$$ [1.1], where *k* is the Boltzmann constant,
>
> The molecular interpretation of **heat capacity** *C* is based upon its definition, $C = q/\Delta T$ [1.5a] where q is a heat input and ΔT is the subsequent temperature change, and the effect that *q* has upon the Boltzmann distribution. When energy levels are very close together, the heat input will promote molecules to excited states that do not differ much from the states populated at the initial temperature. Thus, the Boltzmann distribution does not differ much at the final temperature and the final temperature differs only slightly from the initial temperature; $\Delta T=T_f-T_i$ is small. Placing a small value of ΔT into the heat capacity definition yields a large heat capacity. We conclude that large heat capacity reflects a multitude of molecular states that have closely spaced energies. For example, the vibrational energies of hydrogen bonds in liquid water are close together, and the heat capacity of water is larger than expected for a substance consisting of small molecules.

Above quotation is from the following reference:
C. Trapp, M. Cady, Solutions Manual to Accompany Physical Chemistry for the Life Sciences, 2nd Ed. p. 21.

**** STUDENT answers should NOT be exact quotations and students should provide references (citations) for all material used to form their 'brief molecular interpretation'.**
**** Award up to 10 pts for creative and good interpretations, along with useful references/citations.**

(B) Award up to 15 pts for students who follow the detailed instructions. This obviously has a subjective component to the points awarded. **An example** of a creative, insightful and clear visual illustration of temperature is the fundaments chapter, section F.3, subsection (b) of Atkin's course textbook (pages 13-16). Specifically, page 16 and fig. F.9, F.10 and F.11. Reproducing these figures in a spreadsheet or plotting package for a range of temperature and gas molecules is an example of a clear visual illustration. As an example, here is a link to a public google sheet (spreadsheet) that was made to illustrate the Maxwell distribution for a bunch of common molecular gases (from BCH341 Exam 1, Question 1 in Spring 2019): https://docs.google.com/spreadsheets/d/1tgXUy4guFY4b5hoAoWotE1nDpuGzgQK4TlIQegOmddE/edit?usp=sharing

A low resolution screenshot of this google sheet is provided below.



Maxwell Speed Distribution

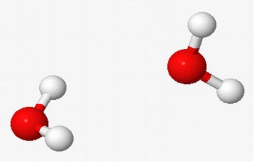
Gas	Molar Mass (kg/mol)
N2	0.028
O2	0.032
Ar	0.03995
CO2	0.044
H2O	0.018
Ne	0.02018
He	0.004
CH4	0.016
Kr	0.0838
H2	0.00102

k	1.38E-23	m2 kg s-2 K-1
T	2300	K
R	8.31446	m2 kg s-2 K-1 mol-1

	Maxwell Speed Distribution Function - f(v)									
Speed (m/s)	N2	O2	Ar	CO2	H2O	Ne	He	CH4	Kr	H2
1	1.41E-09	1.73E-09	2.41E-09	2.78E-09	7.29E-10	8.65E-10	7.63E-11	6.11E-10	7.32E-09	9.83E-12
10	1.41E-07	1.73E-07	2.41E-07	2.78E-07	7.29E-08	8.65E-08	7.63E-09	6.11E-08	7.32E-07	9.83E-10
20	5.65E-07	6.91E-07	9.63E-07	1.11E-06	2.91E-07	3.46E-07	3.05E-08	2.44E-07	2.93E-06	3.93E-09
30	1.27E-06	1.55E-06	2.17E-06	2.50E-06	6.55E-07	7.78E-07	6.87E-08	5.49E-07	6.57E-06	8.85E-09
40	2.26E-06	2.76E-06	3.85E-06	4.45E-06	1.16E-06	1.38E-06	1.22E-07	9.76E-07	1.17E-05	1.57E-08

Another great way to visually represent molecular details is through computational chemistry/biochemistry programs (molecular dynamic programs and electronic structure programs). The program that is most easily accessible for students is molcalc (https://molcalc.org/). Molcalc has a good molecular viewer and allows the calculation of molecular properties, including heat capacity. I provide more details about computational programs, software, apps at biopchem.education in the computational section: https://biopchem.education/bch341fall2019/computational-molecular-sciences/

I have found molcalc to be a bit buggy because of Java/Javascript in some browsers. However, there are tons of similar programs and excellent molecular GUI interfaces (e.g, Avogadro, VMD, Atomify, etc).



This molecular illustration is a screenshot from the Jmol in-browser viewer used my molcal.org. It is a molecular 'ball-stick' model of a water dimer. As an example of something that students could use as a good molecular example, one could comparing a single water molecule to water dimers in various geometries can reveal some fundaments about the thermodynamics of hydrogen bonding.

A few resources for simulating, illustrating, plotting, visualizing molecular systems are provided below:

- PHET: https://phet.colorado.edu/en/simulation/gas-properties
- Kinetic Theory: Atomic and Molecular Explanation of Temperature.
- Molecular Video Temperature – YouTube.

The best student examples will be posted on the biopchem.education website. I am excited to see what creative examples and illustrations students come up with for this question/project.

**** Award up to 15 pts for creative, interesting, novel, visual and illustrative examples.**

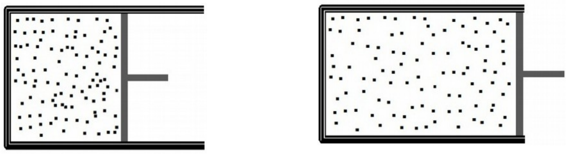
2. (A) Calculate the change in enthalpy (ΔH) for 1.0 mol of carbon dioxide (CO_2) initially at a volume of 5.00 L and a temperature of 298 K to a final volume of 10.00 L and a temperature of 373 K. Explicitly state all assumptions along with a justification for any and all assumptions made. Express your answer in units of kilojoules per mole (kJ/mol) (15 pts).
(B) The enthalpy is a common form of energy used in biochemical thermodynamics and is a state function, meaning the change in enthalpy (ΔH) for the process above should be independent of the path. Explicitly illustrate this point by calculating the change in enthalpy for the expansion process above along a different path than you did in part (A) of this problem (5 pts).
(C) This problem is inspired from a Module 1 quiz question and further YellowDig discussion. The numerical value that was correct on the quiz is NOT the answer to part (A) of this problem. Why? The change of system from helium to carbon dioxide plays a critical role (another example of understanding thermodynamics from a molecular perspective). Calculate the change in enthalpy for the exact initial and final conditions stated in part (A) but using helium instead of carbon dioxide as the molecular system. Explain or illustrate how this change in molecular system changes the calculated change in enthalpy (ΔH) for this process. (5 pts)

(A) So, we are asked to look at the change in energy (specifically the enthalpy) for the expansion of CO_2 gas. My advise for working biopchem numerical problems is to first reason through a general prediction or estimation before starting to work through the problem numerically. Second, summarize all known values from both the information given in the problem and any external sources of information, i.e., standard thermodynamic tables. Also, I really like making or using a plot, sketch or diagram to try and 'visualize' the problem. Third, start considering implied assumptions or necessary assumptions that need to work the problem. When considering assumptions, it is useful to (or in this case required!) that you justify any and all assumptions used to solve the problem. As an advanced step it is very useful to estimate or calculate the potential impact of the assumption on any numerical calculation. Now we are (finally) ready to either derive or state the necessary equation(s) and computational steps needed to numerically solve the problem. Lastly, it is often useful to summarize your results and put the calculated numerical values in context along with the appropriate units.

(i) Estimate/prediction: This is the expansion of a gas by increasing the temperature, meaning energy in the form of heat is added to the system. It is not obvious if this expansion is done under isobaric conditions or if there is a change in pressure. Why does this matter? Because this would add the potential for energy exchange in the form of work (VdP mechanical work in the case of enthalpy). Overall, I would estimate or predict an increase in the systems 'energy', with enthalpy being the specific energy being considered in this problem. So, I would expect a positive value for ΔH (endothermic). Doubling the volume (5 to 10 L) with an increase in temperature of much less than doubling (~20% temp change, 298 to 373 K) and no change in the number of moles (closed system, dN=0), this makes me guess that there is a change in pressure and that overall the positive dH is a small value, because it will mostly be just the change in heat and the heat capacity of gases are generally small. To put a quick estimated value, I would just quickly calculate CpΔT over the range of 298 to 373 K.

(ii) Summarize known information (5 pts)

Initial State	Final State	Assumption (A) or Explicitly Stated (ES) or Implicitly Stated (IS)
N = 1.0 mol CO_2	N = 1.0 mol CO_2	IS (problem implies no reaction and closed system (dN = 0))
V = 5.0 L	V = 10.0 L	ES
T = 298 K	T = 373 K	ES



Helpful Sketch of initial and final states. In my opinion, this really helps frame some questions, for example, whats the pressure (is this an isobaric expansion or does the piston have a different force on it between the initial and final states?

We want to know how the much the system changes its enthalpy (a form of energy) during this gas expansion process. Energy/Enthalpy can involve both work and heat terms (1st law). Hence, before we can directly calculate the value we want, dH, we first need to look at the work (VdP) and heat (TdS). This will require us to use an equation of state (EoS) or have experimental data on CO_2 under the stated conditions. Also, we will definitely need to make some assumptions.

(iii) Assumptions (and justifications) (5 pts)

- Assume this expansion is being performed in a reversible manner (TdS equal to heat) and the initial and final states are in thermal equilibrium. This is a general implicit assumption of the problem. Otherwise, more information would be necessary.
- Assume ideal gas behavior.
    - The justification is that the system is the low pressure and large volume regime, well within the vapor phase region of CO_2. This assumption is not obvious and could really use further justification. So, how to go about testing this assumption? Start by calculating the pressures of the intial and final state using the ideal gas law and an equation of state that takes into account non-ideal behavior, e.g., the van der Waals EoS. Also, look up the know phase diagram (PV diagram) for CO_2. Does the initial and final pressure-volumes fall well within the vapor phase (far from the liquid and solid phases).

So, from assumption of ideal gas (perfect gas):
PV = nRT
Cp-Cv = nR
enthalpy, H, and heat capacities (Cv & Cp) are functions of temperature only and not of pressure.
* https://en.wikipedia.org/wiki/Perfect_gas

$$P_i = \frac{nRT}{V} = \frac{(1\,mol)(0.082\,L\,atm/K\,mol)(298\,K)}{5\,L} = 4.9\,atm$$

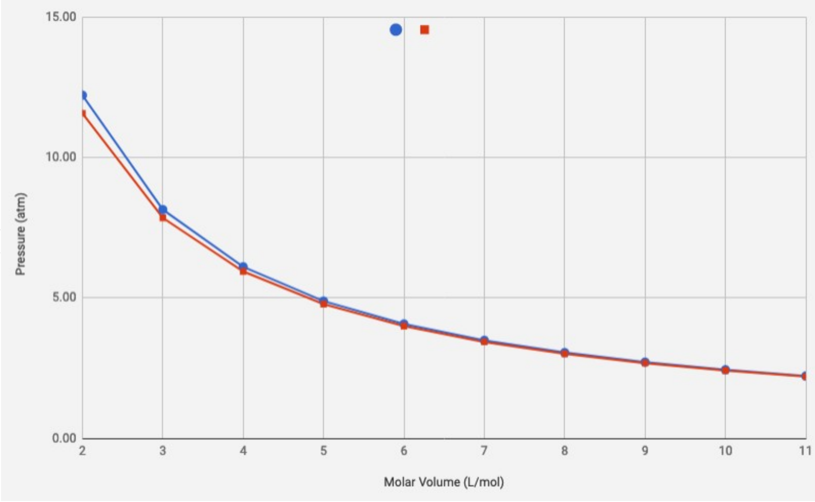
$$P_f = \frac{nRT}{V} = \frac{(1\,mol)(0.082\,L\,atm/K\,mol)(373\,K)}{10\,L} = 3.1\,atm$$

So, not an isobaric (dP = 0) gas expansion.

Also, if you look at these pressure-volumes on the CO_2 phase diagram, it is not obvious that the assumption of being an ideal gas is valid. Hence, compare the VDW EoS calculated pressures for the initial and final states, or better yet, I made a Van der Waals versus Ideal Gas EoS spreadsheet (google sheets) and publicly shared it: https://docs.google.com/spreadsheets/d/1b2g1ec_P4naeB0TWENrx71sQmymQR2MHWEsUBQfWx38/edit?usp=sharing

Screenshot of the associated plot:
Blue Circles – Ideal Gas EoS
Red Squares – VDW Gas EoS

* Helps justify Ideal gas assumption and even provides estimate of the error involved in making this assumption.



(iv) Derive or state the necessary equation(s) and computational steps needed to numerically solve the problem. (5 pts)

I always prefer to derive the necessary equation(s) and computational steps and then numerically solve while keeping track of units. The biggest mistake students often make it to search of the 'right' equation and then plug and chug!! The problem is did you really pick the right equation(s)?? You will find a TON of equations for the change in enthalpy in your textbook. Which is the correct one to use? Depends on the conditions and assumptions and system and…..
Hence, instead of memorizing a bunch of equations for the same variable under specific conditions, I prefer to exercise the method shown above, where we now use our assumptions to derive the correct equations and computational steps.

The definition of enthalpy:

$$H \equiv U + PV$$

we want the change in enthalpy, dH (and eventually ΔH), so

$$dH = dU + d(PV)$$

assuming ideal gas EoS and closed system (no change in number of moles)

$$dH = dU + d(nRT) = C_V\, dT + d(nRT) = n(C_V + R)\, dT = nC_P\, dT$$

assuming ideal gas also means constant value for the heat capacity, which makes integration easy

$$\int dH = nC_P \int dT$$

$$\Delta H = nC_P\, \Delta T = (1\, mol)(\frac{7}{2}R)(373\, K - 298\, K) = (1\, mol)(\frac{7}{2}(8.314\, J/K\, mol))(75\, K) = 2.2\, kJ$$

(A) ΔH = 2.2 kJ

(B) The above derivation allows for you to consider multiple paths. For example, an isotherm expansion which will have a ΔH = 0 kJ, followed by an adiabatic compression, which will drive the internal temperature up to 373 K with a ΔH = 2.2 kJ. The isothermal-adiabatic expansion and/or compression is the basis of the Carnot cycle and can be used to get to anywhere on the PV diagram for an ideal gas. Your textbooks cover this in great detail, so I won't bother reproducing it here. (5 pts)

(C) The same derivation as part (iv) all holds true and the assumption of ideal gas behavior is even better for helium (a monatomic noble gas in a pressure-volume range far far from its liquid or solid phases). What does change is the heat capacity value, which for a monatomic ideal gas is Cv = 3/2R or Cp = 5/2R

$$\Delta H = nC_P\, \Delta T = (1\, mol)(\frac{5}{2}R)(373\, K - 298\, K) = (1\, mol)(\frac{5}{2}(8.314\, J/K\, mol))(75\, K) = 1.6\, kJ$$

(C) ΔH = 1.6 kJ

Specifically, the Equipartition Theorem (https://en.wikipedia.org/wiki/Equipartition_theorem) predicts that the constant for a monatomic, diatomic, triatomic gases (and then you need to apply symmetry relations to get the reduction for the triatomic CO_2). This is a great foundational theorem to understand in foundations of molecular thermodynamics.
(5 pts)

3. (A) Predict whether the change in entropy (ΔS) is positive, negative or near zero for the following processes at 298K (4 pts). Provide a molecular level explanation or justification for your prediction (8 pts). (B) Now calculate the change in entropy (ΔS) for the following processes at 298K (8 pts). Write a brief explanation on how your predicted vs. calculated results compare (5 pts).

i. H_2O (*s*) → H_2O (*l*), melting of ice.
ii. Formation reaction for steam (water vapor, H_2O (*g*)).
iii. C_3H_8 (*l*) → C_3H_8 (*aq*), Liquid propane going to aqueous propane.
iv. The hydrolysis of the dipeptide glycylglycine.

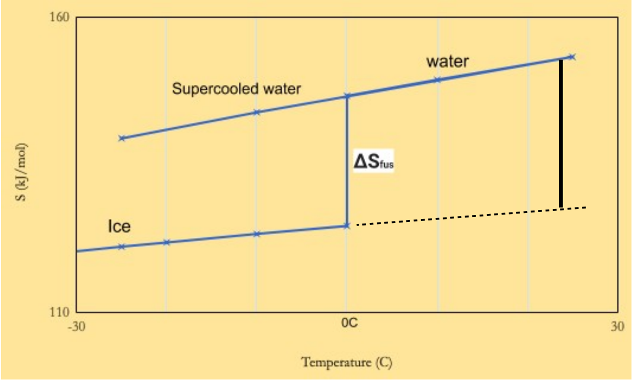
H_2O (*s*) → H_2O (*l*), melting of ice.

(A) Positive

(B) ΔS = 22 J/Kmol (calculate from absolute molar entropy for water and ice), this is at 0°C. To calculate the ΔS_{fus} at 25°C, you will need to determine Cp/T dT of ice from 0 to 25°C. You can see this on my google sheet and see visually that ΔS_{fus} at 25°C will clearly be larger than at 0°C.
Specifically, it is ~ 30 J/Kmol. (represented in the plot with a black solid line)

Google sheet that helps visualize the entropy thermodynamics of H_2O (*s*) to H_2O (*l*) phase change:
https://docs.google.com/spreadsheets/d/1Fd4hWnJBU2s9SiZQ-mwRdeoqAxg1BBaiThLvjl2ayug/edit?usp=sharing

Screenshot:



This is classic disordering transition and is discussion in detail in your textbooks, on yellowdig, and in my videos.

Formation reaction for steam (water vapor, H_2O (*g*)).

(A) Negative

(B) $H_2 (g) + \frac{1}{2} O_2 (g) \rightarrow H_2O (g)$

S_o (J/Kmol) =130.8 205.35 188.93

$\Delta S_f = S^o(H_2O\,(g)) - [S^o(H_2\,(g)) + \frac{1}{2} S^o(O_2\,(g))] = -44.5$ J/Kmol

Again, this is a very classic reaction and the negative change in entropy is most easily described as all the gas molecules having high entropy (as can be seen from the molar entropy values above) but you are reducing the total number of moles from 1.5 to 1 in this formation reaction.

C_3H_8 (*l*) → C_3H_8 (*aq*), Liquid propane going to aqueous propane.

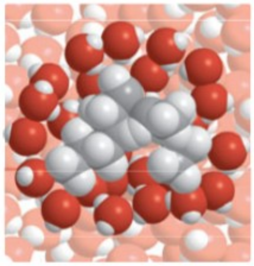


Fig. 2.14 When a hydrophobic molecule (in shades of gray) is surrounded by water, the H_2O molecules (with their oxygen atoms shown in red) form a cage, of which a cross-section is shown here. As a result of this acquisition of structure, the entropy of water decreases, so the dispersal of the hydrophobic molecule into the water is entropy opposed; its coalescence is entropy favored.

(A) Negative
(B) $C_3H_8 (l) \rightarrow C_3H_8 (aq)$

$\Delta S_f = S^o(C_3H_8\ (aq)) - S^o(C_3H_8\ (l)) = -80$ J/Kmol
* biopchem.education website

This is very well discussion in the course textbook, so I will refrain from a lengthy explanation in this document. However, I will reproduce one of the textbook figures (citation above) that well illustrates the more ordered of water around a hydrophobic molecule. This is a great example of where a molecule picture can really illustrate the point.

The hydrolysis of the dipeptide glycylglycine.

(A) Positive (or near zero) (would be my predictions… why? Cause most/all aqueous hydrolysis reactions have a positive Δs_{rxn})

(B) Glycylglycine + Water → 2 Glycine

$^+H_3NCH_2CONHCH_2COO^-\ (aq) + H2O\ (l) \rightarrow 2\ ^+H_3NCH_2COO^-\ (aq)$

$\Delta S_{rnx} = 2S^o(Gly\ (aq)) - S^o(GlyGly\ (aq)) - S^o(H_2O\ (l))$

* The solid Gly and Gly-Gly dipeptide values are listed at biopchem.education and in the textbook. However, finding good aqueous values is not easy and have quite an error associated with them. Assuming all the molecules are very water soluble and ionic, then hydrolysis almost always leads to a positive ΔS. From the quiz, you are told that this reaction has a negative ΔS, which would make it unusual an exception to the general rule. Why?? Damn good question!! The common reason is a large hydrophobic effect (like the problem above). However, Gly and Gly-Gly are both hydrophilic and well ionized (zwitterion) in aqueous solution. I honestly doubt this result is true and I bet the aqueous hydrolysis has a typical positive value for ΔS. I think what happens is that people use the assumption that the solid state Gly and Gly-Gly values can be substituted in for the aqueous values. This is a very poor assumptions and probably the mistake that leads this problem to be misinterpreted.
So, why include this on the exam if its so problematic? Biological samples are OFTEN problematic and thinking deeply about all the different possible molecular effects on energy (thermodynamics) is a great 'real-world' exercise. This problem isn't about right or wrong, its about interpretation and estimation.

4. (A) A sample of the monosaccharide (sugar) D-threose of mass 1.15 g was placed in a constant volume calorimeter and then ignited in the presence of excess oxygen. The temperature rose by 1.48°C. In a separate experiment in the same calorimeter, the combustion of 0.917 g of benzoic acid, for which the internal energy of combustion is -3226 kJ/mol, gave a temperature rise of 1.94°C. Calculate the enthalpy of formation of D-threose (10 pts). (B) Calculate the enthalpy of formation of D-threose and benzoic acid using either an arithmetic method (e.g., bond dissociation energies) or a computational method (e.g, *ab initio* electronic structure computational program like molcalc.org) (10 pts). (C) Compare the results from the calorimetric method used in part-A to the method used in part-B and provide a brief molecular level explanation for any potential differences (5 pts).

Similar to suggested homework exercise question 1.31 (P. Atkins et. al., Physical Chemistry for the Life Sciences, 2nd Ed.).

- https://en.wikipedia.org/wiki/Benzoic_acid
- https://en.wikipedia.org/wiki/Threose
- https://en.wikipedia.org/wiki/Calorimeter

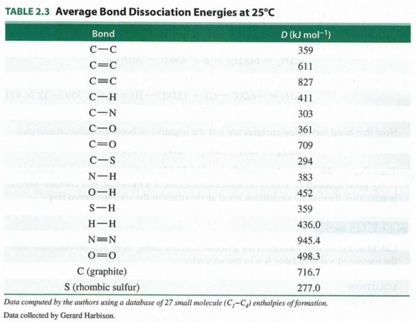


TABLE 2.3 Average Bond Dissociation Energies at 25°C

Bond	*D* (kJ mol^{-1})
C—C	359
C=C	611
C≡C	827
C—H	411
C—N	303
C—O	361
C=O	709
C—S	294
N—H	383
O—H	452
S—H	359
H—H	436.0
N≡N	945.4
O=O	498.3
C (graphite)	716.7
S (rhombic sulfur)	277.0

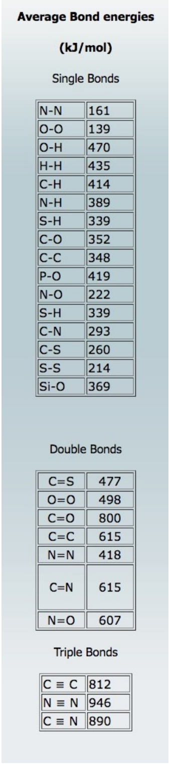
Data computed by the authors using a database of 27 small molecule (C_1–C_4) enthalpies of formation.

Data collected by Gerard Harbison.

$$C=\frac{q_{Vcal}}{\Delta T}=\frac{q_{Vba,comb}}{\Delta T}=\frac{-n\Delta U_{ba}}{\Delta T}=-\frac{0.917\,g(-3226\,kJ/mol)}{122.13\,g/mol(1.94\,K)}=12.5\,kJ/K$$

C = 12.5 kJ/K

Internal energy change of D-threose combustion is



Average Bond energies

(kJ/mol)

Single Bonds

N-N	161
O-O	139
O-H	470
H-H	435
C-H	414
N-H	389
S-H	339
C-O	352
C-C	348
P-O	419
N-O	222
S-H	339
C-N	293
C-S	260
S-S	214
Si-O	369

Double Bonds

C=S	477
O=O	498
C=O	800
C=C	615
N=N	418
C=N	615
N=O	607

Triple Bonds

C ≡ C	812
N ≡ N	946
C ≡ N	890

$$\Delta U=\frac{q_V}{n}=\frac{q_{Vcal}}{n_{threose}}=\frac{(C\,\Delta T)_{cal}}{(m/M)_{threose}}=\frac{12.5\,kJ/mol*1.48\,K*120.1\,g/mol}{1.15\,g}=-1930\,kJ/mol$$

$\Delta U_c = \Delta H_c$ = -1930 kJ/mol

$C_4H_8O_4$ (s) + $4O_2$ (g) → $4CO_2$ (g) + $4H_2O$ (l) - threose

$\Delta H_{comb} = 4\Delta H_f(CO_2) + 4\Delta H_f(H_2O) - (\Delta H_f(\text{threose}) + 4\Delta H_f(O_2))$

$\Delta H_f(\text{threose}) = 4\Delta H_f(CO_2) + 4\Delta H_f(O_2) - 4\Delta H_f(O_2) - \Delta H_{comb}$

ΔH_f (threose) = 4(-393.5 kJ/mol) + 4(-285.8 kJ/mol) – 4(0) – (-1930 kJ/mol) = -787.2 kJ/mol

(10 pts)

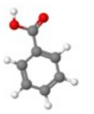
- **Arithmetic method (e.g., bond dissociation energies)**

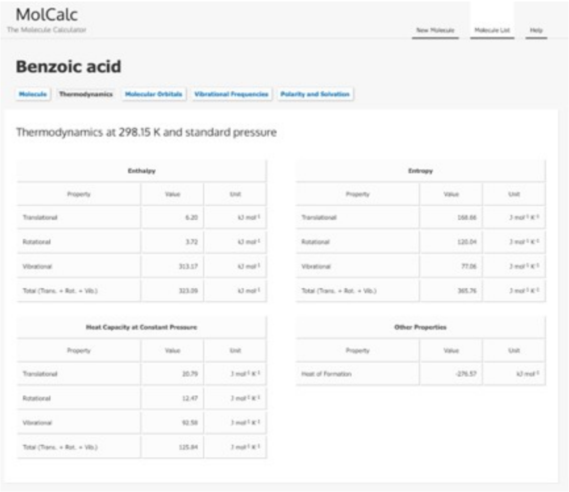
H_c (threose) = [4(O=O) + (3(C-C) + 3(O-H) + 5(C-H) + 3(C-O))] - [8(C=O) + 8(O-H)]
= [4(498 kJ/mol)+(3(359 kJ/mol)+3(452 kJ/mol)+5(411 kJ/mol)+3(361 kJ/mol))] - [8(709 kJ/mol) +8(452 kJ/mol)]
ΔH_c (threose) = - 1725 kJ/mol

(the same procedure can be done for benzoic acid)

(10 pts)

- **Computational method (molcalc.org)**
- Threose Heat of Formation (molcalc): -709.57 kJ/mol
- Benzoic Acid Heat of Formation (molcalc): -276.57 kJ/mol
- The exact ΔH_c can be calculated by also using molcalc to get the heat of formation of CO_2 and H_2O, then using the combustion balanced equation to determine.





Benzoic acid

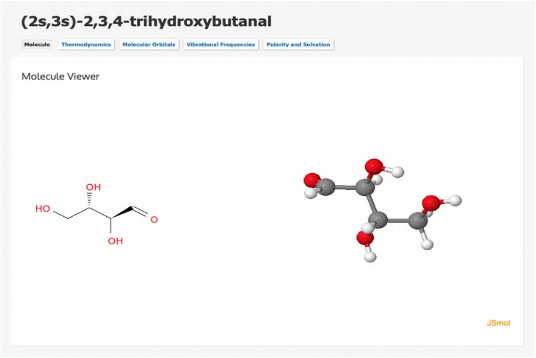
Thermodynamics at 298.15 K and standard pressure

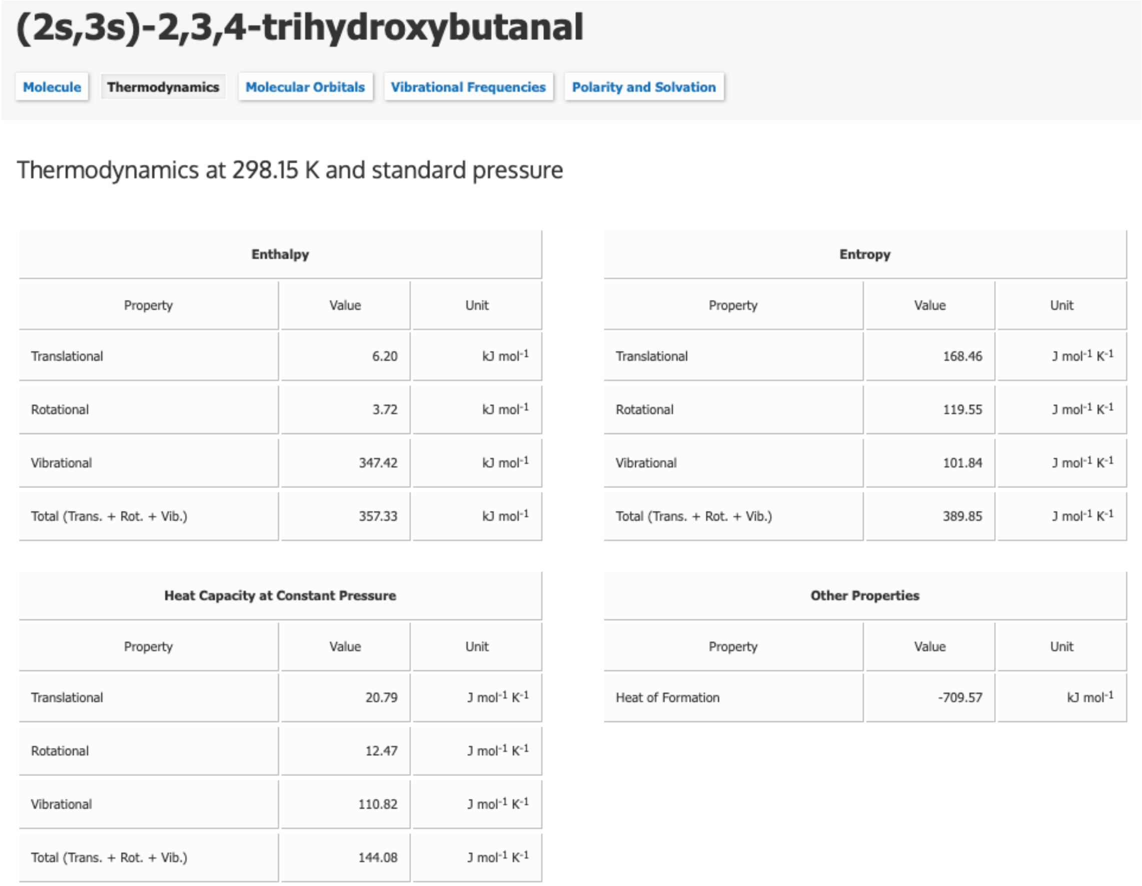
Enthalpy		
Property	Value	Unit
Translational	6.20	kJ mol^{-1}
Rotational	3.72	kJ mol^{-1}
Vibrational	313.17	kJ mol^{-1}
Total (Trans. + Rot. + Vib.)	323.09	kJ mol^{-1}

Entropy		
Property	Value	Unit
Translational	168.66	J mol^{-1} K^{-1}
Rotational	120.04	J mol^{-1} K^{-1}
Vibrational	77.06	J mol^{-1} K^{-1}
Total (Trans. + Rot. + Vib.)	365.76	J mol^{-1} K^{-1}

Heat Capacity at Constant Pressure		
Property	Value	Unit
Translational	20.79	J mol^{-1} K^{-1}
Rotational	12.47	J mol^{-1} K^{-1}
Vibrational	92.58	J mol^{-1} K^{-1}
Total (Trans. + Rot. + Vib.)	125.84	J mol^{-1} K^{-1}

Other Properties		
Property	Value	Unit
Heat of Formation	-276.57	kJ mol^{-1}





(2s,3s)-2,3,4-trihydroxybutanal

Thermodynamics at 298.15 K and standard pressure

Enthalpy		
Property	Value	Unit
Translational	6.20	kJ mol^{-1}
Rotational	3.72	kJ mol^{-1}
Vibrational	347.42	kJ mol^{-1}
Total (Trans. + Rot. + Vib.)	357.33	kJ mol^{-1}

Entropy		
Property	Value	Unit
Translational	168.46	J mol^{-1} K^{-1}
Rotational	119.55	J mol^{-1} K^{-1}
Vibrational	101.84	J mol^{-1} K^{-1}
Total (Trans. + Rot. + Vib.)	389.85	J mol^{-1} K^{-1}

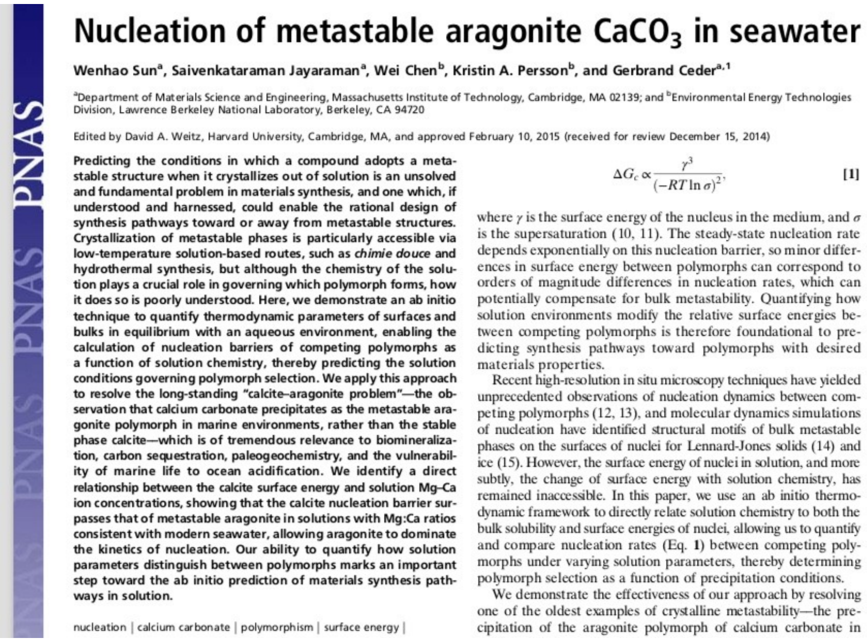
Heat Capacity at Constant Pressure		
Property	Value	Unit
Translational	20.79	J mol^{-1} K^{-1}
Rotational	12.47	J mol^{-1} K^{-1}
Vibrational	110.82	J mol^{-1} K^{-1}
Total (Trans. + Rot. + Vib.)	144.08	J mol^{-1} K^{-1}

Other Properties		
Property	Value	Unit
Heat of Formation	-709.57	kJ mol^{-1}

The bond enthalpy method assumes no intermolecular interactions and hence can deviate significantly from calorimetry methods, especially with solids or liquids with significant intermolecular interactions like hydrogen bonding, London dispersion forces, etc. This is also true for single molecule electronic structure calculations (the molcalc example). Sugars are well known to have strong hydrogen bonding in the solid and liquid phase. These molecules are further complex by their ability to form linear and cyclic structures. The ability to cyclize reduces in low number monosaccharides (like threose), but can still be significant. (5 pts)

5. Find and read a recent and original paper in the scientific literature that sounds interesting to you and which common thermodynamic parameters (i.e., ΔH, ΔS, ΔG, or C_p …) have been measured or computed. (A) Record the reference (citation) to this scientific paper (5 pts). (B) Summarize the significance of the paper in one paragraph (5 pts). (C) List the thermodynamic parameters determined and what methods were used to measure or compute the thermodynamics presented in the paper (15 pts).

Please try to choose a public open-access journal article and provide a link to the web or pdf version of the manuscript. If you choose a copyrighted article that is not publicly accessible, please provide a method of linking to this article. It is recommended that you make a web-accessible (publicly available) shared link to a pdf electronic version of the paper. This can be done from any of the commonly used cloud-storage services, i.e., Dropbox, Google Drive, Amazon Drive, Box, etc.



Nucleation of metastable aragonite $CaCO_3$ in seawater

Wenhao Sun[a], Saivenkataraman Jayaraman[a], Wei Chen[b], Kristin A. Persson[b], and Gerbrand Ceder[a,1]

[a]Department of Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, MA 02139; and [b]Environmental Energy Technologies Division, Lawrence Berkeley National Laboratory, Berkeley, CA 94720

Edited by David A. Weitz, Harvard University, Cambridge, MA, and approved February 10, 2015 (received for review December 15, 2014)

Predicting the conditions in which a compound adopts a metastable structure when it crystallizes out of solution is an unsolved and fundamental problem in materials synthesis, and one which, if understood and harnessed, could enable the rational design of synthesis pathways toward or away from metastable structures. Crystallization of metastable phases is particularly accessible via low-temperature solution-based routes, such as *chimie douce* and hydrothermal synthesis, but although the chemistry of the solution plays a crucial role in governing which polymorph forms, how it does so is poorly understood. Here, we demonstrate an ab initio technique to quantify thermodynamic parameters of surfaces and bulks in equilibrium with an aqueous environment, enabling the calculation of nucleation barriers of competing polymorphs as a function of solution chemistry, thereby predicting the solution conditions governing polymorph selection. We apply this approach to resolve the long-standing "calcite–aragonite problem"—the observation that calcium carbonate precipitates as the metastable aragonite polymorph in marine environments, rather than the stable phase calcite—which is of tremendous relevance to biomineralization, carbon sequestration, paleogeochemistry, and the vulnerability of marine life to ocean acidification. We identify a direct relationship between the calcite surface energy and solution Mg–Ca ion concentrations, showing that the calcite nucleation barrier surpasses that of metastable aragonite in solutions with Mg:Ca ratios consistent with modern seawater, allowing aragonite to dominate the kinetics of nucleation. Our ability to quantify how solution parameters distinguish between polymorphs marks an important step toward the ab initio prediction of materials synthesis pathways in solution.

nucleation | calcium carbonate | polymorphism | surface energy |

$$\Delta G_c \propto \frac{\gamma^3}{(-RT\ln\sigma)^2}, \qquad [1]$$

where γ is the surface energy of the nucleus in the medium, and σ is the supersaturation (10, 11). The steady-state nucleation rate depends exponentially on this nucleation barrier, so minor differences in surface energy between polymorphs can correspond to orders of magnitude differences in nucleation rates, which can potentially compensate for bulk metastability. Quantifying how solution environments modify the relative surface energies between competing polymorphs is therefore foundational to predicting synthesis pathways toward polymorphs with desired materials properties.

Recent high-resolution in situ microscopy techniques have yielded unprecedented observations of nucleation dynamics between competing polymorphs (12, 13), and molecular dynamics simulations of nucleation have identified structural motifs of bulk metastable phases on the surfaces of nuclei for Lennard-Jones solids (14) and ice (15). However, the surface energy of nuclei in solution, and more subtly, the change of surface energy with solution chemistry, has remained inaccessible. In this paper, we use an ab initio thermodynamic framework to directly relate solution chemistry to both the bulk solubility and surface energies of nuclei, allowing us to quantify and compare nucleation rates (Eq. **1**) between competing polymorphs under varying solution parameters, thereby determining polymorph selection as a function of precipitation conditions.

We demonstrate the effectiveness of our approach by resolving one of the oldest examples of crystalline metastability—the precipitation of the aragonite polymorph of calcium carbonate in

(A) Sun, Wenhao; Jayaraman, Saivenkataraman; Chen, Wei; Persson, Kristin; Ceder, Gerbrand. Nucleation of Metastable Aragonite $CaCO_3$ in Seawater, *Proceedings of the National Academy of Sciences of the United States of America,* 112(11), 3199-3204 (2015).

Or

Sun, W., Jayaraman, S., Chen, W., Persson, K., Ceder, G., *PNAS USA*, 112(11), 3199-3204 (2015).

(B) The common occurrence in natural environments of $CaCO_3$ polymorphs has long been noted and is very important in biology, geology and the interface of these two fields. Also, ocean acidification and the dissolution of $CaCO_3$ could play a huge role in changing the earth's oceans and marine life. Therefore, a complete understanding of the thermodynamics in $CaCO_3$ is critical. One important 'problem' has been the observation of natural environmental aragonite phase of $CaCO_3$ found in oceans, where to the best of our thermodynamic understanding, it is not the expected or stable phase. In spite of an early recognition that the occurrence and persistence of these coexisting solid phases (Calcite and Aragonite) is anomalous, the explanation of the phenomenon has remained remarkably elusive. The ability of this PNAS paper to identify a direct relationship between the calcite thermodynamic surface energy and solutions Mg-Ca ion concentrations, showing that the calcite nucleation barrier surpasses that of aragonite in solutions with Mg:Ca ratios found in seawater, allowing aragonite to dominate the kinetics of nucleation. The ability to quantify how solution parameters distinguish between polymorphs marks an important step toward the thermodynamic prediction pathways in solution for this process.

(C) Density Functional Theory (DFT) using VASP was used for all thermodynamic calculations. The primary thermodynamic parameters plotted, determined and calculated where $CaCO_3$ polymorphs (Calcite and Aragonite) ΔG, Equilibrium Constants (K), Surface Energy and K_{sp} (solubility constants). All four figures in this paper are plots of thermodynamic parameters associated with $CaCO_3$ polymorphs (Calcite and Aragonite).

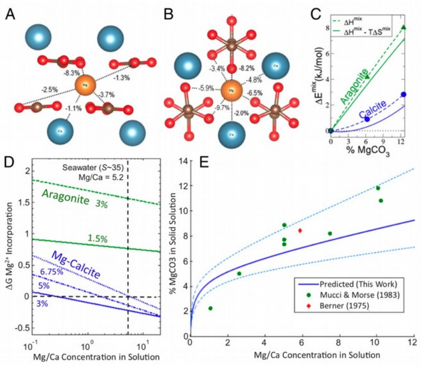


Fig. 1. Structural distortions in the (*A*) calcite and (*B*) aragonite lattices from Mg^{2+} substitution on the Ca^{2+} site. The Ca^{2+} site is ninefold coordinated in aragonite and sixfold coordinated in calcite, resulting in higher enthalpy of mixing of Mg^{2+} in the aragonite structure. (*C*) Calculated solid-state mixing energies of $CaCO_3$–$MgCO_3$. (*D*) Free energy of Mg^{2+} incorporation into $CaCO_3$ in open exchange with aqueous solution of given Mg:Ca ratio. Equilibrium $MgCO_3$ concentration of Mg–calcite corresponds to $\Delta G = 0$. Aragonite is not energetically favorable to incorporate Mg^{2+} at any Mg:Ca ratio. (*E*) Predicted equilibrium $MgCO_3$ concentration in calcite at a given solution Mg:Ca ratio, compared with experiments (23, 25) under similar conditions. Dashed lines correspond to uncertainties in the experimental $\log_{10} K_{sp}^{MgCO_3} = -7.8 \pm 0.3$.

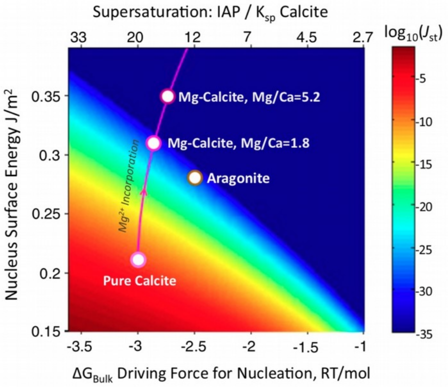


Fig. 3. Dimensionless $\log_{10}$ steady-state nucleation rates of calcium carbonate polymorphs at 25 °C plotted (color-coded) as a function of the nucleus surface energy and the bulk driving force for nucleation. Inhibition of calcite nucleation upon Mg uptake is primarily due to an increase in the surface energy, rather than from a reduction of bulk driving force from increased solubility. Example nucleation rates for aragonite and calcite at given Mg:Ca ratios are plotted at $\sigma = [a_{Ca^{2+}}][a_{CO_3^{2-}}]/K_{sp}^{calcite} = 20$, near the onset of aragonite nucleation.

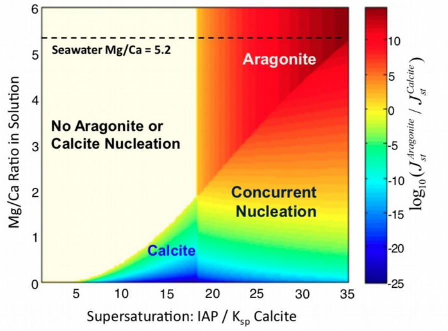


Fig. 4. Kinetic phase diagram of the relative nucleation rate between calcite and aragonite (color-coded) as a function of solution Mg:Ca ratio and the supersaturation. For Mg:Ca = 5.2 (modern seawater) only aragonite is preferred to nucleate. Concurrent nucleation of calcite and aragonite occurs for a broad span of supersaturations near Mg:Ca = 2.

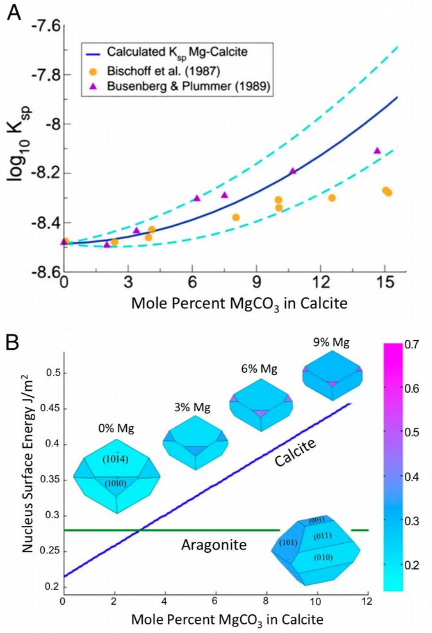


Fig. 2. (*A*) Predicted equilibrium solubility product of Mg–calcite. Dashed lines correspond to different reference states for the aqueous ion formation energies (*SI Appendix*, section S.I.5). (*B*) Morphology-averaged surface energies for hydrated Mg–calcite and aragonite as a function of Mg^{2+} uptake in calcite. Colors correspond to facet-specific surface energies. Aragonite does not incorporate Mg^{2+}.

Extra Credit: After your exam is turned in, it will be put into an anonymous peer review system and students will have 1-2 days to peer review (peer grade) three randomly assigned exams. Students who provide insightful comments and accurate evaluation (correct number of points) will receive 15 extra credit points (5 pts/exam). These points will only be given to students that provide detailed corrections, scores and comments on each of the 3 assigned exams and for each problem within the submitted exam. These comments and recommended scoring (points) for each problem can be done directly as comments in the Canvas LMS. However, it is recommended that the peer reviewer be provided as a separate single PDF annotated document with the associated corrections, comments, scores/points, etc (i.e., a graded annotated PDF document) added to the students originally submitted document.

I hope this rubric provides students a good template for how to organize and typeset solutions to exam and homework problems. This document was do in Libre Office. I chose this software because it is free, available for all major operating systems (pc, mac and linux) and has a suite of apps that is similar and compatible to MS-Office. I alternate between googles in-browser apps (google docs, sheets, etc) and Libre Office for basic word processing, spreadsheets, plotting and equation/formula typesetting. However, as the mathematics gets more complex and the scientific concepts and problems more difficult, it really really helps to learn at least one application or software package that is designed for math and science. I typically default to jupyter notebooks, mathematica and latex to create more complex documents that even now have the ability to be interactive and help illustrate very complex ideas and in our case molecular concepts.

Okay, this solution set / rubric has gotten long enough without me rambling more!!

Please please email me at yarger@biopchem.education if you find any typos are errors. In a document made in less than 5 hrs and being in a rush, I am sure there are several typos or small mistakes.

Cheers, Jeff Yarger
Sept. 11, 2019