Exam 1 – Fall 2018
BCH 341 - Physical Chemistry with a Biological Focus
Professor Jeff Yarger

Aug 26-28, 2018

DUE Tuesday, Aug 28, 2018 by 11:59 PM (UTC-7). Turn in completed exam as a single PDF document into the assignment link on ASU Canvas. Please make sure the completed exam is organized, self-contained and legible.

Name: ____ (as recorded on ASU Canvas)

ASU Email: ______________________________ ASU ID: __________________________

There are 6 multiple-choice questions and 6 numerical problems. Pick 5 multiple-choice questions and 5 numerical problems to work on this examination, for a total of 10 questions. The exam is worth a total of 100 points. Each multiple-choice question is worth 5 points and each numerical problem is worth 15 points. Please record your answers in the summary area on this first page of the exam. IF you do provide more than 5 answers on the multiple-choice section, then the first 5 answered will be graded. Please completely fill in ONE bubble per multiple choice question and fill in the blank with the numerical answer(s) and the associated units in the spaces below for the numerical problems (write N/A, if there is not a numerical answer associated with a specific problem).

Answer Summary

1. ⓐ ⓑ ⓒ ⓓ [✓ ⓔ]
2. ⓐ ⓑ [✓ ⓒ] ⓓ ⓔ
3. ⓐ ⓑ ⓒ ⓓ [✓ ⓔ]
4. [✓ ⓐ] ⓑ ⓒ ⓓ ⓔ
5. ⓐ ⓑ [✓ ⓒ] ⓓ ⓔ
6. ⓐ [✓ ⓑ] ⓒ ⓓ ⓔ

Multiple Choice Points (25 possible): 25
(Answer 5 of the 6 questions)

7. (A) 0.39-0.45 GPa (0°C-500°C), (B) No

Numerical Problem Points (75 possible): 75
(Answer 5 of the 6 questions)

8. (A) $q = -36.6\ kJ$ (glucose), (B) $q = -30.9\ kJ$ (galactose)

9. (A) $\Delta H^{o}_{iso} = \pm 4.45\ {}^{kJ}/_{mol}$ (butene), (B) 1,2-dichloroethylene, (C) t-butyl-ethene

10. fat releases more energy than sugar… by ~ factor of 2.

11. ~0.1°C to 0.3 °C (depending on body weight and heat capacity used).

12. Not numeric answer.

Total Points (100 possible): _________

1. State the condition(s) under which the following equation can be applied: $\Delta H = T \Delta S$

a) Constant Pressure
b) Reversible Process
c) Constant Temperature
d) None of the above (a-c)
e) All of the above (a-c)

2. Calculate the molar heat capacity of methane (CH_4) computationally (http://molcalc.org/ or some similar *ab initio* computational chemistry program) at standard temperature and pressure (STP). What molecular 'degree of freedom' contributes the most to the total heat capacity of methane at STP?

a) Vibrational
b) Rotational
c) Translational
d) None contribute
e) All contribute equally

3. Estimate (or calculate) the change in enthalpy (ΔH) of the process of carbon dioxide gas (CO_2 *(g)*) expanding from an initial volume of 20.0 liters at a temperature of 25°C to a final volume of 25.0 liters at a temperature of 100°C. Assume the gas obeys the idea gas equation of state under these conditions and that the gas is expanding under constant pressure conditions.

a) 0 kJ/mol
b) -1.6 kJ/mol
c) 1.6 kJ/mol
d) -2.5 kJ/mol
e) 2.5 kJ/mol

4. The melting of ice (H_2O (*s*)) at 0°C and 1 atm is

a) Endothermic
b) Exothermic
c) Isoenthalpic
d) Zero
e) none of the above

5. Which of the following combinations of conditions most influences a gas to behave ideally?
(i.e., follow the ideal gas equation of state, PV=NRT)

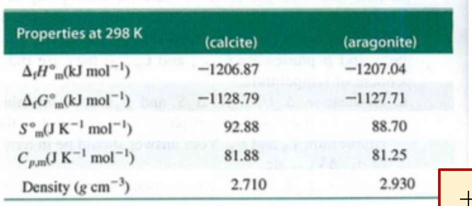
a) low pressure and low temperature
b) high pressure and low temperature
c) low pressure and high temperature
d) high pressure and high temperature

6. Predict whether the change in entropy (ΔS) is positive, negative or near zero for the hydrolysis of the dipeptide glycylglycine (Gly-Gly) at 5°C.

a) Positive
b) Negative
c) Near Zero

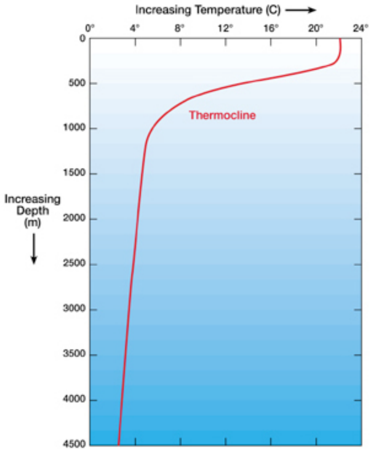
7. The shells of many marine organisms contain $CaCO_3$ (s), largely in the crystalline form known as calcite. There is a second crystalline form of $CaCO_3$ (s) know as aragonite. (A) Based on known thermodynamic and physical properties of these two crystalline forms, what conditions (pressures and temperatures) are required to make the direct conversion from calcite to aragonite spontaneous? (B) Are there any known places in the ocean where the aragonite crystalline form of $CaCO_3$ (s) would be expected to be the stable phase? [Report pressures in gigapascal, GPa, and temperatures in degrees Celsius (°C). Put a box around your Temperature-Pressure conditions for part-A]

* Ref. Tinoco Chp 3, Problem 15.



Properties at 298 K	(calcite)	(aragonite)
$\Delta_f H^\circ_m$(kJ mol^{-1})	−1206.87	−1207.04
$\Delta_f G^\circ_m$(kJ mol^{-1})	−1128.79	−1127.71
S°_m(J K^{-1} mol^{-1})	92.88	88.70
$C_{p,m}$(J K^{-1} mol^{-1})	81.88	81.25
Density (g cm^{-3})	2.710	2.930

+1 pt



(A) $CaCO_3$ (Calcite) → $CaCO_3$ (Aragonite)

+1 pt

$$\Delta G^o_{298K} = \Delta G^o_{298K}(Aragonite) - \Delta G^o_{298K}(Calcite)$$

$$\Delta G^o_{298K} = -1127.71 \, {}^{kJ}/_{mol} - \left(-1128.79 \, {}^{kJ}/_{mol}\right)$$

$$\Delta G^o_{298K} = 1.08 \, {}^{kJ}/_{mol}$$

+5 pts

$$dG = VdP - SdT + \sum_i \mu_i dN_i$$

+1 pt

$dG = VdP$ (constant T and N)

$\Delta G = V\Delta P$

$\Delta_r G(P_2) - \Delta_r G(P_1) = \Delta_r V(P_2 - P_1)$

$\Delta_r V(P_2 - P_1) = \Delta_r G(P_2) - \Delta_r G(P_1) = 0$ kJ – 1.08×10^3 J = -2.7731×10^{-6} m^3 (P_2 – 100,000 Pa)

$P_2 = 3.9 \times 10^8$ Pa = 0.39 GPa (or 3.9 kbar) at room temperature (298 K or 25°C)

This pressure corresponds to a depth of around 40,000 meters (http://docs.bluerobotics.com/calc/pressure-depth/)

This is way deeper than the oceans on earth exist.

+5 pts

As can be seen by the Temperature vs. Depth plot, at increasing depth, which corresponds to increasing pressure, we will generally have colder temperatures. Hence, instead of room temperature we can more accurately look at this transition at closer to 0°C.

With Cp values for both calcite and aragonite, you can calculate the ΔG at 0°C. However, the similar heat capacities and small temperature change indicates that this will NOT make much of an effect on the resulting pressure for the equilibrium phase transition between calcite and aragonite. Basically, iI will stay about the same, ~0.4 GPa.

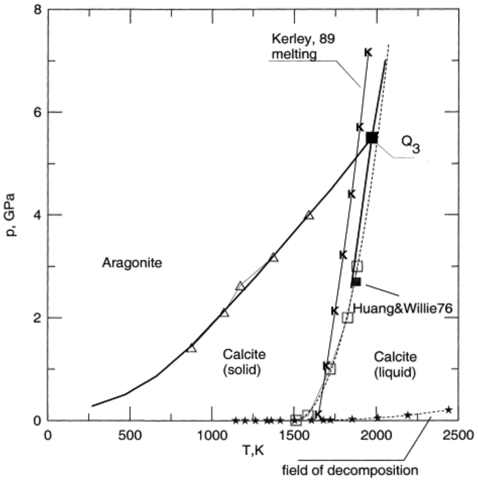
What about high temperatures? There do exist hydrothermal vents at significant depth in the ocean. Maybe this gets to conditions for this transformation to take place. About the hottest hydrothermal vent know is around 500°C. So, lets determine what pressure one can convert calcite to aragonite at 500°C.

$\Delta_f G$ (calcite, 0°C) = $\Delta_f H$ (0°C) – T $\Delta_f S$ (0°C)
$\Delta_f G$ (aragonite, 0°C) = $\Delta_f H$ (0°C) – T $\Delta_f S$ (0°C)

+1 pt

- This can be done explicitly or through ΔC_p (aragonite-calcite) = -0.63 J/Kmol
- 0.00068 kJ/mol difference (so very small)

$$\Delta G^o_{273K} = 1.08\, {}^{kJ}/_{mol}$$



$\Delta_f G$ (calcite, 500°C) = $\Delta_f H$ (500°C) – T $\Delta_f S$ (500°C) =
$\Delta_f G$ (aragonite, 500°C) = $\Delta_f H$ (500°C) – T $\Delta_f S$ (500°C) =

- 0.16455 kJ/mol difference

$$\Delta G^o_{773K} = 1.24\, {}^{kJ}/_{mol}$$

+5 pts

$dG = VdP$ (constant T and N)

+1 pt

$\Delta G = V\Delta P$

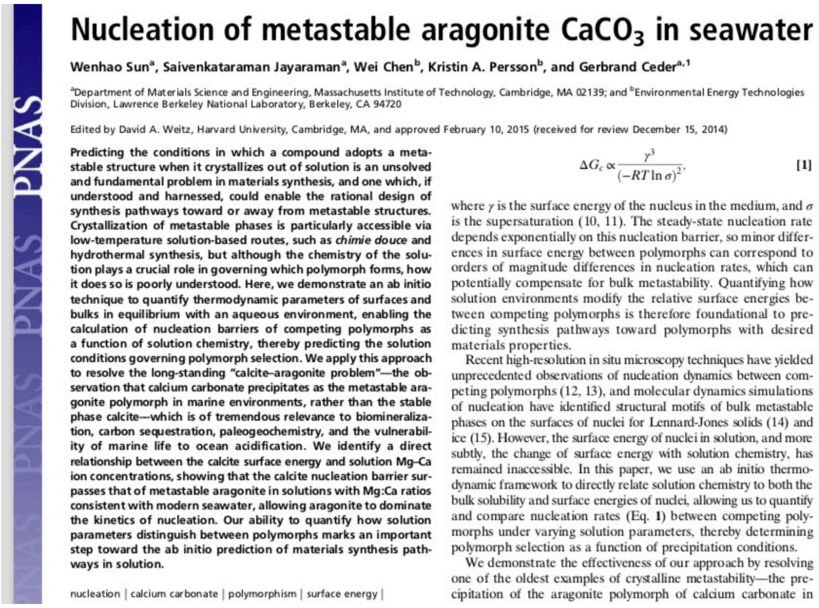
$\Delta_r G(P_2) - \Delta_r G(P_1) = \Delta_r V(P_2 - P_1)$

$\Delta_r V(P_2-P_1) = \Delta_r G(P_2) - \Delta_r G(P_1) = 0$ kJ – 1.24×10^3 J = -2.7731×10^{-6} m^3 (P_2 – 100,000 Pa)

$P_2 = 4.5 \times 10^8$ Pa = 0.45 GPa (or 4.5 kbar) at room temperature (773 K or 500°C)

(B) NO

+5 pts



Nucleation of metastable aragonite $CaCO_3$ in seawater

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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

www.pnas.org/cgi/doi/10.1073/pnas.1423898112

PNAS, March 17, 2015
Vol. 112 no. 11 pgs 3199-3204.

Proceedings of the National Academy of Sciences of the United States of America, 112(11), 3199-3204 (2015)

8. Alcoholic fermentation by microorganisms typically involves the breakdown of glucose into ethanol and carbon dioxide by the reaction

$$C_6H_{12}O_6\,(s) \rightarrow 2\,CO_2\,(g) + 2\,C_2H_5OH\,(l)$$

Controlling the temperature and pressure conditions of this reaction is critical in most alcoholic fermentation processes. Hence, being able to estimate how much heat is absorbed or liberated in this process is extremely important. (A) Calculate the amount of heat (*q*) liberated (or adsorbed) in a yeast brew upon fermentation of 100 g of glucose at 25°C and a pressure of 1 bar (STP). (B) There are numerous 'simple sugars' (monosaccharides) that can be substituted in place of glucose in this fermentation process. Assuming any monosaccharide can be catalytically broken down into ethanol and carbon dioxide in a similar manner as glucose (microorganisms), suggest an alternative monosaccharide to glucose if the goal is to reduce the amount of heat liberated during the alcoholic fermentation process, and where the starting amount of material (sugar) is always 100 grams. Show the calculations of heat (*q*) in support of your suggestion for a new monosaccharide to use in this new reduced heat liberation process.
[Express your answers for heat in units of kilojoules, kJ. Put a box around your numerical answers and the chemical formula, name and structure of your proposed monosaccharide alternative]

Tinoco Chp 2, Problem 22
& Quiz
& Practice Exam from Spring 2018

+1 pt

This can be assumed to be performed at constant pressure so, dH = d*q*

$$q_p = \Delta H = 2\Delta H_f^o(EtOH,l) + 2\Delta H_f^o(CO_2,g) - \Delta H_f^o(glucose,s)$$

$$= 2(-267.98) + 2(-393.51) - (-1274.4) = -66.6\,{}^{kJ}\!/_{mol}$$

+1 pt

100g glucose / 180.156 g/mol = 0.555 mol

$$q_p = -66.6\,{}^{kJ}\!/_{mol}(0.555\,mol) = -36.6\,kJ \text{ (glucose)}$$

+5 pts

(B) $C_3H_6O_3\,(s) \rightarrow 1\,CO_2\,(g) + C_2H_5OH\,(l)$ +1 pt

$$q_p = \Delta H = \Delta H_f^o(EtOH,l) + \Delta H_f^o(CO_2,g) - \Delta H_f^o(dihydroxyacetone,s)$$

$$= (-267.98) + (-393.51) - (-601.99) = -59.5\,{}^{kJ}\!/_{mol}$$

+1 pt

100g dihydroxyacetone / 90.08 g/mol = 1.11 mol

+1 pt

$$q_p = -59.5\,{}^{kJ}\!/_{mol}(1.11\,mol) = -66.1\,kJ \text{ (dihydroxyacetone)}$$

- So it liberates more heat. This is common for 'smaller' monosaccharides (even though I have not calculated them all, and it is possible one liberates less heat… but unlikely).

+5 pts

The easiest solution is another hexose with a more negative heat of formation, like Galactose.

$$q_p = \Delta H = 2\Delta H_f^o(EtOH,l) + 2\Delta H_f^o(CO_2,g) - \Delta H_f^o(galactose,s)$$

+2 pts

$$= 2(-267.98) + 2(-393.51) - (-1285.4) = -55.6\,{}^{kJ}\!/_{mol}$$

100g galactose / 180.156 g/mol = 0.555 mol

$$q_p = -55.6\,{}^{kJ}\!/_{mol}(0.555\,mol) = -30.9\,kJ \text{ (galactose)}$$

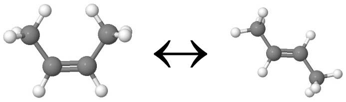
+5 pts

- So galactose liberates less heat.

9. Determine the standard enthalpies (energies) of gaseous *trans*-2-butene and *cis*-2-butene using a computational chemistry program (e.g., http://molcalc.org/ or any other *ab initio* computational chemistry package you want to use). (A) Calculate the thermodynamic enthalpy attributed to the steric repulsion in the *cis* compound relative to the *trans* compound (i.e., enthalpy of isomerism, ΔH_{iso}). Replace the methyl groups with several common functional groups, atoms or molecular moieties (R-groups) to (B) minimize and (C) maximize the ΔH_{iso}. [Report all enthalpies (ΔH) in kJ/mol. Put a box around your numerical answers (ΔH) and the chemical formula, name and structure of your proposed cis and trans compounds that (B) minimize and (C) maximize the enthalpy of isomerism]

Tinoco Chp 2, Problem 35

(A) Using Molcalc:



+2 pts

-14.85 kJ/mol -10.40 kJ/mol (MolCalc STP Heat of Formation)

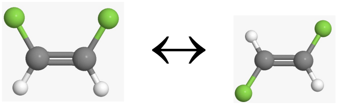
$$\Delta H^o_{iso}(cis \rightarrow trans) = \Delta H^o_f(trans) - \Delta H^o_f(cis) = -10.40 - (-14.85) = -4.45\, {}^{kJ}/_{mol}$$

$$\Delta H^o_{iso}(trans \rightarrow cis) = \Delta H^o_f(cis) - \Delta H^o_f(trans) = -14.85 - (-10.40) = 4.45\, {}^{kJ}/_{mol}$$

$$\Delta H^o_{iso} = \pm 4.45\, {}^{kJ}/_{mol}$$

+5 pts

(B) Using Molcalc:



16.68 kJ/mol 14.89 kJ/mol

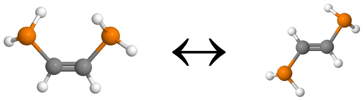
+2 pts

$$\Delta H^o_{iso} = \pm 1.79\, {}^{kJ}/_{mol}$$

+5 pts

- H, Cl are R-groups that would have a smaller ΔH_{iso}, but there are probably lots more.
- The example shown is 1,2-dichloroethylene

(C) Using Molcalc:



94.23 kJ/mol 78.71 kJ/mol

$$\Delta H^o_{iso} = \pm 15.52\, {}^{kJ}/_{mol}$$

+5 pts

- T-butyl, F, OH, CF_3, PH_2 are the R-groups that would have a smaller ΔH_{iso}, but there are probably lots more.
- The example shown is 1,2-diphosphine-ethylene

10. The thermodynamic properties of foods can be discussed in terms of the enthalpy of combustion per gram of food. Do you get more energy from the metabolism of one gram of 'sugar' or one gram of 'fat'? Answer this question quantitatively and with as much thermodynamic detail as possible. Use two of the following three methods to quantify your answer: (A) arithmetic method, (B) calorimetry, and/or (C) computational. The best way to quantitatively answer this question is to pick a simple 'sugar' and a simple 'fat' and perform exact thermodynamic calculations of the change in energy when undergoing 'metabolism' (or an idealized chemical reaction that represents metabolism).
[Report all thermodynamic values in SI units. Underline all assumptions and put a box around the calculated thermodynamic energies]

Tinoco Chp 2, Problem 21

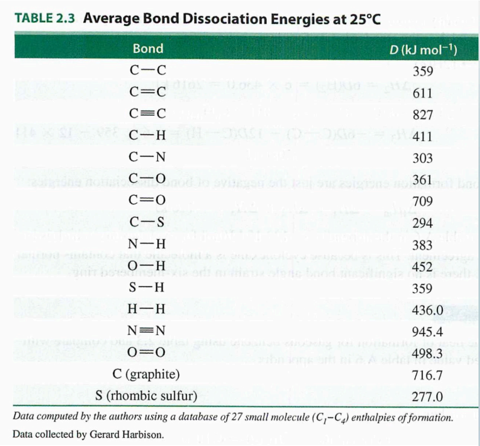
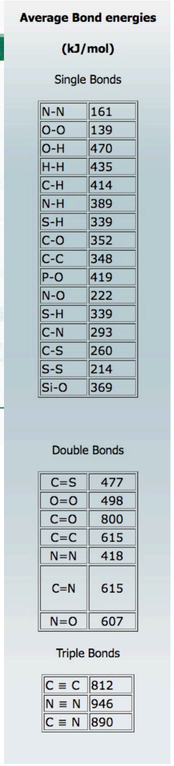


TABLE 2.3 Average Bond Dissociation Energies at 25°C

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.



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

Sugar: Glucose ($C_6H_{12}O_6$) – 180.156 g/mol
Fat: Lauric Acid ($C_{12}H_{24}O_2$) – 200.32 g/mol

+2 pts

Combustion Rxn:
$C_6H_{12}O_6\,(s) + 6\,O_2\,(g) \rightarrow 6\,CO_2\,(g) + 6\,H_2O\,(g)$
$C_{12}H_{24}O_2\,(s) + 17\,O_2\,(g) \rightarrow 12\,CO_2\,(g) + 12\,H_2O\,(g)$

NIST WebBook & Wikipedia
ΔH_c (Glucose) = -2805 kJ/mol (-15.6 kJ/g)
ΔH_c (Lauric Acid) = -7377 kJ/mol (-36.8 kJ/g)

+5 pts

(A) Arithmetic method

Bond Energies, Dissociation energies – Table 2.3 (Tinoco)

+2 pts

ΔH_c (Glucose) = [6(O=O) + (5(C-C) + 5(O-H) + 7(C-H) + 7(C-O))] - [12(C=O) + 12(O-H)]
= [6(498 kJ/mol)+(5(359 kJ/mol)+5(452 kJ/mol)+7(411 kJ/mol)+7(361 kJ/mol))] - [12(709 kJ/mol)+12(452 kJ/mol)]
ΔH_c (Glucose) = - 1483 kJ/mol = -8.2 kJ/g

ΔH_c (Lauric Acid) = [17(O=O) + (11(C-C) + 1(O-H) + 23(C-H) + (C-O) + (C=O)] - [24(C=O) + 24(O-H)]
= [17(498 kJ/mol)+(11(359 kJ/mol)+(452 kJ/mol)+23(411 kJ/mol)+(361 kJ/mol)+(709 kJ/mol)] - [24(709 kJ/mol)+24(452 kJ/mol)]
ΔH_c (Lauric Acid) = - 4474 kJ/mol = -22.3 kJ/g

Bond Energies, Dissociation energies – **AGAIN** using Avg Bond Energies Table
ΔH_c (Glucose) = [6(498 kJ/mol) + (5(348 kJ/mol) + 5(470 kJ/mol) + 7(414 kJ/mol) + 7(352 kJ/mol))] - [12(800 kJ/mol) + 12(470 kJ/mol)]
ΔH_c (Glucose) = - 2800 kJ/mol = -15.5 kJ/g

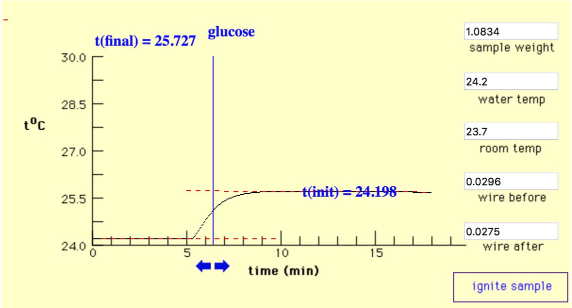
ΔH_c (Lauric Acid) = [17(498 kJ/mol) + (11(348 kJ/mol) + (470 kJ/mol) + 23(414 kJ/mol) + (352 kJ/mol) + (800 kJ/mol)] - [24(800 kJ/mol) + 24(470 kJ/mol)]
ΔH_c (Lauric Acid) = - 7042 kJ/mol = -35.2 kJ/g

+5 pts

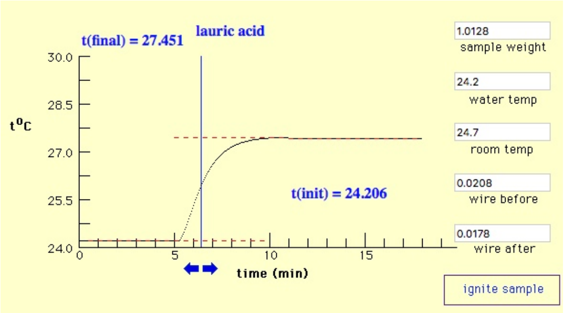
- http://sci-culture.com/chemistry/calculate_enthalpy.php
- Either arithmetic method shows that Lauric Acid (fat) releases more energy than Glucose (sugar).

(B) Calorimetry

Using Simulated Bomb Calorimeter (http://web.mst.edu/~gbert/cal/cal.html)



1.0834 sample weight
24.2 water temp
23.7 room temp
0.0296 wire before
0.0275 wire after

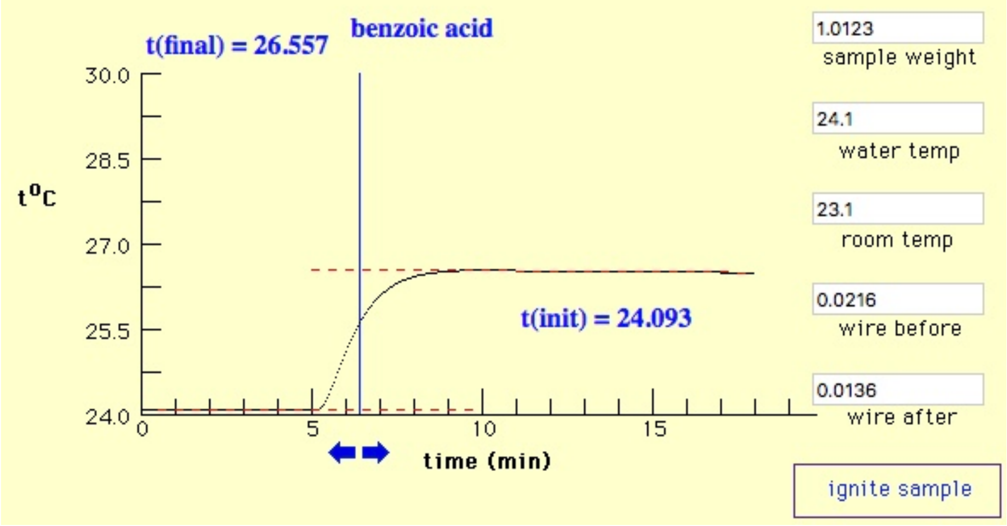


1.0128 sample weight
24.2 water temp
24.7 room temp
0.0208 wire before
0.0178 wire after

+5 pts

- You can tell just from the rate of the ΔT, that Lauric Acid (fat) releases more energy than Glucose (sugar).
- Exact Calculation is explained on website and requires Benzoic Acid Calibration to get the 'calorimeter constant'.

+5 pts



1.0123 sample weight
24.1 water temp
23.1 room temp
0.0216 wire before
0.0136 wire after

If you do an exact calculation, you get values similar to the ideal values:

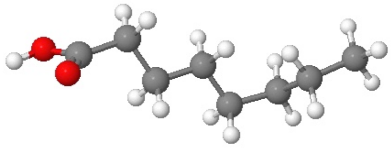
ΔH_c (Glucose) = -2800 kJ/mol (-15.5 kJ/g)
ΔH_c (Lauric Acid) = -7400 kJ/mol (-36.9 kJ/g)

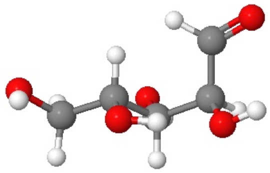
+5 pts

- Website with Bomb Calorimetry (calculation) explanation: https://youtu.be/6PxPz_-bv6U

(C) Computational

- Computational thermochemistry methods are covered at: https://biopchem.education/biopchem/courses/asu-bch-341-fall-2018/computational-biopchem/
- ASU has a site license for Gaussian 09 and 16 (and Gaussview 5 and 6) for linux and mac os. This is the commercial package I use most often. I also have some videos on using this package at:
  - https://www.youtube.com/user/PchemLab
  - https://www.youtube.com/watch?v=An35qX0fX7Q&t=4s
- For simplicity molcalc is more commonly used by students. However, it is limited on the number of atoms in the molecule and cannot run glucose or lauric acid. Instead we need to use smaller sugar and fat molecules. e.g. Caprylic Acid (fat) and Ribose (sugar)





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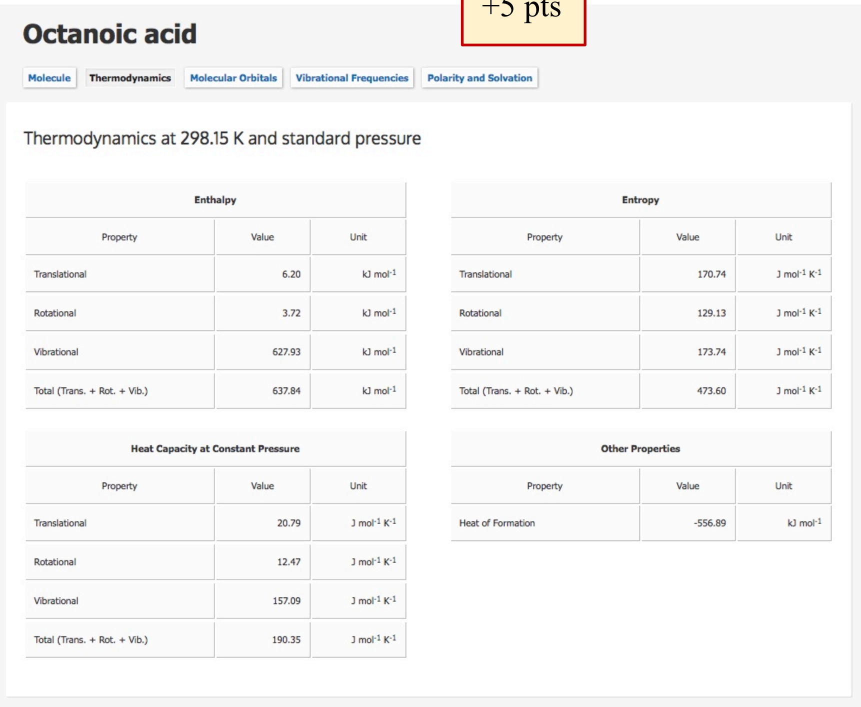


Octanoic acid

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	627.93	kJ mol^{-1}
Total (Trans. + Rot. + Vib.)	637.84	kJ mol^{-1}

Entropy		
Property	Value	Unit
Translational	170.74	J mol^{-1} K^{-1}
Rotational	129.13	J mol^{-1} K^{-1}
Vibrational	173.74	J mol^{-1} K^{-1}
Total (Trans. + Rot. + Vib.)	473.60	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	157.09	J mol^{-1} K^{-1}
Total (Trans. + Rot. + Vib.)	190.35	J mol^{-1} K^{-1}

Other Properties		
Property	Value	Unit
Heat of Formation	-556.89	kJ mol^{-1}

- Ribose Heat of Formation (molcalc): -900.36 kJ/mol

+5 pts

- For comparison (ΔH_f (glucose) = -1273 kJ/mol and ΔH_f (lauric acid) = -775 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.
- Caprylic Acid (fat) releases more energy than ribose (sugar).

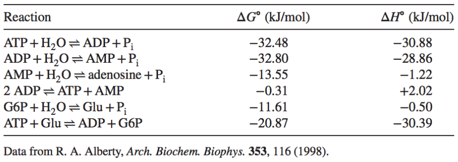
+2 pts

Students exams can be graded by reproducing their molcalc (computational) results and associated calculations.

11. Adenosine triphosphate (ATP) is a complex organic molecule that provides energy to drive many processes in living cells, often referred to as the 'molecular unit of currency' of intracellar energy transfer. When consumed, ATP converts either to adenosine diphosphate (ADP) or to adenosine monophosphate (AMP). A person will typically use a kilogram (1 kg) of ATP per hour or more. So, to get an idea of how much energy this can transfer, estimate the following: If all the energy from the hydrolysis of 1 kg of ATP into ADP was used to heat up your body, how much would your temperature increase? [Report the temperature increase in degrees Celsius. Underline all assumptions and put a box around your final answer]

Tinoco Chp 2, Problem 31

+5 pts



Reaction	$\Delta G°$ (kJ/mol)	$\Delta H°$ (kJ/mol)
$ATP + H_2O \rightleftharpoons ADP + P_i$	−32.48	−30.88
$ADP + H_2O \rightleftharpoons AMP + P_i$	−32.80	−28.86
$AMP + H_2O \rightleftharpoons \text{adenosine} + P_i$	−13.55	−1.22
$2\ ADP \rightleftharpoons ATP + AMP$	−0.31	+2.02
$G6P + H_2O \rightleftharpoons Glu + P_i$	−11.61	−0.50
$ATP + Glu \rightleftharpoons ADP + G6P$	−20.87	−30.39

Data from R. A. Alberty, *Arch. Biochem. Biophys.* **353**, 116 (1998).

In humans, approximately 60% of the energy released from the hydrolysis of ATP produces metabolic heat rather than fuel the actual reactions taking place. We are going to assume 100% for this problem (as the maximum amount of heat we could get from this chemical process. Also, the energy change (and heat) due to ATP hydrolysis depends upon the concentrations of the various participants in the reaction and physiological conditions. But we are going to use -30.88 kJ/mol (but it can vary between -20 and -70 kJ/mol, which is a very large variation and interesting to read about why!).

1000.0 g ATP / 507.18 g/mol = 1.97 mol of ATP

So, -30.88 kJ/mol * 1.978 mol = -60.89 kJ of heat

+5 pts

The **average specific heat capacity** of a **human body** is approximately 3500 J/(kg.K) at normal conditions. The average body mass globally is ~62 kg. So,

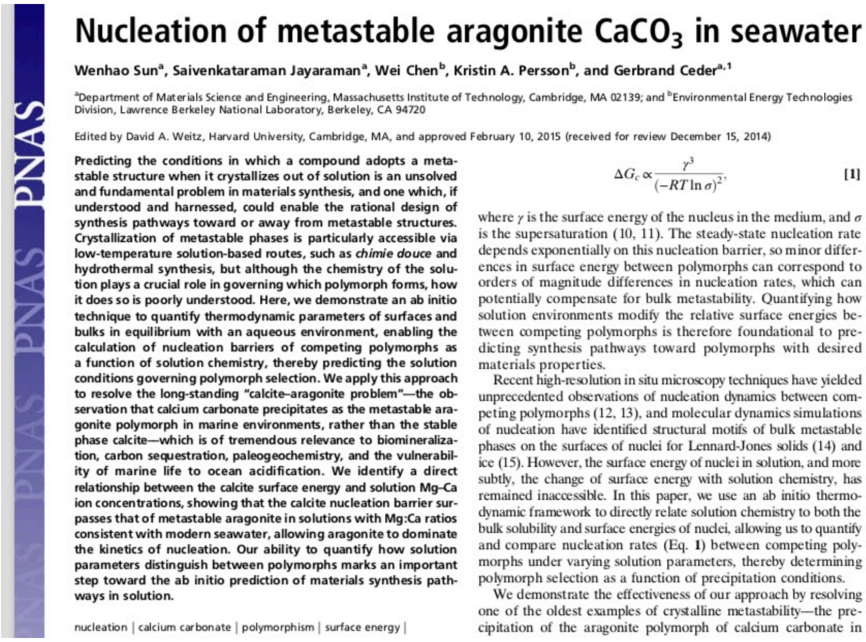
$$\Delta T = \frac{\Delta H}{C_p} = \frac{60.89 kJ}{(62 kg)\ 3.5\ {}^{kJ}/_{kgK}} = 0.3K\ or\ 0.3^oC$$

+5 pts

0.3°C…. So, not a lot every hour.

12. Find and read a paper in the scientific literature that sounds interesting to you. It needs to be a scientific paper in 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. (B) Summarize the purpose of the paper and why it was worthwhile in one paragraph. (C) List the thermodynamic parameters determined and what methods were used to measure or compute the thermodynamics presented in the paper.

Tinoco Chp 1, Problem 2



Nucleation of metastable aragonite $CaCO_3$ in seawater

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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).

+5 pts

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.

+5 pts

(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 (γ) and K_{sp} (solubility constants). All four figures in this paper are plots of thermodynamic parameters associated with $CaCO_3$ polymorphs (Calcite and Aragonite).

+5 pts

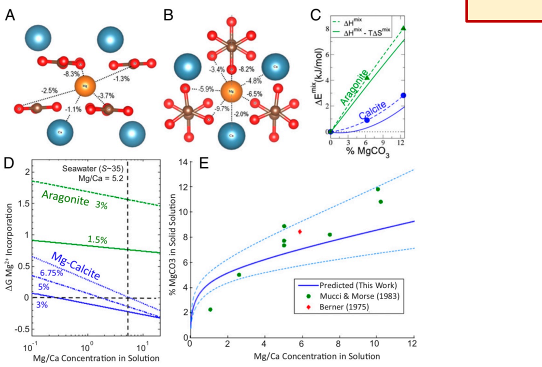

Fig. 1. Structural distortions in the (*A*) calcite and (*B*) aragonite lattices from Mg^{2+} substitution on the Ca^{2+} site. The Ca^{2+} site is ninefold coordinated in aragonite and sixfold coordinated in calcite, resulting in higher enthalpy of mixing of Mg^{2+} in the aragonite structure. (*C*) 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 $\log_{10} K_{sp}^{MgCO_3} = -7.8 \pm 0.3$.

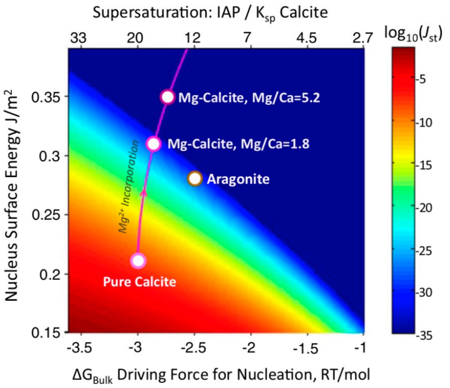

Fig. 3. Dimensionless $\log_{10}$ steady-state nucleation rates of calcium carbonate polymorphs at 25 °C plotted (color-coded) as a function of the nucleus surface energy and the bulk driving force for nucleation. Inhibition of calcite nucleation upon Mg uptake is primarily due to an increase in the 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.

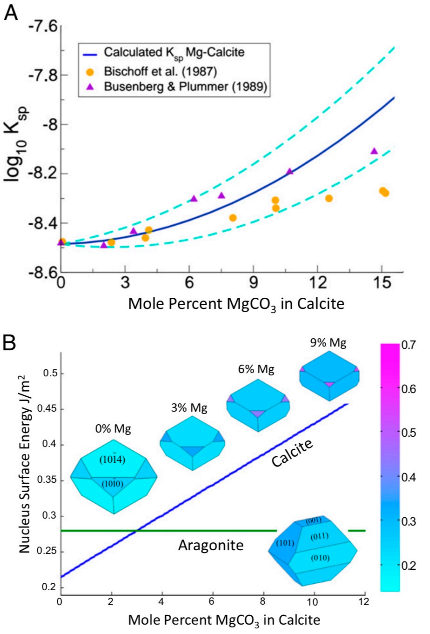

Fig. 2. (*A*) Predicted equilibrium solubility product of Mg–calcite. Dashed lines correspond to different reference states for the aqueous ion formation energies (*SI Appendix*, section S.I.5). (*B*) Morphology-averaged surface energies for hydrated Mg–calcite and aragonite as a function of Mg^{2+}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

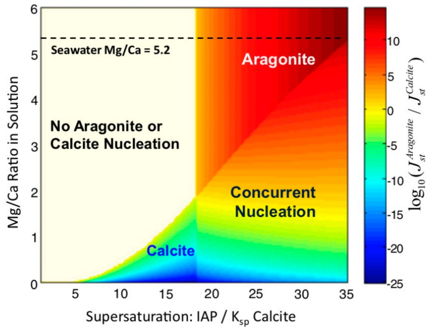

Fig. 4. Kinetic phase diagram of the relative nucleation rate between calcite and aragonite (color-coded) as a function of solution Mg:Ca ratio and the supersaturation. For Mg:Ca = 5.2 (modern seawater) only aragonite is preferred to nucleate. Concurrent nucleation of calcite and aragonite occurs for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