# Exam 1 – Spring 2019

BCH 341 - Physical Chemistry with a Biological Focus

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January 23-24, 2019

**DUE Thursday, Jan 24, 2019 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.**

Initials: _KEY____ Email: ___yarger@biopchem.education_____

To aid in the anonymous peer review process, you do NOT need to include your full name, just your first and last initials, and an email address for contact purposes. The exam consists of 8 numerical problems. The first 4 problems are worth 10 pts each and the last 4 problems are worth 15 pts each. Hence, the exam is worth a total of 100 points. You are required to explicitly show all equations, numerical calculations and associated units. 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.

1. The composition of planetary atmospheres is determined in part by the speeds of the molecules of the constituent gases because the faster moving molecules can reach escape velocity and leave the planet (often called Jeans escape, named after British astronomer Sir James Jeans). The major constituents of earth's atmosphere (air) are nitrogen, oxygen, argon, carbon dioxide, dihydrogen monoxide, neon, helium, methane, krypton and hydrogen gases. In general, the earth is too large to lose a significant proportion of its atmosphere through Jeans escape. (A) Of the major constituent gases in the earth's atmosphere, which are most susceptible to Jeans escape? (B) The exosphere is the high-altitude region where atmospheric density is sparse and Jeans escape occurs. For the atmospheric gases susceptible to Jeans escape (part-A), estimate the fraction of molecules traveling at a speed above the earth's escape velocity.

*Similar to suggested homework exercise question F.33 (P. Atkins et. al., Physical Chemistry for the Life Sciences, 2nd Ed.)*

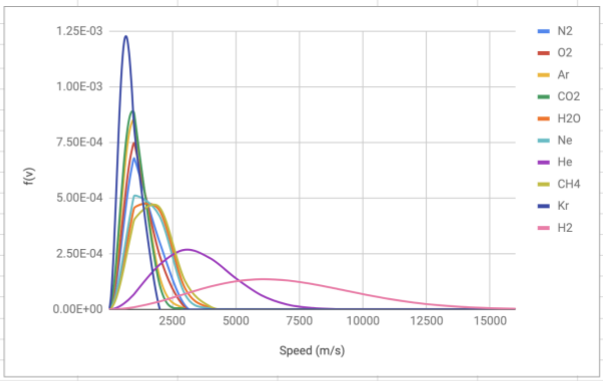
Wikipedia – Maxwell Speed Distribution

$$f(\nu) = 4\pi\left[\frac{m}{2\pi k_B T}\right]^{3/2} \nu^2 e^{-m\nu^2/2k_B T}$$

- Google Sheet Document.

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 |




+5 pts

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 |
| 8000 | 4.06E-22 | 6.14E-25 | 1.43E-30 | 1.88E-33 | 3.87E-15 | 1.20E-16 | 6.05E-06 | 9.21E-14 | 5.90E-62 | 1.14E-04 |
| 9000 | 2.02E-27 | 5.17E-31 | 3.51E-38 | 7.65E-42 | 1.64E-18 | 1.93E-20 | 1.29E-06 | 9.51E-17 | 4.97E-78 | 9.18E-05 |
| 10000 | 2.27E-33 | 7.96E-38 | 1.04E-46 | 3.04E-51 | 2.65E-22 | 1.05E-24 | 2.19E-07 | 4.15E-20 | 5.11E-96 | 6.83E-05 |
| 11000 | 5.78E-40 | 2.25E-45 | 3.75E-56 | 1.18E-61 | 1.64E-26 | 1.96E-29 | 2.95E-08 | 7.67E-24 | 6.43E-116 | 4.72E-05 |
| 12000 | 3.35E-47 | 1.18E-53 | 1.65E-66 | 4.54E-73 | 3.88E-31 | 1.25E-34 | 3.17E-09 | 6.05E-28 | 9.96E-138 | 3.04E-05 |
| 13000 | 4.42E-55 | 1.14E-62 | 8.81E-78 | 1.72E-85 | 3.53E-36 | 2.75E-40 | 2.72E-10 | 2.04E-32 | 1.90E-161 | 1.83E-05 |
| 14000 | 1.34E-63 | 2.04E-72 | 5.77E-90 | 6.46E-99 | 1.24E-41 | 2.07E-46 | 1.87E-11 | 2.94E-37 | 4.48E-187 | 1.03E-05 |
| 15000 | 9.23E-73 | 6.80E-83 | 4.63E-103 | 2.40E-113 | 1.68E-47 | 5.38E-53 | 1.04E-12 | 1.82E-42 | 1.30E-214 | 5.48E-06 |
| 16000 | 1.46E-82 | 4.21E-94 | 4.56E-117 | 8.89E-129 | 8.84E-54 | 4.83E-60 | 4.61E-14 | 4.82E-48 | 4.71E-244 | 2.73E-06 |
| | | | | | | | | | | |
| Mean Speed (m/s) | 1,319 | 1,234 | 1,104 | 1,052 | 1,645 | 1,553 | 3,489 | 1,745 | 762 | 6,910 |

$$\bar{\nu} = \left[\frac{8RT}{\pi M}\right]^{1/2}$$ *mean speed according to the Maxwell distribution.*

(A) Hydrogen and to a lesser extent Helium
(B) Integrate above ~ 11 km/s (earth's escape velocity) – Hydrogen ~ 5% , Helium ~ 0.05%.

+5 pts

2. (A) The helix to coil transition of an alanine peptide in water has been observed using numerous experimental techniques, which includes standard calorimetry. The two conformations of neighboring peptide groups in a polypeptide are shown to differ in energy by 1.3 kcal/mol. At body temperature what is the expected ratio of populations of the two conformations? (B) How do you expect the population of these two conformations to change over that standard temperature range of water (0°C to 100°C)? The 1.3 kcal/mol per residue was determined from the following journal article: Scholtz, J., et. al., *Proc. Natl. Acad. Sci. USA*, 88, 2854-2858 (1991). There are numerous other journal articles on the helix to coil transition in alanine peptides. It sometimes helps to look up other journal articles to get several perspectives and determine the variation in the experimentally determined energy. [Put a box around your numerical answer in part-A. For part-B, the recommended way to illustrate the answer is through a plot of population versus temperature.]

*Similar to suggested homework exercise question F.31 (P. Atkins et. al., Physical Chemistry for the Life Sciences, 2nd Ed.) and a brief illustration on F.3 p. 15.*

Body temperature is 310K

1.3 kcal/mol = 5.44 kJ/mol

(A) $$\frac{N_{coil}}{N_{helix}} = e^{-(E_{coil}-E_{helix})/RT} = e^{-(5440J/mol)/(8.3145J/Kmol*310K)} = 0.12$$

- In cymath: e^(-5440/(8.1345*310))

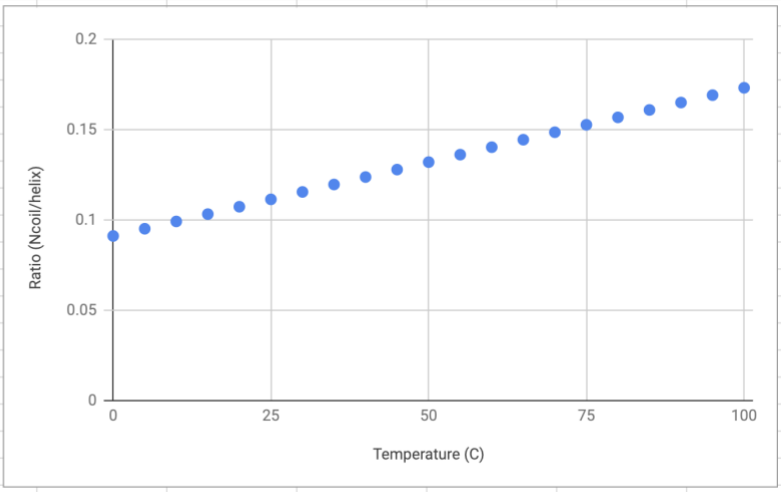
+5 pts

(B) Plot in Google Sheet.

Boltzmann Distribution for Helix to Coil Transition in Alanine Peptide in Water

| | | |
|---|---|---|
| ΔE (Helix-Coil) | 5440 | J/mol |
| R | 8.3145 | J/Kmol |

| T (oC) | Ratio (Ncoil/Nhelix) |
|---|---|
| 0 | 0.09114450543 |
| 5 | 0.09515470915 |
| 10 | 0.09919040408 |
| 15 | 0.1032483195 |
| 20 | 0.1073253508 |
| 25 | 0.1114185541 |
| 30 | 0.1155251418 |
| 35 | 0.1196424764 |
| 40 | 0.1237680656 |
| 45 | 0.127899556 |
| 50 | 0.1320347283 |
| 55 | 0.1361714909 |
| 60 | 0.1403078751 |
| 65 | 0.1444420289 |
| 70 | 0.1485722123 |
| 75 | 0.1526967918 |




+5 pts

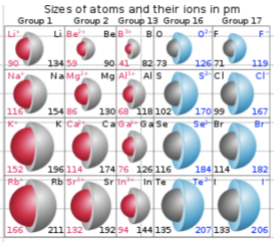
Looking that the PNAS paper, this is only the ΔH energy and lacks the TΔS component.

3. (A) Plot the Coulomb potential due to the nuclei at a point in a $Li^+ F^-$ ion pair located on a line half-way between the nuclei as the point approaches from infinity and ends at the mid-point between the nuclei. (B) Formation of LiF from the elements releases one of the highest energy per mass of reactants. What is the energy per mass of reactants for LiF and briefly discuss (from a chemical and/or molecular point of view) why it has one of the highest energies per mass of reactants. Also, provide the name and chemical formula of a compound that has a higher energy per mass of reactants.

*Similar to suggested homework exercise question F.28 (P. Atkins et. al., Physical Chemistry for the Life Sciences, 2nd Ed.).*

*(A) Google Sheet*

Coulomb Potential - Lithium Fluoride

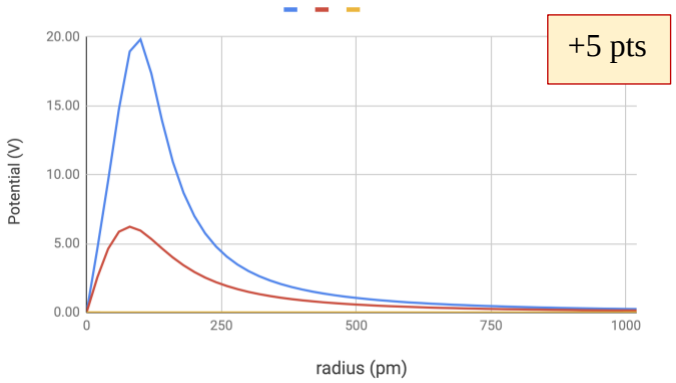



$$E_P = \frac{Q_1 Q_2}{4\pi\epsilon_o r}$$

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| Li+ radius | 90 | pm | | | | | |
| F- radius | 119 | pm | | | | | |
| Internuclear Sep. | 209 | pm | | | | | |
| rc | 104.5 | pm | | | | | |
| | | | | | | | |
| e | 1.60E-19 | C | | | | | |
| 4 pi epsilon | 1.11E-10 | J-1 C2 m-1 | | | | | |
| ke | 9.00E+09 | N m2 C-2 | | | | | |
| e*ke/10-12 | 1440 | J/C = Volt | | Angle = | 30 | 60 | 90 |

* Coulomb Potential
* https://en.wikipedia.org/wiki/Electric_potential_energy
*https://en.wikipedia.org/wiki/Coulomb%27s_law
* Q = Z e
* Wikipedia (https://en.wikipedia.org/wiki/Ionic_radius)

| r (pm) | 30 Degree - Potential (V) | 60 Degree - Potential (V) | 90 Degree - Potential (V) |
|---|---|---|---|
| 0 | 0.00 | 0.00 | 0.00 |
| 20 | 4.63 | 2.55 | 0.00 |
| 40 | 9.57 | 4.62 | 0.00 |




+5 pts

- *Blue curve is 30-degrees, Red curve is 60-degrees, and Yellow curve is 90-degrees.*
- *This is based on the position of the lithium and fluorine ions as the charge approaches the center point between the two ions along a straight line at the angle, theta, to the internuclear line. If we interpret the problem as specifying that the approach be at the angle theta equal 90-degrees, then r(Li+) = r(F-) all along the approach and the above relation tells us that the Coulomb potential is zero. All all values of r. The law of cosines is used for any other angle and two are shown, 30 and 60-degrees.*

(B) $\Delta H_f$ = -616 kJ/mol for LiF (https://en.wikipedia.org/wiki/Lithium_fluoride). Only BeO has a higher energy per mass of reactants, with a $\Delta H_f$ = -600 kJ/mol and a molecular mass that is 4 % less than LiF (while the $\Delta H_f$ are 3% different).

+5 pts

4. Each student has been assigned a common gas or volatile liquid compound. (A) Do you expect the compound you have been assigned to behave like an ideal gas at standard temperature and pressure? This can be quantified by comparing the molar volume (density) of the compound using the Van der Waals equation of state to that of the ideal gas equation of state. (B) For the compound you have been assigned, under what temperature and/or pressure conditions do you start to get significant deviations from ideality? This can be quantified by comparing the Van der Waals equation of state to that of the ideal gas equation of state at various temperatures and/or pressures and determining where the two equations of state start to vary significantly (e.g., there is a > 10% deviation between the two equations of state).

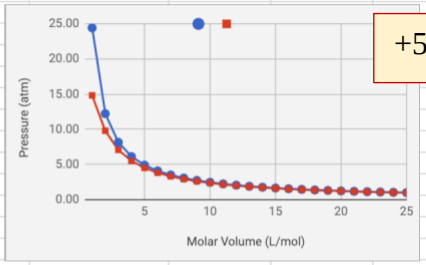
*Similar to suggested homework exercise question 1.6 (J. Allen, Biophysical Chemistry, 1st Ed.).*

- There is an error in Allen's textbook regarding the VDW gas problem and table. See the following public google sheet link for known errors in the textbook: https://docs.google.com/spreadsheets/d/1XRxjo6IyI94qLOqnAp72-lfv14GYZV_PVp3JuP90eh8/edit?usp=sharing
- https://en.wikipedia.org/wiki/Van_der_Waals_equation
    - Error regarding ref 23 – Become a Wikipedia contributor and get this corrected for extra credit. Salzman is a professor at U of A (not ASU) and contributing to Wikipedia is a GREAT thing to do and contribute to decentralized free information. Also, this is a great topic to contribute on… Normalizing Equations of State to critical point temperature, pressure, volume, etc is really useful and it would be great to get this point corrected on Wikipedia and potentially even expanded upon!! Extra extra credit for anyone that expands upon this concept. You can propose new material for Wikipedia and Prof. Yarger or Mujica are happy to proofread any material you want to add to Wikipedia before submitting it to ensure everything is correct and written properly.
- https://en.wikipedia.org/wiki/Van_der_Waals_constants_(data_page)
- Plotting the VDS EoS vs. the Ideal Gas EoS below Tc, Pc (reduced form) is where things really get interesting and educational. I will save this idea for the final exam.

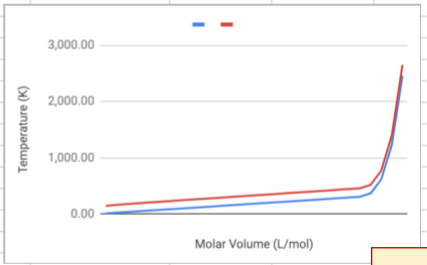
Example for Acetic Acid Below. This will vary a lot depending on the assigned molecule.
(A) Yes or No, depending on Molecule assigned. (B) EoS are more alike at large molar volumes.

**Van der Waals versus Ideal Gas - Equation of State**

| Isothermal: | T (Kelvin) = | 298 | | | | |
|---|---|---|---|---|---|---|
| | Idea Gas EoS | VDW EoS | % Variation in | VDW Constants | | |
| V (L/mol) | P (atm) | P (atm) | Pressure | a (L2 bar / mol2) | b (L / mol) | Cmpd |
| 1 | 24.44 | 14.83 | 39.33% | 11.77 | 0.07685 | *Acetic Acid* |
| 2 | 12.22 | 9.79 | 19.88% | | | |
| 3 | 8.15 | 7.06 | 13.33% | | | |
| 4 | 6.11 | 5.50 | 10.03% | | | |
| 5 | 4.89 | 4.49 | 8.05% | | | |
| 6 | 4.07 | 3.80 | 6.73% | | | |
| 7 | 3.49 | 3.29 | 5.79% | | | |
| 8 | 3.05 | 2.90 | 5.08% | | | |
| 9 | 2.72 | 2.59 | 4.53% | | | |
| 10 | 2.44 | 2.34 | 4.09% | | | |
| 11 | 2.22 | 2.14 | 3.73% | | | |
| 12 | 2.04 | 1.97 | 3.42% | | | |
| 13 | 1.88 | 1.82 | 3.17% | | | |
| 14 | 1.75 | 1.69 | 2.95% | | | |
| 15 | 1.63 | 1.58 | 2.76% | | | |
| 16 | 1.53 | 1.49 | 2.60% | | | |
| 17 | 1.44 | 1.40 | 2.45% | | | |
| 18 | 1.36 | 1.33 | 2.32% | | | |
| 19 | 1.29 | 1.26 | 2.20% | | | |
| 20 | 1.22 | 1.20 | 2.10% | | | |
| 21 | 1.16 | 1.14 | 2.00% | | | |
| 22 | 1.11 | 1.09 | 1.92% | | | |
| 23 | 1.06 | 1.04 | 1.84% | | | |
| 24 | 1.02 | 1.00 | 1.77% | | | |
| 25 | 0.98 | 0.96 | 1.70% | | | |
| 30 | 0.81 | 0.80 | 1.43% | | | |
| 50 | 0.49 | 0.48 | 0.90% | Blue (circles) | Ideal Gas EoS | |
| 100 | 0.24 | 0.24 | 0.50% | Red (squares) | VDW EoS | |
| | | | | | | |
| Isobaric: | P (atm) = | 1.01 | | | | |
| | Idea Gas EoS | VDW EoS | % Variation in | | | |
| V (L/mol) | T (K) | T (K) | Temperature | | | |
| 1 | 12.31 | 146.38 | -1089.26% | | | |
| 2 | 24.62 | 164.52 | -568.33% | | | |
| 3 | 36.92 | 178.92 | -384.56% | | | |




+5 pts




+5 pts

5. Use the equipartition theorem to calculate the contribution of molecular motion to the total energy of a sample of 1 mole of (i) argon, (ii) nitrogen, (iii) carbon dioxide, (iv) water vapor and (v) methane at room temperature and pressure. (B) Compare the values calculated using the equipartition theorem to those from ab initio electronic structure computational calculates (from a program like molcalc.org).

*Similar to suggested homework project question 1.47(f) (P. Atkins et. al., Physical Chemistry for the Life Sciences, 2nd Ed.).*
** https://en.wikipedia.org/wiki/Equipartition_theorem*
** 1/2KT – for each degree of freedom – Translation, Rotation, Vibration*
** Assumption is vibrations are not significant in small molecular near room temperature.*

Equipartition Theorem & Electronic Structure Calculations (AM1 level, Molcalc.org)

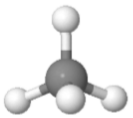
| | | |
|---|---|---|
| U = n/2 R T | | |
| R | 8.3145 | J/Kmol |
| T | 298.15 | K |

+5 pts

+5 pts

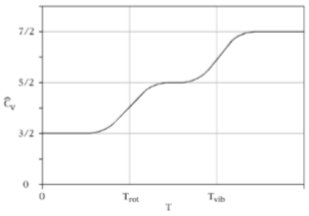
Cp = Cv + R

| | Equipartition | | | | | Heat Capacity (Cv) | | | Heat Capcity (molcalc) | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **Molecule** | **Trans.** | **Rot.** | **Vib.** | **Total** | **U (kJ/mol)** | **Trans.** | **Rot.** | **Vib.** | **Trans.** | **Rot.** | **Vib.** | **U (kJ/mol)** |
| Ar | 3 | 0 | 0 | 3 | **3.72** | 3/2 R | | 0 | 20.8 | | | **3.72** |
| N2 | 3 | 2 | 0 | 5 | **6.20** | 3/2 R | R | 0 | 20.8 | 8.31 | 0 | **6.20** |
| CO2 | 3 | 2 | 0 | 5 | **6.20** | 3/2 R | R | 0 | 20.8 | 8.31 | 10.5 | **9.33** |
| H2O | 3 | 3 | 0 | 6 | **7.44** | 3/2 R | 3/2 R | 0 | 20.8 | 12.5 | 0.13 | **7.49** |
| CH4 | 3 | 3 | 0 | 6 | **7.44** | 3/2 R | 3/2 R | 0 | 20.8 | 12.5 | 2.3 | **8.14** |



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 | 2.25 | J mol⁻¹ K⁻¹ |
| Total (Trans. + Rot. + Vib.) | 35.51 | J mol⁻¹ K⁻¹ |




** Molcal.org

+5 pts

* $CO_2$ would be close if vib. was taken into account.
* Show one of the molcal.org, CH4, all calculated at molcalc.org

6. (A) A sample of the sugar D-ribose of mass 1.525 g was placed in a constant volume calorimeter and then ignited in the presence of excess oxygen. The temperature rose by 1.91°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-ribose. (B) Calculate the enthalpy of formation of D-ribose 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). (C) Briefly compare the results from the calorimetric method used in part-A to the method used in part-B.

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

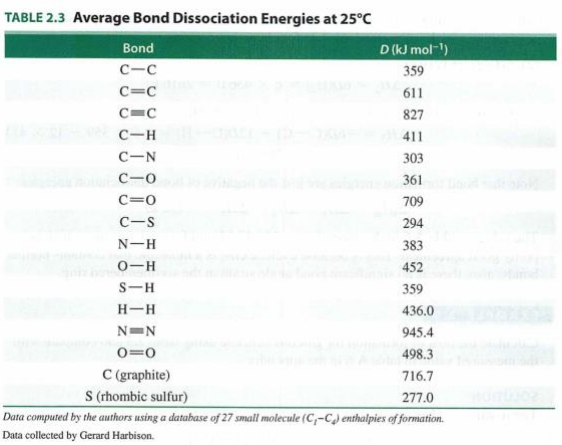


TABLE 2.3 Average Bond Dissociation Energies at 25°C

| 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.

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

$$C = \frac{q_{Vcal}}{\Delta T} = \frac{q_{Vba\ combustion}}{\Delta T} = \frac{-n\Delta U_{ba}}{\Delta T} = \frac{-0.916g(-3226kJ/mol)}{122.13g/mol(1.94K)}$$

C = 12.5 kJ/K

Internal energy change of D-ribose combustion is

$$\Delta U = \frac{q_V}{n} = \frac{-q_{Vcal}}{n_{ribose}} = -\frac{(C\Delta T)_{cal}}{(m/M)_{ribose}} = -\frac{12.5kJ/mol * 0.94K * 150.1g/mol}{1.525g}$$

$\Delta U_c = \Delta H_c$ = -2387 kJ/mol +5 pts

$C_5H_{10}O_5$ (s) + $5O_2$ (g) → $5CO_2$ (g) + $5H_2O$ (l)

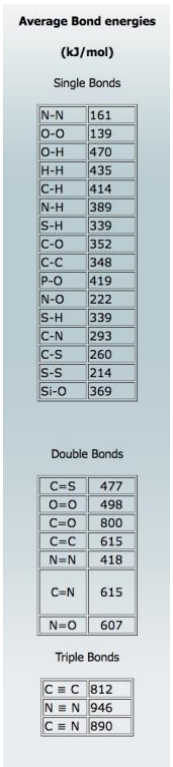
$\Delta H_{comb} = 5\Delta H_f(CO_2) + 5\Delta H_f(H_2O) - (\Delta H_f(\text{Ribose}) + 5\Delta H_f(O_2))$

$\Delta H_f$ (ribose) = $5\Delta H_f(CO_2) + 5\Delta H_f(O_2) - 5\Delta H_f(O_2) - \Delta H_{comb}$ +5 pts

$\Delta H_f$ (ribose) = 5(-393.5 kJ/mol) + 5(-285.8 kJ/mol) – 5(0) – (-2387 kJ/mol) = -1009 kJ/mol

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

$H_c$ (Ribose) = [5(O=O) + (4(C-C) + 4(O-H) + 6(C-H) + 4(C-O))] - [10(C=O) + 10(O-H)]
= [5(498 kJ/mol)+(4(359 kJ/mol)+4(452 kJ/mol)+6(411 kJ/mol)+4(361 kJ/mol))] - [10(709 kJ/mol)+10(452 kJ/mol)]
$\Delta H_c$ (Ribose) = - 1966 kJ/mol +5 pts



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 |

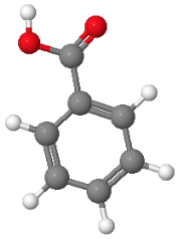
Triple Bonds

| | |
|---|---|
| C ≡ C | 812 |
| N ≡ N | 946 |
| C ≡ N | 890 |

- **Computational method (molcalc.org)**
- Ribose Heat of Formation (molcalc): -900.36 kJ/mol
- Benzoic Acid Heat of Formation (molcalc): -276.57 kJ/mol
- The exact $\Delta H_c$ can be calculated by also using molcalc to get the heat of formation of $CO_2$ and $H_2O$,

MolCalc
The Molecule Calculator

New Molecule



## Benzoic acid

Molecule | Thermodynamics | Molecular Orbitals | Vibrational Frequencies | Polarity and Solvation

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**

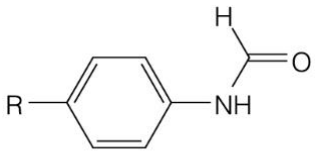
| Property | Value | Unit |
|---|---|---|
| Heat of Formation | -276.57 | kJ mol$^{-1}$ |

then using the combustion balanced equation to determine.

| Constant Volume Calorimetry - Heat of Combustion & Formation | | | | | | |
|---|---|---|---|---|---|---|
| | | | | | | |
| Compound | M (g/mol) | Mass (g) | ΔT (K) | ΔU (kJ/mol) | ΔHcomb (kJ/mol) | ΔHfus (kJ/mol) |
| Benzoic Acid (ba) | 122.12 | 0.917 | 1.94 | -3226 | -3226 | -385.2 |
| D-Ribose | 150.13 | 1.525 | 1.91 | -2,387 | -2,387 | -1,009 |

- Google Sheet

7. The following is an example of a structure-activity relation (SAR), in which it is possible to correlate the effect of a structural change in a compound with its biological function. The use of SARs can improve the design of drugs for the treatment of disease because it facilitates the prediction of the biological activity of a compound before it is synthesized. The binding of non-polar groups of amino acid to hydrophobic sites in the interior of proteins is governed largely by hydrophobic interactions. (A) Consider a family of hydrocarbons R-H. The hydrophobicity constants, π, for R = $CH_3$, $CH_2CH_3$, $(CH_2)_2CH_3$, $(CH_2)_3CH_3$, and $(CH_2)_4CH_3$, are, respectively, 0.5, 1.0, 1.5, 2.0 and 2.5. Use these data to predict the π value of $(CH_2)_7CH_3$. (B) The equilibrium constant $K_1$ for the dissociation of inhibitors (1) from the enzyme chymotrypsin (Atlas P3) were measured from different substituents R:




1

| **R** | **$CH_3CO$** | **CN** | **$NO_2$** | **$CH_3$** | **Cl** | **$(CH_2)_2CH_3$** |
|---|---|---|---|---|---|---|
| **π** | -0.20 | -0.025 | 0.33 | 0.50 | 0.90 | 1.5 |
| **$K_1$** | $2.34x10^{-2}$ | $1.26x10^{-2}$ | $3.72x10^{-3}$ | $1.78x10^{-3}$ | $3.98x10^{-4}$ | $5.01x10^{-5}$ |

Plot $K_1$ against π and determine the best fit to the data that allows for extrapolation. Hint: If the direct plot of $K_1$ against π is not linear, it is typically possible to find a functional form of $K_1$ and π that produces a linear plot and then use a standard linear fitting algorithm for the best fit to the data. (C) Predict the value of $K_1$ for R = H and R = $(CH_2)_7CH_3$.

*Similar to suggested homework project question 2.31 (P. Atkins et. al., Physical Chemistry for the Life Sciences, 2nd Ed.).*

$C_nH_{2n+2}$
Or
R-H where R= $C_nH_{2n+1}$
π = n/2

| n | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 |
|---|---|---|---|---|---|---|---|---|
| π | 0.5 | 1 | 1.5 | 2 | 2.5 | 3 | 3.5 | 4 |

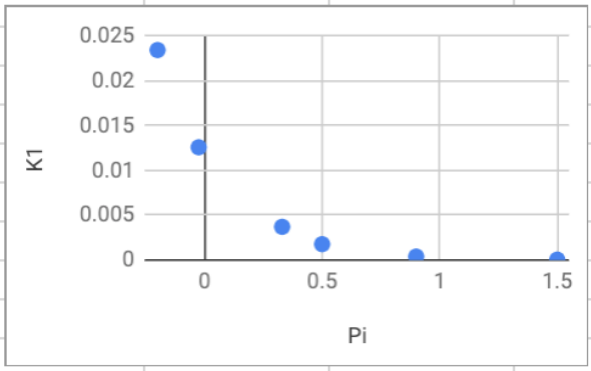
**(A)**
**$(CH_2)_7CH_3 = C_nH_{2n+1} = C_8H_{17}$**
**n=8**
**π = 4**

+5 pts

- Google Sheet for (B) and (C) - Next Page.

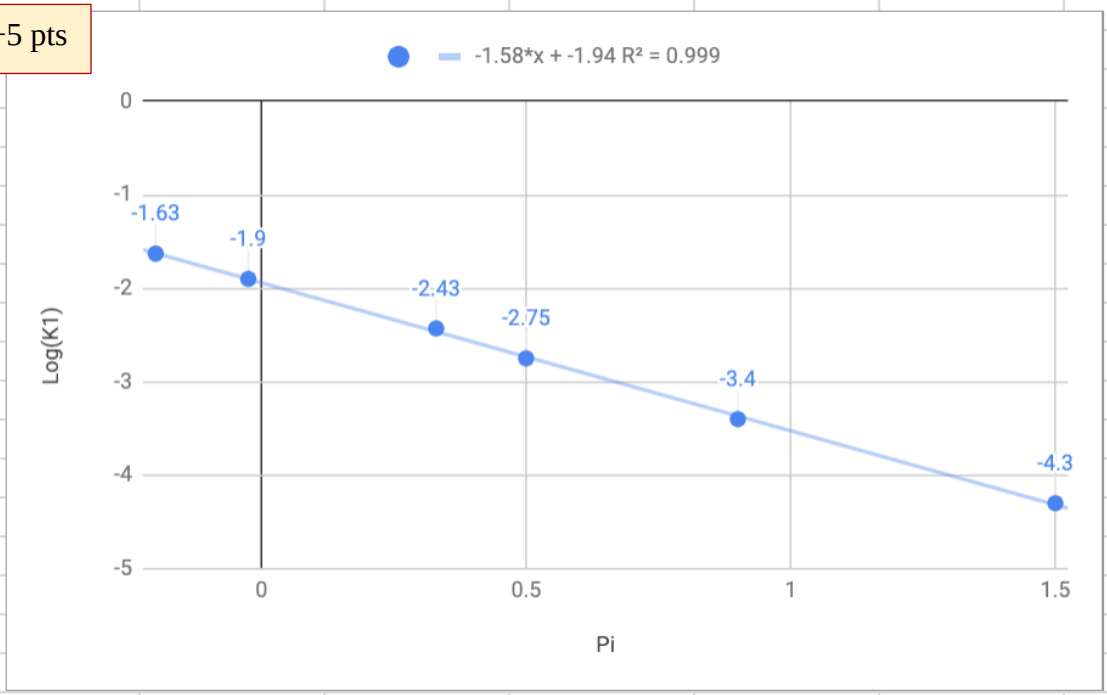
## Equilibrium Constant - Binding

| p | log K1 | K1 |
|---|---|---|
| -0.2 | -1.63 | 0.02344228815 |
| -0.025 | -1.9 | 0.01258925412 |
| 0.33 | -2.43 | 0.003715352291 |
| 0.5 | -2.75 | 0.00177827941 |
| 0.9 | -3.4 | 0.000398107170 |
| 1.5 | -4.3 | 0.000050118723 |




* Not Linear

+5 pts

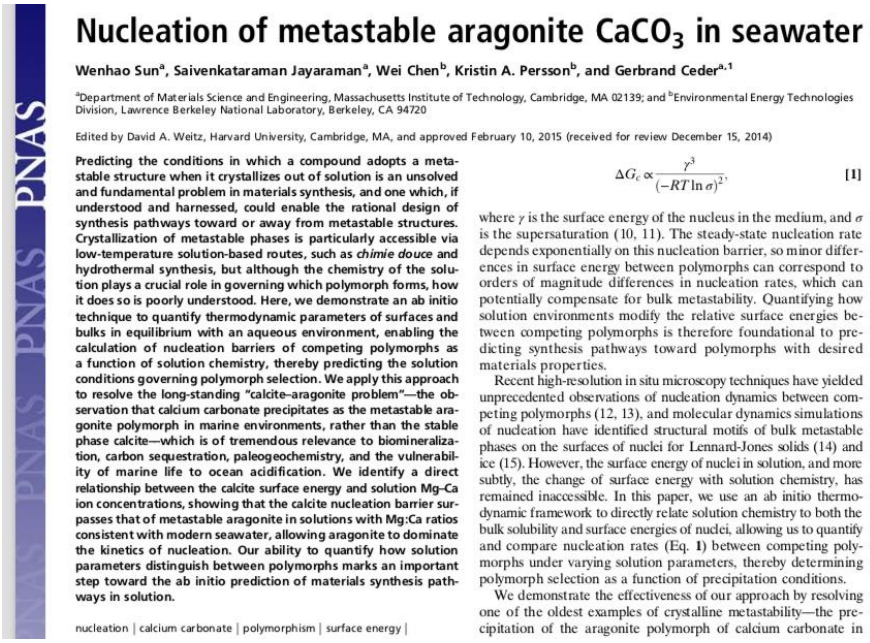



| | | |
|---|---|---|
| Pi = 4 | Log(K1) = | -8.26 |
| **R = (CH2)7CH3** | K1 = | 5.50E-09 |

+5 pts

| | | |
|---|---|---|
| Pi = 0 | Log(K1) = | -1.94 |
| **R=H** | K1 = | 1.15E-02 |

8. Find and read a recent paper in the scientific literature that sounds interesting to you and which common thermodynamic parameters (i.e., $\Delta H$, $\Delta S$, $\Delta G$, or $C_p$ …) have been measured or computed. (A) Record the reference (citation) to this scientific paper. (B) Summarize the significance of the paper in one paragraph. (C) List the thermodynamic parameters determined and what methods were used to measure or compute the thermodynamics presented in the paper. 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

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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 |

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

where $\gamma$ is the surface energy of the nucleus in the medium, and $\sigma$ 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).

+5 pts

(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) $\Delta G$, Equilibrium Constants (K), Surface Energy ($\gamma$) 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

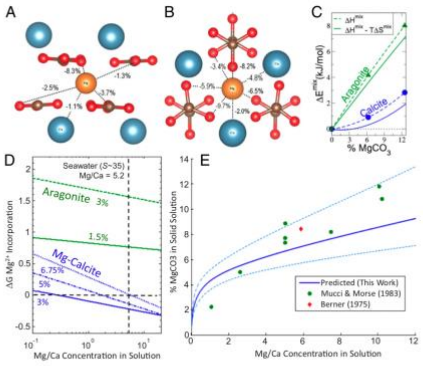


**Fig. 1.** Structural distortions in the (*A*) calcite and (*B*) aragonite lattices from $Mg^{2+}$ substitution on the $Ca^{2+}$ site. The $Ca^{2+}$ site is ninefold coordinated in aragonite and sixfold coordinated in calcite, resulting in higher enthalpy of mixing of $Mg^{2+}$ in the aragonite structure.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

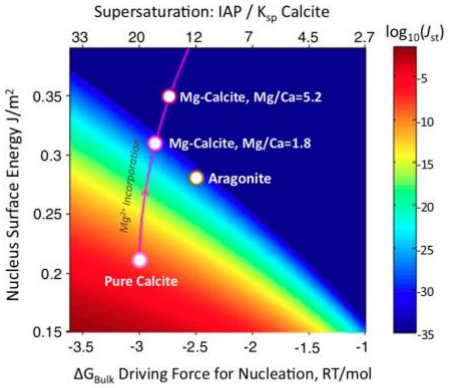


**Fig. 3.** Dimensionless $\log_{10}$ steady-state nucleation rates of calcium carbonate polymorphs at 25 °C plotted (color-coded) as a function of the nucleus surface energy and the bulk driving force for nucleation. Inhibition of calcite nucleation upon Mg uptake is primarily due to an increase in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

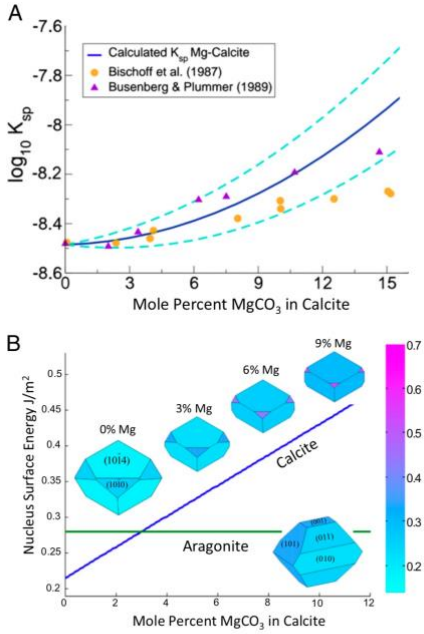


**Fig. 2.** (*A*) Predicted equilibrium solubility product of Mg–calcite. Dashed lines correspond to different reference states for the aqueous ion formation energies (*SI Appendix*, section S.I.5). (*B*) Morphology-averaged surface energies for hydrated Mg–calcite and aragonite as a function of $Mg^{2+}$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

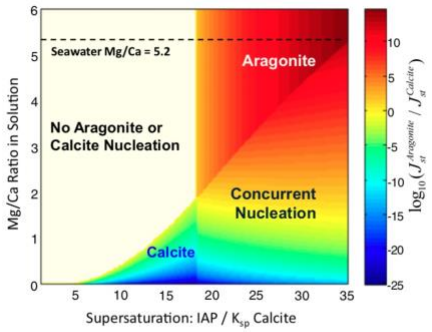


**Fig. 4.** Kinetic phase diagram of the relative nucleation rate between calcite and aragonite (color-coded) as a function of solution Mg:Ca ratio and the supersaturation. For Mg:Ca = 5.2 (modern seawater) only aragonite is preferred to nucleate. Concurrent nucleation of calcite and aragonite occurs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