Department of Chemistry
Cumulative Examinations

March 24, 2018

You may choose to answer any exam from any area covered in the examination booklet. Each exam may contain multiple parts. You may answer more than one exam but each exam is scored separately and is treated as an individual examination result. Thus, answering parts of two exams with a score of 50% would not yield a 100% grade for this cumulative exam. Instead you would receive 50% on each examination attempted.

This booklet contains five examinations.

1) Analytical Cumulative Examination,       Page 1
2) Biochemistry Cumulative Examination,      Page 2
3) Inorganic Cumulative Examination,         Page 3
4) Organic Cumulative Examination,           Pages 4-11
5) Physical Cumulative Examination,          Pages 12-14

On your examination booklet:

1) Print your student ID number.
2) Print the Exam Booklet number.
3) Print the question number you are answering.
4) Print the Exam Date.

Do not write your name anywhere on the examination booklet. Each exam will be scored anonymously. If you attempt more than one exam, you must use a separate examination booklet for each examination.

When you complete the examination, return the examination and your answer booklet to the proctor. Exam results will be posted on bulletin board #2B on the north side of the hall near BRWN 2124.
1) (20 points) (a) Sketch a diagram of a fluorescence microscope, labeling the beam path and any important parts.
   (b) Estimate the percentage of photons collected by a 1 cm² detector located 1 cm from a point emitter, selecting reasonable values for quantities required.
   (c) Sketch a Jablonski diagram for fluorescence (standard fluorescence, no need for two-photon here) and a reasonable graph of absorption and emission spectra for a fluorophore. Label the Stokes shift in both diagrams.
   (d) If a fluorophore with an excitation maximum in the green exhibits a 20 nm shift in its emission peak, calculate the corresponding difference in energy, making a reasonable choice for a green wavelength.

2) (20 points) (a) Sketch a diagram of an FTIR spectrometer, labeling the beam path and all relevant parts.
   (b) Add to the sketch the mechanical motions in the instrument that lead to formation of the interferogram, labeling any important distances.
   (c) Describe (using 1-2 complete sentences) differences in the roles of a Nernst glower and a laser in a standard FTIR spectrometer.
   (d) Use an energy level diagram sketch and one complete sentence to describe the quantity typically graphed in Raman spectroscopy.

3) (10 points) Briefly describe (2-3 sentences) the principle of operation of either stimulated emission depletion (STED) microscopy, or stochastic optical reconstruction microscopy (STORM), making clear which technique you are describing, and how it enables imaging below the diffraction limit.

4) (10 points) Briefly explain, using a simple diagram and 2-3 sentences, the photoelectric effect and how it is related to X-Ray Photoelectron Spectroscopy (XPS). Include in your description an explanation of the information that is learned about the sample in XPS.

5) (10 points) Sketch an SEM instrument diagram, labeling relevant parts and the beam path.

6) (10 points) Sketch a TEM instrument diagram, labeling relevant parts and the beam path. Briefly describe two key considerations related to the sample structure, in achieving reasonable contrast in a TEM image.

7) (20 points) (a) Sketch an STM tunneling junction, labeling important parts, distances, and potentials. Describe in 1-2 sentences how the feedback loop works.
   (b) Sketch an AFM instrument diagram, labeling relevant parts. Describe in 1-2 sentences two different imaging modes that are commonly employed.
   (c) Compare the typical lateral and vertical resolutions of STM and AFM.
Biochemistry Cumulative Exam Questions for March 24, 2018

1. Although the bond energy for a hydrogen bond in a vacuum is estimated to be ~20 kJ/mol, we find that a hydrogen bond in an average folded protein contributes <5kJ/mol. Explain this discrepancy. (10 points)

2. If you wished to synthesize a peptide that would insert into a lipid bilayer and then assemble into hexamer that would form an aqueous pore across the membrane, how would you optimally design this peptide? Included in your description should be its length, amino acid sequence, and orientation/assembly to form the aqueous channel in the lipid bilayer. A diagram might be useful in your response to the last request. Please also include a mechanistic explanation for each of your choices. (36 points)

3. The Hill coefficient for the interaction of oxygen with human hemoglobin in the red cell is ~2.8. Explain in detail i) what this number means, ii) what molecular mechanism leads to this behavior, and iii) why it is important for oxygen delivery to the tissues. (30 points) why it is important to hemoglobin function.

4. Draw the structure of the following peptide: DRLKGW. (24 points)
Inorganic Chemistry Cumulative
Exam March 24, 2018

1. (10 pt) Given the standard potentials of half reactions (i) and (ii), calculate that of (iii).
   (i) \( \text{Fe}^{2+} + 2e^- \rightarrow \text{Fe(s)} \) \( E^0 = -0.440 \text{ V} \)
   (ii) \( \text{Fe}^{3+} + 1e^- \rightarrow \text{Fe}^{2+} \) \( E^0 = 0.771 \text{ V} \)
   (iii) \( \text{Fe}^{3+} + 3e^- \rightarrow \text{Fe(s)} \)

2. (15 pt) The electron self-exchange reaction between [Co(NH₃)₆]³⁺ and [Co(NH₃)₆]²⁺ is much slower than that between the Ru analogues. Provide a concise rationale.

3. (15 pt) Calculate the equilibrium constant of the reaction \((F = 96485 \text{ C/mol}; \ R = 8.31 \text{ J/(K mol)})\)
   \( \text{Au}^{3+}(\text{aq}) + 2 \text{CN}^- (\text{aq}) \leftrightarrow [\text{Au(CN)}₂]^- (\text{aq}) \)
   From the standard potentials
   \( \text{Au}^{3+}(\text{aq}) + 1e^- \rightarrow \text{Au(s)} \) \( E^0 = 1.680 \text{ V} \)
   \( [\text{Au(CN)}₂]^- (\text{aq}) + 1e^- \rightarrow \text{Au(s)} + 2 \text{CN}^- (\text{aq}) \) \( E^0 = -0.600 \text{ V} \)

4. (20 pt) Consider a six coordinated V³⁺ complex of an effective \(D_3\) symmetry. Determine the ligand field terms originated from the free ion ground state term.
   Hint: \( \chi(\alpha) = [\sin(L + \frac{1}{2})\alpha]/[\sin(\alpha/2)] \)

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<tr>
<th>(D_3)</th>
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5. (30 pt) Use projection operator method to generate the SALCs of ligand \(\sigma\) donor orbitals for an ML₅ (\(C_{4v}\)) type complex.

<table>
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Organic Cumulative Exam
March 24, 2018

The following questions relate to the recently published paper entitled “Intermolecular Anti-Markovnikov Hydroamination of Unactivated Alkenes with Sulfonamides Enabled by Proton-Coupled Electron Transfer”, *JACS 2018 140, 741-747* that is attached to this exam.

1. (15 pts) Briefly describe three advantages of this methodology.

2. (15 pts) Briefly describe three limitations of this methodology.

3. (10 pts) How could you accelerate the transformations listed in Table 1 that describe 15 h reaction times?

4. (5 pts) The authors suggest that the catalytic cycle in Figure 3 involves proton transfer from the phosphorodiester to thiolate, based on pKₐ values measured in acetonitrile. Given that the reactions are run in trifluorotoluene, is this a valid argument? Why or why not?

5. (10 pts) Draw an intermediate that helps explain why an oxidant/base catalyst pair with an effective bond strength of 103 kcal/mole is capable of activating N-H bonds that range as high as 115 kcal/mole. HINT: This intermediate should also explain why the reaction is unsuccessful in THF (Table 1, Entry 12).

6. (15 pts) Write a plausible mechanism for the transformation of $63 \rightarrow 64 \rightarrow 65$.

7. (15 pts) Rationalize the Stern-Volmer quenching observations in Figure 4 (top).

8. (15 pts) Rationalize the cyclic voltammetry observations in Figure 4 (bottom).
Intermolecular Anti-Markovnikov Hydroamination of Unactivated Alkenes with Sulfonamides Enabled by Proton-Coupled Electron Transfer

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Department of Chemistry, Princeton University, Princeton, New Jersey 08544, United States

Supporting Information

ABSTRACT: Here we report a catalytic method for the intermolecular anti-Markovnikov hydroamination of unactivated alkenes using primary and secondary sulfonamides. These reactions occur at room temperature under visible light irradiation and are jointly catalyzed by an iridium(III) photocatalyst, a dialkyl phosphate base, and a thiol hydrogen atom donor. Reaction outcomes are consistent with the intermediacy of an N-centered sulfonamidyl radical generated via proton-coupled electron transfer activation of the sulfonamide N–H bond. Studies outlining the synthetic scope (>60 examples) and mechanistic features of the reaction are presented.

INTRODUCTION

Olefin hydroamination is an ideal method for the synthesis of aliphatic amines, combining alkenes and simple N–H functional groups in a direct and atom-economical fashion. While appealing in principle, these transformations are often challenging in practice: general methods for the intermolecular hydroamination of unactivated alkenes are rare, and even fewer provide access to the anti-Markovnikov series of addition products. New olefin amination technologies that address these limitations have the potential to create a significant synthetic benefit.

To this end, our group recently reported a photo-driven olefin amination method based on the proton-coupled electron transfer (PCET) activation of anilide N–H bonds. In this work, an excited-state redox catalyst and a weak phosphate base jointly mediate the concerted homolytic activation of the strong N–H bonds of N-aryl amide derivatives under visible light irradiation to afford a transient amide radical. While cyclizations of these reactive N-centered radicals onto pendant alkenes were highly efficient, efforts to extend this protocol to intermolecular C–N bond formation proved unsuccessful (Figure 1A). This lack of reactivity likely stems from the comparatively high stability of N-aryl amidoalkyls, which enables charge recombination between the reduced photocatalyst and the N-radical to occur at rates faster than bimolecular olefin addition. To overcome this limitation, we sought to develop PCET activations of alternative N–H functional groups, where the resulting N-radical intermediate would undergo intermolecular olefin addition at rates competitive with back electron transfer. In particular, we focused on the PCET activation of sulfonamide N–H bonds (Figure 1B). In a recent report describing a directed C–H alkylation method, we demonstrated that an N-radical species derived from the PCET activation of a sulfonamide could activate distal aliphatic C–H bonds via 1,3-hydrogen atom transfer (HAT). As sulfon-

Figure 1. (A) PCET-mediated intramolecular hydroamination with N-aryl amides. (B) PCET-mediated intermolecular hydroamination with sulfonamides.

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catalytic method for the intermolecular hydroamination of electron-rich alkenes with sulfonamides and a variety of azoles. In these reactions, a highly oxidizing excited-state organic photocatalyst converts an alkene substrate to its corresponding radical cation. These electrophilic intermediates can then react with nucleophilic amine donors in the key C–N bond-forming event. While powerful, these methods are limited by the thermodynamic challenges associated with one-electron oxidation of terminal and disubstituted olefins, and intermolecular variants of these aminations are currently limited to the reactions of styrenes and trisubstituted alkyl olefins. With respect to other examples of anti-Markovnikov hydroamination catalysis, Hall has recently reported an elegant method for the directed addition of aliphatic amines to simple alkenes. Also, numerous anti-Markovnikov aminations of styrenes have been reported, including seminal early reports from Beller and Hartwig.

RESULTS AND DISCUSSION

We envisioned a prospective catalytic cycle for a PCET-based olefin amination as shown in Figure 3. In analogy to our previous work, we anticipated that the phosphate base would first form a hydrogen bonded complex with the sulfonamide N–H bond. The resulting non-covalent adduct would participate in a concerted PCET event with the excited state of the iridium photocatalyst [Ir(dF(CF3)2ppy)2(S,S’-dcF(ppy))PF6] (A), resulting in formal homolysis of the N–H bond and formation of the key sulfonamidyl radical intermediate. When considered as a formal hydrogen atom acceptor, the oxidant/base catalyst pair has an effective bond strength of 103 kcal/mol. As such, the homolytic activation of the strong N–H bonds in both primary and secondary sulfonamides (bond dissociation free energy (BDDE) for N–H ~105 and ~97 kcal/mol, respectively) is feasible on thermochemical grounds. Next, in accord with literature precedent, we expected the N-radical species to undergo anti-Markovnikov addition to an olefin partner to furnish a new C–N bond and a vicinal carbon-centered radical. This alkyl radical can then be reduced by the thiol cocatalyst via HAT, and the resulting thiol radical can undergo single-electron reduction (E(Fe3+/Fe2+) = −0.22 V vs Fe3+/Fe2+) to the corresponding thiolate by the reduced Ir(III) state of the photocatalyst (E(Ir(III)/Ir(III)) = −1.07 V vs Fe3+/Fe2+). Favorable proton transfer between the thiolate (pKb[PhSH] ≈ 21 in MeCN) and the phosphoric acid (pKa ≈ 12 in MeCN) should follow, returning the active forms of all three catalysts.

Notably, success in the proposed scheme requires that PCET activation of the substrate N–H bond occurs in the presence of the aryl thiol—a known substrate class for multi-site PCET—that exhibits a much weaker S–H bond (S–H BDDE ~79 kcal/mol). Moreover, the thiol H atom donor must not preemptively reduce the highly reactive and electrophilic sulfonamidyl radical intermediates, which are known to be potent hydrogen atom abstractors. While seemingly problematic, recent PCET methods for olefin amination and alcohol β-scission have demonstrated these surprising selectivities and implied the feasibility of the proposed transformation.
Accordingly, we were pleased to find that under conditions similar to our C–H abstraction work, treatment of model terminal olefin substrate 4-methyl-N-(pent-4-en-1-yl)-benzenesulfonamide with 2 mol% of Ir photocatalyst A, 20 mol% of tetrabutylammonium dibutylphosphate base, and 30 mol% of 2,4,6-trisopropyl-thiophenol (TRIP thiol) provided the desired hydroamination product 1 in 78% GC yield following irradiation with blue LEDs in trifluoroacetone at room temperature (Table 1, entry 1). We next explored the sensitivity of these reactions to various changes in the standard conditions. Other hydrogen atom donors were moderately successful, but uniformly less effective than TRIP thiol (entries 2–5). Similarly, a number of iridium photocatalysts structurally similar to A were also effective in these reactions (entries 6, 7), but the reaction yields diminished as the potential of the excited-state species decreased (entries 8, 9). Also, the reaction is moderately successful in dichloromethane (entry 10), but considerably less so in other solvents (entries 11, 12). Notably, control reactions of 1 lacking the phosphate base, photocatalyst A, light, or TRIP thiol were uniformly unsuccessful (entries 13–16).

In the intramolecular version of this reaction we found that a number of olefin substitution patterns were accommodated, including terminal (1, 2, and 4), 1,2-disubstituted (3), and trisubstituted olefins (5) (Table 2). For a substrate containing two electronically similar alkynes, only the double bond proximal to the nitrogen was aminated (6). Various bicyclic and bridged ring systems can also be accessed using this method with high levels of diastereoselectivity (7–10). We also found these conditions were successful for aminations with a wide range of aryl- and alkyl-substituted sulfonamides. A para-methoxyphenyl-substituted sulfonamide was found to cyclize in 96% yield (11). Similarly, tosyl- and phenylsulfonyl-bearing substrates afforded the desired amination products 12 and 13 in 74% and 66% yield, respectively. Halogenated and more electron-deficient sulfonamides also afford the corresponding products 14–17 in more moderate yields. Aminations with substrates bearing meta- (18) and ortho-substituted (19) methoxyphenyl groups also proceed smoothly under the standard conditions, as did cyclization of a hindered mesityl derivative (20, 21). Heterocyclic sulfonamides were also tolerated in this reaction, furnishing products 22–25. Alkyl-substituted sulfonamides were also successful substrates, affording the desired cyclization products 26–31 in good yields. We also observed that both a primary alkyl chloride (28) and phthalimide (30, 31) were tolerated under these photoredox conditions. In addition, two different dimethylamino sulfonamides substrates delivered hydroamination products 32 and 33 in 91% and 80% yield, respectively. Notably, in this series of substrates, several sterically and electronically distinct sulfonamides were shown to react comparably well with both the trisubstituted model olefin and a much less reactive terminal alkenes (21, 24, 31, and 33), suggesting that more reactive olefins are not required for efficient intramolecular cyclizations.

Next, we examined the viability of more difficult intramolecular alkyne aminations (Table 3). We were pleased to find that numerous alkynes are effective reaction partners for the N-centered radicals generated from sulfonamide 34. A wide range of olefin substitution patterns are tolerated, including 1,1-disubstituted (35–37), 1,2-disubstituted (38, 39), tri- and tetracsubstituted (40, 41), and even terminal alkynes (42). Both cyclic and acyclic alkene partners can be employed, and the reaction is not sensitive to alkene configuration, as both cis- and trans-4-octene afford the same product with similar efficiency (39). As sulfonamidyl radicals are electrophilic, they are
Table 3. Scope of the Intermolecular Hydroamination

Yields are for isolated material following chromatography on silica gel and are the average of two experiments. Reactions were conducted on 0.5 mmol scale with 3 equiv of olefin unless otherwise noted. "Yields were determined by 1H NMR analysis of the crude reaction mixture." 3 equiv of olefin was used.

Scheme 1. Tandem Amination/C–H Alkylation\textsuperscript{a}

\textsuperscript{a}Yields are for isolated material following chromatography on silica gel and are the average of two experiments. Reactions were conducted on 0.5 mmol scale with 5.0 equiv of 63 and 66 in the first step and 2.0 equiv of alkene in the second step.
expected to react most readily with nucleophilic olefin partners. Accordingly, we found that a silyl enol ether can be efficiently aminated to afford vicinal amino alcohol product 44 following desilylation. In terms of functional group tolerance, carbamates (45), acetates (46, 47), phthalimides (48), silyl ethers (49, 50), ketones (51), primary alkyl chlorides (52), and methyl esters (53) are all tolerated under the standard conditions. In addition, an unsymmetrical but electronically biased 1,2-disubstituted alkene could be hydrosilylated to provide 54 as a 3:1 mixture of regiosomers. The major isomer exhibits connectivity consistent with attack of the electrophilic N-radical on the more electron-rich carbon of the alkene. We also found that both vinyl and allyl silane could hydrosilylated, though with modest reaction efficiencies (55, 56). Several more complex substrates, including natural product and pharmaceutical derivatives, were also aminated successfully (57, 58). In this study, we generally found that the 2° sulfonamide products resulting from hydrosilylation with 34 do not participate in a second olefin amination step to furnish 3° sulfonamide products. This selectivity for monoaiklation likely results from the increased stability of the 2° N-radical species formed upon PCET activation, which should decrease the rate of olefin addition relative to that of charge recombination. However, we observed that with more nucleophilic olefin partners, such as methylene-cyclopentanone, secondary N-allyl sulfonamides could also be aminated effectively (59, 60). We also observed that a lysine-based amino acid derivative (61) and a steroid conjugate (62) could be successfully alkylated. Notably, in 61 the secondary sulfonamide was selectively alkylated in the presence of a secondary amide N—H bond, a potentially competitive site for PCET. With respect to limitations, the intermolecular reactions are generally less efficient with sulfonamide donors other than 34 (37) and styrene was found to be a poor substrate (43) in this reaction. Efforts to address these constraints are the focus of future work.

Lastly, we attempted to highlight the synthetic versatility of sulfonamide PCET activation in the context of a tandem olefin amination-directed C—H bond alylation sequence (Scheme 1). First, the terminal alkenes 63 and 66 were subjected to the intermolecular anti-Markovnikov hydrosilylation protocol described above to afford the alkylated sulfonamides in 75% and 74% yield, respectively. The newly installed secondary sulfonamide was then activated in a second oxidative PCET event using the same Ir/phosphate pair, leading to site-selective abstraction of the δ-C—H bond to afford a carbon-centered radical that can be trapped by an electron-deficient olefin (64, 65, 67). These reactions underscore the synthetic benefits of PCET-based methods for homolytic bond activation, generating versatile radical intermediates from common organic functional groups under mild catalytic conditions.22

In addition to these synthetic methods, we also sought to understand the elementary steps leading to N-radical generation. Using cyclic voltammetry, we found the oxidation of N-propyl-4-methoxybenzenesulfonamide occurs at +1.8 V vs FeC/FeC. As such, direct electron transfer between this sulfonamide and the excited state of photocatalyst A [{Ir(ppy)3}(4-methoxybenzenesulfonamide) +1.30 V vs FeC/FeC is endergonic by nearly 500 mV. Accordingly, we found that solutions of sulfonamide alone do not quench the luminescence of A. Other sulfonamides that do not bear electron-rich aromatic groups have even higher oxidation potentials (Ep(1/2)(N-propyltosylamide) = +2.2 V vs FeC/FeC, Ep(1/2)(N-propyl-4-cyanobenzenesulfonamide) > +3.0 V vs FeC/FeC). These values indicate that a stepwise ET-PT mechanism for sulfonamidyl radical formation is unlikely to be operative. Similarly, the pKs of benzenesulfonamide is approximately 27 in MeCN—roughly 15 pKs units less acidic (ΔG° = +20.6 kcal/mol) than the conjugate acid of the dibutylphosphate base. This highly unfavorable equilibrium discounts mechanisms involving an initial proton transfer step between the sulfonamide and the phosphate base to form a more easily oxidized sulfonamide anion. Lastly, the potentials required for oxidation of terminal and disubstituted alkenes are more than 600 mV endergonic relative to the excited-state potential of A, inconsistent with the viability of alkene radical cation formation under these conditions.

Based on these outcomes, we reasoned that concerted PCET might be the operative mechanism of N-radical generation. Consistent with this view, we observed quenching of *A in CH2Cl2 solutions containing varied concentrations of N-propyl-
4-methoxybenzenesulfonamide in the presence of a constant concentration of dibutyl phosphate. While the degree of quenching was modest ($K_{\text{Q}} = 3.0 \text{ M}^{-1}$), the decrease in luminescence intensity was linearly correlated to the sulfonamide concentration, consistent with a first-order kinetic dependence (Figure 4, top panel). As described in detail in prior work from our group, the dialkyl phosphate base alone also quenches the luminescence of A in CH$_3$Cl$_2$ solution at $\lambda$. However, the concentration dependence of the quenching process is complex and exhibits saturation behavior—a feature that may reflect the formation of a favorable iridium-phosphate hydrogen-bonded adduct under these reaction conditions. Therefore, we note that phosphate oxidation occurs at potentials significantly more positive than those of $\Delta \Delta G = +1.0 \text{ V}$, arguing against the possible role of phosphoryl radicals in the N–H activation step. The thermodynamic driving force for the proposed excited-state PCET process is favorable ($\Delta G^\circ = -6.0 \text{ kcal/mol}$) based on the N–H BDE of N-ethylbenzenesulfonamide of 97 kcal/mol and an effective BDE of 103 kcal/mol for the Ir/phosphate pair.

We further evaluated the role of PCET in sulfonamide activation using electrochemical techniques. Specifically, we carried out cyclic voltammetry studies on 4-methoxybenzenesulfonamide in CH$_3$Cl$_2$ containing 0.1 M NBu$_4$PF$_6$ in the presence of varying concentrations of monobutyl phosphate (Figure 4, middle panel). While all of the voltammograms were irreversible, we observed that the onset potentials were shifted to less positive potentials and current response increases with increasing concentrations of phosphate. Control experiments revealed that analogous scans of sulfonamide or phosphate alone do not give rise to these current features (Figure 4, bottom panel). Qualitatively, these outcomes are also consistent with the proposed PCET process.

**CONCLUSIONS**

We have developed a catalytic anti-Markovnikov hydroamination of unactivated alkenes with simple sulfonamides enabled by a PCET activation of the sulfonamide N–H bond. This work further demonstrates the potential of PCET for the direct homolytic activation of strong heteroatom–hydrogen bonds found in many common organic functional groups, and utilization of the resulting radical intermediates in synthetically useful transformations.

**ASSOCIATED CONTENT**

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.7b11144.

Experimental details; characterization data and NMR spectra; voltammetric, thermochemical, and luminescence quenching data (PDF)

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Notes

The authors declare no competing financial interest.

**ACKNOWLEDGMENTS**

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**REFERENCES**


(14) Zhao, Y.; Bordwell, F. G.; Cheng, J.; Wang, D. J. Am. Chem. Soc. 1997, 119, 9135. Also see DFT calculation in Supporting Information.
(15) (a) Romero, N. J.; Nieves, D. A. J. Am. Chem. Soc. 2014, 136, 17024. Also see S–H BDFE = 79 kcal/mol in the following:
(23) Estimated from Bordwell’s pKₐ table: pKₐ(PhSO₂NH₂) = 16 in DMSO.
P-CHEM CUME: SOME POSSIBLY USEFUL INFORMATION

First law of thermodynamics:

\[ dU = dq + dw = C_v \cdot dT - P \cdot dV \]  
\[ (U \equiv \text{internal energy}, P-V \text{ work only}) \]

Definitions of important state functions:

\[ H = U + P \cdot V \]  
\[ (H \equiv \text{enthalpy}) \]

\[ dS = dq_{\text{rev}} / T \]  
\[ (S \equiv \text{entropy}) \]

\[ G = H - T \cdot S \]  
\[ (G \equiv \text{Gibbs energy}) \]

Gibbs equations:

\[ dU = T \cdot dS - P \cdot dV \]
\[ dH = T \cdot dS + V \cdot dP \]
\[ dA = -S \cdot dT - P \cdot dV \]
\[ dG = -S \cdot dT + V \cdot dP \]

Definition of constant pressure and constant volume heat capacities:

\[ C_v = \left( \frac{\partial U}{\partial T} \right)_V, \; C_p = \left( \frac{\partial H}{\partial T} \right)_P \]

Definition of the chemical potential:

\[ \mu_i = \left( \frac{\partial G_i}{\partial n_i} \right)_{T,P,n_{j \neq i}} \]

Chemical potential of A in an ideal solution:

\[ \mu_A = \mu_A^* + R \cdot T \cdot \ln \chi_A \]  
\[ (\text{note: } \mu_A^* \text{ depends on } T \text{ and } P) \]

Equation of state of a perfect gas:

\[ P \cdot V = R \cdot T \]

Chemical potential of a perfect gas:

\[ \mu_A = \mu_A^* + R \cdot T \cdot \ln \left( \frac{P_A}{P^o} \right) \]  
\[ (\text{note: } \mu_A^* \text{ depends on } T; ^* \text{ symbol indicates standard state pressure}) \]

Taylor expansion of \( \ln(x) \):

\[ \ln(1 + x) = x - \frac{x^2}{2} + \frac{x^3}{3} - \ldots \]
1. (a) Show that the molar heat capacity difference for a real gas is given by:

$$
\overline{C}_p - \overline{C}_v = \left( \frac{\partial \overline{V}}{\partial T} \right)_P \cdot \left\{ P + \left( \frac{\partial \overline{U}}{\partial \overline{V}} \right)_T \right\}
$$

The bars over $C_p$, $C_v$, $V$, and $U$ indicate molar quantities. (20 points)

(b) Show that $\overline{C}_p - \overline{C}_v = R$ for a perfect (i.e., ideal) gas. (5 points)

(c) Explain why $\overline{C}_p > \overline{C}_v$ for a real gas. (10 points)

2. Consider the chemical potential of $A$ in an ideal liquid solution:

$$
\mu_A = \mu_A^* + R \cdot T \cdot \ln \chi_A
$$

where $\mu_A^*$ is the chemical potential of pure $A$, and $\chi_A$ is the mole fraction of $A$.

(a) Show that the entropy change of mixing $n_A$ moles of $A$ with $n_B$ moles $B$ at constant $T$ and $P$ is:

$$
\Delta S_{\text{mix}} = -n_{\text{TOT}} \cdot R \cdot \left[ \chi_A \cdot \ln(\chi_A) + \chi_B \cdot \ln(\chi_B) \right]
$$

where $n_{\text{TOT}}$ is $n_A + n_B$. (15 points)

(b) Use chemical potentials to show that the vapor pressure of $A$ over an ideal liquid solution of $A$ and $B$ is equal to $\chi_A \cdot P_A^*$, where $P_A^*$ is the vapor pressure of pure $A$. Treat $A$ in the vapor phase as a perfect gas. (10 points)

3. Copper and nickel are completely miscible in both the solid and liquid states at 1 bar pressure. The melting point of pure copper at 1 bar pressure is 1085 °C, and that of nickel is 1455°C.

(a) Sketch the phase diagram of the Cu + Ni system in the solid and liquid regions, with copper mole fraction in the $x$-axis and temperature in the $y$-axis. Identify the single and two-phase regions of the diagram. (10 points)
(b) Consider a region of the phase diagram in which the solid and liquid solution phases are in equilibrium. Which phase is enriched in Cu relative to the other (i.e. which phase has the higher mole fraction of Cu)? (5 points)

4. A is a non-ionic solute that dissolves in water to form an ideal solution. A solution of A in water is decanted into one side of a U-tube, the two sides of which are separated by a membrane that is permeable only to water. An equivalent volume of pure water is decanted into the other side of the U-tube. At equilibrium, liquid on one side of the U-tube is at a different height than liquid on the other side, as shown in the diagram to the right.

(a) Which side of the tube contains of pure water? Explain your answer. (10 points)

(b) Show that \( h \), the height difference between the two sides of the U-tube at equilibrium, is approximately proportional to the molarity of A for small concentrations of A. (15 points)
### Periodic Classification of the Elements

<table>
<thead>
<tr>
<th>I A</th>
<th>1 H 1.00797</th>
<th>II A</th>
<th>3 Li 6.939</th>
<th>4 Be 9.0122</th>
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</thead>
<tbody>
<tr>
<td>I B</td>
<td>11 Na 22.9888</td>
<td>II B</td>
<td>12 Mg 24.312</td>
<td></td>
</tr>
<tr>
<td>37 Rb 85.47</td>
<td>38 Sr 88.905</td>
<td>39 Y 91.22</td>
<td>40 Zr 92.906</td>
<td>41 Nb 95.94</td>
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<tr>
<td>55 Cs 132.905</td>
<td>56 Ba 137.34</td>
<td>57 La* 138.91</td>
<td>72 Hf 178.49</td>
<td>73 Ta 180.948</td>
</tr>
<tr>
<td>87 Fr (223)</td>
<td>88 Ra (226)</td>
<td>89 Ac† (227)</td>
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<td></td>
</tr>
</tbody>
</table>

#### *Lanthanides*
- 58 Ce 140.12
- 59 Pr 140.907
- 60 Nd (144.24)
- 61 Pm (150.39)
- 62 Sm (157.25)
- 63 Eu (158.924)
- 64 Gd (162.50)
- 65 Tb (164.930)
- 66 Dy (167.26)
- 67 Ho (168.934)
- 68 Er (173.04)
- 69 Tm (174.97)

#### †Actinides
- 90 Th 232.033
- 91 Pa (231)
- 92 U (238.03)
- 93 Np (237)
- 94 Pu (242)
- 95 Am (243)
- 96 Cm (247)
- 97 Bk (247)
- 98 Cf (249)
- 99 Es (254)
- 100 Fm (253)
- 101 Md (256)
- 102 Lw (257)

(Numbers in parentheses are the mass numbers of the most stable isotopes.)