1. For water ($\text{H}_2\text{O}$) in a 1 L box, what will be the relative numbers of different quantized energy levels within an energy window of 10,000 cm$^{-1}$ above $D_0$ for the electronic ground state?

(a) translational < rotational < vibrational < electronic
(b) rotational < translational < vibrational < electronic
(c) electronic < vibrational < rotational < translational
(d) translational < vibrational < rotational < electronic
(e) translational < electronic < rotational < vibrational
(f) the same number of all levels will be found

2. A certain gas is well described by the van der Waals equation of state at a certain temperature $T$. As the molar volume is increased, to what value does the compressibility factor $Z$ converge?

(a) Zero
(b) One
(c) $R$
(d) $k_B$
(e) $e$
(f) $\pi^2$

3. For a linear molecule, what is the contribution to the molar constant volume heat capacity from rotation?

(a) $(3/2)k_B$
(b) $N_A$
(c) $k_B$
(d) 1 cm$^{-1}$
(e) It depends on the mass
(f) $R$

4. Which of the following statements about energy levels and states is true at thermal equilibrium?

(a) There can be greater population of a higher energy state compared to a lower energy state
(b) There are always more levels than states
(c) There may be more states than levels
(d) There can be greater population of a higher energy level compared to a lower energy level
(e) (c) and (d)
(f) All of the above
5. The below plot shows the second virial coefficient, $B_{2V}$, as a function of $T$ for 4 different gases. If you have the same number of moles in the same size container for each gas at 300 K, which gas has the lowest pressure, $P$?

(a) He  
(b) N$_2$  
(c) CH$_4$  
(d) CO$_2$  
(e) All pressures will be equal  
(f) (not used)

6. Consider the following empirically developed gas partition function:

$$Q(N,V,T) = \frac{1}{N!} \left( \frac{2\pi mk_B T}{h^2} \right)^{3N/2} (V - Nb)^N e^{aN^2/k_BT}$$

where $a$ and $b$ are non-negative empirical constants. If $a$ and $b$ are both greater than zero, what is the pressure for the gas?

(a) $P = \frac{Nk_B T}{V}$
(b) $P = \frac{Nk_B T}{V - Nb} - \frac{aN^2}{V^2}$
(c) $P = P_c$
(d) $P = \frac{Nk_B T}{V - b} - \frac{aN^2}{T^{1/2} V^2}$
(e) $P = \frac{Nk_B T}{V} + \frac{Nab}{V^2} + \frac{Na^2 b^2}{V^3} + \cdots$
(f) 1 bar
7. The partition function $Q$ for a system of all non-degenerate levels, and having a ground state energy of 0, is equal to 2. What fraction of the population is in the ground state?

(a) 0%  
(b) 11%  
(c) 50%  
(d) 67%  
(e) 75%  
(f) 100%

8. Which of the following are state functions?

(a) Energy $U$  
(b) Gibbs free energy $G$  
(c) Entropy $S$  
(d) Helmholtz free energy $A$  
(e) (a) and (c)  
(f) All of the above

9. One mole of an ideal gas is expanded adiabatically to twice its original volume. What is the net transfer of heat $q$ from the surroundings?

(a) $-(3/2)RT$  
(b) $-2\text{ J}$  
(c) $0\text{ J}$  
(d) $(3/2)RT$  
(e) $-w$  
(f) $\Delta U$

10. Consider the reversible, isothermal expansion of an ideal gas from a pressure of 10 bar to 2 bar. Defining the system as the gas and the surroundings as the universe, the change in the entropy of the system at 300 K is $13.4 \text{ J mol}^{-1}\text{ K}^{-1}$. Now, which of the following statements is always true if the same isothermal expansion is carried out, but not reversibly?

(a) The entropy change for the system will be $13.4 \text{ J mol}^{-1}\text{ K}^{-1}$  
(b) The entropy change for the surroundings will be positive  
(c) The total entropy change (sum of system and surroundings) will be larger than in the reversible case.

(d) (a) and (b)  
(e) (a) and (c)  
(f) all of the above
11. To what is \( \left( \frac{\partial S}{\partial P} \right)_T \) equal?

(a) \( \left( \frac{\partial P}{\partial V} \right)_T \)  \hspace{1cm}  (d) \( \left( \frac{\partial P}{\partial S} \right)_T \)

(b) \( \left( \frac{\partial A}{\partial T} \right)_V \)  \hspace{1cm}  (e) \( -\left( \frac{\partial V}{\partial T} \right)_P \)

(c) \( \left( \frac{\partial G}{\partial T} \right)_S \)  \hspace{1cm}  (f) \( \left( \frac{\partial P}{\partial T} \right)_V \)

12. The below plot is of the chemical potential as a function of pressure for a pure substance having a negative value of \( \Delta V_{\text{fus}} \). Which of the following statements is false?

(a) The line marked A is the liquid  \hspace{1cm}  (d) The line marked C is the gas

(b) The line marked B is the solid  \hspace{1cm}  (e) At no point are all three phases in equilibrium

(c) Raising the temperature would lower line B relative to line A  \hspace{1cm}  (f) The temperature is below the critical point
13. The pressure on an incompressible solid having a molar volume of 0.2 L is increased from 10 bars to 20 bars at a constant temperature 300 K. By how much does the molar free energy of the solid increase? (All answers have units of L-bar/mol, you may assume \( R = 0.1 \) L-bar/K-mol)

(a) 0  
(b) 1  
(c) 2  
(d) 30  
(e) 30 \ln 2  
(f) 60

14. When two liquids having a total number of molecules that sums to one mole are mixed, what is the final volume? In the answers \( V \) is an initial pure volume, \( \bar{V} \) is a partial molar volume, \( n \) is number of moles, and \( x \) is mole fraction.

(a) \( \bar{V}_1 + \bar{V}_2 \)  
(b) \( x_1 V_1 + x_2 V_2 \)  
(c) \( n_1 \bar{V}_1 + n_2 \bar{V}_2 \)  
(d) \( V_1 + V_2 \)  
(e) \( x_1 \bar{V}_1 + x_2 \bar{V}_2 \)  
(f) (c) and (e)

15. Consider 0.001 mol of the strong electrolyte \( \text{Na}_2\text{SO}_4 \) dissolved into 1 L of water at 300 K. Which of the below statements is/are true?

(a) The conductivity of the solution is the same as that measured for pure water  
(b) The mean ionic activity coefficient is less than 1  
(c) The mean ionic activity coefficient is greater than 1  
(d) The freezing point depression is smaller than what would be observed if 0.001 mol \( \text{CaCl}_2 \) were substituted for \( \text{Na}_2\text{SO}_4 \)  
(e) The ionic strength of the solution is 0.002 mol L\(^{-1}\)  
(f) The inverse Debye length \( \kappa^{-1} \) will decrease at higher temperatures

16. Given the electrochemical cell reaction \( \text{H}_2(g) + \text{PbSO}_4(s) \rightleftharpoons 2\text{H}^+(aq) + \text{SO}_4^{2-}(aq) + \text{Pb}(s) \), which of the following changes would not decrease the cell voltage?

(a) Increase in the size of the lead electrode  
(b) Decreased solution pH  
(c) Dissolution of \( \text{K}_2\text{SO}_4 \)  
(d) Dissolution of HBr  
(e) Decreased pressure of \( \text{H}_2 \)  
(f) (not used)
17. Consider the below composition diagram. Which of the below statements is/are true for either 1 or 2 as a solute in solution (in the mole fraction Henry’s law standard state)?

(a) \( k_{H,1} = P_1^* \)  
(b) \( \gamma_1 \) is less than 1 over the range \( 0.2 \leq x_1 \leq 0.8 \)  
(c) Molecules of each component have less favorable interaction energies with each other than with themselves  
(d) \( k_{H,2} < 200 \) torr  
(e) \( \gamma_2 = 1 \) for \( x_1 \sim 0.55 \)  
(f) The solution behaves ideally

18. Consider the dissociation of dilithium in the gas phase \( \text{Li}_2 \Leftrightarrow 2\text{Li} \). If we start with 2 moles of dilithium and zero moles of lithium, which of the following equations correctly expresses the equilibrium constant as a function of the extent of reaction \( \xi \) and the total pressure \( P \) assuming ideal behavior of the gases?

(a) \( K_P = \frac{4\xi_{eq}^2}{4 - \xi_{eq}^2} P \)  
(b) \( K_P = \frac{4\xi_{eq}^2}{2 - \xi_{eq}} P \)  
(c) \( K_P = \frac{2\xi_{eq}^2}{4 - \xi_{eq}^2} P^2 \)  
(d) \( K_P = \frac{2\xi_{eq} (1 - \xi_{eq})}{4(1 - \xi_{eq})} P \)  
(e) \( K_P = \frac{2\xi_{eq}^2}{2 + \xi_{eq}} P \)  
(f) \( K_P = \xi_{eq} P^{-1} \)
19. What is the purpose of a salt bridge in an electrochemical cell?

(a) It carries current corresponding to the non-reversible work that can be harvested from the full cell

(b) It permits the Gibbs-Duhem equation to govern the Debye-Hückel behavior of the ions in solution

(c) It maintains all electrolyte solutions at unit activity to ensure constant voltage

(d) It transfers heat efficiently from one half cell to the other so that the temperature remains constant

(e) It permits transfer of non-redox active ions between half-cells to maintain charge balance during cell operation

(f) It makes the cell taste much better when sprinkled in sparingly

20. Standard reduction potentials are shown for 2 half-cells below. What is the standard notation for a full cell constructed from these two half cells, the standard potential for the full cell, and the correct value of \( n \) to be used in relating the potential to free energy?

\[
\text{Cd}^{2+}(aq) + 2e^- \rightarrow \text{Cd}(s) \quad E^o = -0.40 \text{ V} \\
\text{In}^{3+}(aq) + 3e^- \rightarrow \text{In}(s) \quad E^o = -0.34 \text{ V}
\]

(a) \( \text{In(s) | In(NO}_3\text{)}_3(aq) \parallel \text{CdCl}_2(aq) \parallel \text{Cd(s)} \), \( E^o = 0.12 \text{ V, } n = 1 \)

(b) \( \text{In(s) | In(NO}_3\text{)}_3(aq) \parallel \text{CdCl}_2(aq) \parallel \text{Cd(s)} \), \( E^o = 0.06 \text{ V, } n = 6 \)

(c) \( \text{In(s) | In(NO}_3\text{)}_3(aq) \parallel \text{CdCl}_2(aq) \parallel \text{Cd(s)} \), \( E^o = 0.01 \text{ V, } n = 6 \)

(d) \( \text{Cd(s) | CdCl}_2(aq) \parallel \text{In(NO}_3\text{)}_3(aq) \parallel \text{In(s)} \), \( E^o = 0.06 \text{ V, } n = 6 \)

(e) \( \text{In(s) | In(NO}_3\text{)}_3(aq) \parallel \text{CdCl}_2(aq) \parallel \text{Cd(s)} \), \( E^o = 0.06 \text{ V, } n = 6 \)

(f) \( \text{In(s) | In(NO}_3\text{)}_3(aq) \parallel \text{CdCl}_2(aq) \parallel \text{Cd(s)} \), \( E^o = 0.06 \text{ V, } n = 6 \)
21. (short answer) A temperature composition diagram for phenol and water is shown below at right. Describe in words what would be observed in a flask containing one mole of water and one mole of phenol as the temperature is raised from 25 to 80 °C.

The mixture is immiscible at 25 °C. Two phases will be observed. The diagram is not perfectly labeled, but the two phases will be of composition roughly 10:90 phenol to water and 70:30 phenol to water. If equal amounts of both of these phases were to be present (e.g., 1 moles worth of each) there would be a total of only 0.8 parts of phenol and 1.2 parts of water, which fails to agree with the initial mass balance, so there will be an excess of the more concentrated (70:30) phenol phase. We can determine how much excess from setting \((1+x)(0.7) + (1-x)(0.1) = 1\) (or, considering water instead of phenol, from \((1+x)0.3 + (1-x)0.9 = 1\) where \(x\) is the number of excess moles in the phase enriched in phenol. The first equation give \(0.6x = 0.2\), or \(x = 0.33\). Thus there would be one phase about 2 parts 70:30 phenol:water solution and one phase one part 10:90 phenol:water solution.

As the temperature is raised, the composition of each immiscible phase will increase in the minority component, i.e., the water rich phase will become less water rich and the phenol rich phase will become less phenol rich. From lever rule consideration, the volume of the water rich phase will shrink until, at about 64 °C, it appears, a single phase having 50:50 composition will be present (and remain present at higher temperatures up to the boiling point of the mixture).
(short derivation) The coefficient of thermal expansion for a substance, $\alpha$, and its isothermal compressibility, $\kappa$, are defined below. Compare and contrast the values for each of these quantities at 1 bar and 300 K for an ideal gas and a hard-sphere gas, where the latter obeys the equation of state $P(\bar{V} - b) = RT$, and $b$ is a positive constant.

$$\alpha = \frac{1}{\bar{V}} \left( \frac{\partial \bar{V}}{\partial T} \right)_P \quad \text{and} \quad \kappa = -\frac{1}{\bar{V}} \left( \frac{\partial \bar{V}}{\partial P} \right)_T$$

Considering the ideal and hard-sphere gas equations of state, we may derive the common equation $\bar{V} = RT/P + b$, where $b = 0$ for the ideal gas. For any value of $b$, it is true that

$$\left( \frac{\partial \bar{V}}{\partial T} \right)_P = \frac{R}{P} \quad \text{and} \quad \left( \frac{\partial \bar{V}}{\partial P} \right)_T = -\frac{RT}{P^2}$$

So, given the definitions of $\alpha$ and $\kappa$, we have

$$\alpha = \frac{1}{\bar{V}} \left( \frac{\partial \bar{V}}{\partial T} \right)_P = \left[ \frac{1}{(RT/P) + b} \right] \frac{R}{P} \quad \text{and} \quad \kappa = -\frac{1}{\bar{V}} \left( \frac{\partial \bar{V}}{\partial P} \right)_T = \left[ \frac{1}{(RT/P) + b} \right] \left( -\frac{RT}{P^2} \right)$$

For the ideal gas, with $b = 0$, the fractions simplify trivially to give $\alpha = (1/T) = (1/300) \text{ K}^{-1}$ and $\kappa = (1/P) = 1 \text{ bar}^{-1}$. If $b$ is positive, though, the fraction in brackets for each expression will be smaller than for the ideal gas. Thus, both the volume increase with increasing temperature and the volume decrease with increasing pressure will be proportionally smaller for the hard sphere gas compared to the ideal gas. Physically, this can be understood by recognizing that the molar volume of the hard sphere gas is already proportionally larger than that of the ideal gas, i.e., while the relevant changes (the derivatives) of the molar volume with respect to temperature and pressure are the same for the two gases, the hard-sphere gas begins by occupying more volume at the same temperature and pressure.
23. Sketch a pressure-temperature phase diagram (pressure on y axis, temperature on x axis) showing colligative effects on boiling and melting for a water solution. Label the diagram to make clear how freezing point changes, boiling point changes, liquid vapor pressure changes, and how lines on the diagram relate to adjacent phases.
24. Considering the total differential of the entropy as a function of temperature and pressure, as well as the total differential of the enthalpy expressed in its natural variables (which can be quickly derived using the 1st and 2nd Laws), derive expressions for (i) the constant-pressure temperature dependence of the entropy, and (ii) the constant-temperature pressure dependence of the entropy.

Start with the expression for the total derivative of the entropy with respect to temperature and pressure:

\[ dS = \left( \frac{\partial S}{\partial T} \right)_p \,dT + \left( \frac{\partial S}{\partial P} \right)_T \,dP \]

while from the first and second laws, and the definition of the enthalpy, we can determine:

\[ dH = dU + PdV + VdP = TdS - PdV + PdV + VdP = TdS + VdP \]

solving for \( dS \) provides

\[ dS = \frac{1}{T} \,dH - \frac{V}{T} \,dP \]

The total derivative of the enthalpy with respect to \( T \) and \( P \) is

\[ dH = \left( \frac{\partial H}{\partial T} \right)_p \,dT + \left( \frac{\partial H}{\partial P} \right)_T \,dP = C_p \,dT + \left( \frac{\partial H}{\partial P} \right)_T \,dP \]

leading to

\[ dS = \frac{C_p}{T} \,dT + \frac{1}{T} \left[ \left( \frac{\partial H}{\partial P} \right)_T - V \right] \,dP \]

and we may finally equate terms to determine

\[ \left( \frac{\partial S}{\partial T} \right)_p = \frac{C_p}{T} \]

\[ \left( \frac{\partial S}{\partial P} \right)_T = \frac{1}{T} \left[ \left( \frac{\partial H}{\partial P} \right)_T - V \right] \]