Problem 1 (20 points)
Indicate whether each of the following statements is true or false (1 point each) and provide suitable explanations and justifications for each of your answers (4 points each).

a) \[ \sum (x_i d\phi_i) = 0 \] by the Gibbs-Duhem relationship.

b) \( S_E \) for an ideal solution = \(-R \sum (x_i \ln x_i)\) in order to accommodate the effects of mixing (i.e., that \( S \) for a solution \( \neq \sum x_i S_i \)).

c) Modified Raoult’s expression assumes that the interactions between molecules in the gas phase and between molecules in the liquid phase are both zero.

d) At equilibrium, a flavoring ingredient dissolved in salad dressing (a phase of oil on a phase of water) would have the same molar concentration.

Problem 2 (35 points)
At atmospheric pressure, acetone (1) and chloroform (2) form an azeotrope that boils at 64.6 °C and has a mole fraction of acetone in the liquid of 0.335. The saturation vapor pressures of acetone and chloroform at 64.6 °C are 1.31 and 0.98 atm, respectively.

a) Calculate the activity coefficients of acetone and chloroform at the azeotrope.

b) Determine a value for \( G_E \) in kcal/mol for the azeotrope. If enthalpic factors were to dominate in influencing \( G_E \) for this system, would the adiabatic mixing of pure acetone with pure chloroform (each at 64.6 °C) to generate a solution at the composition of the azeotrope produce a solution that was warmer or cooler than 64.6 °C? If you were unable to solve part a), assume that \( G_E/RT = 2 \).

c) Using your values in part a), calculate the composition of the vapor over a liquid solution at 64.6 °C that contains 12 mol percent acetone. Consider the van Laar equations, p.433 of SVNA, to describe the behavior of this system and note that:

\[
\frac{\ln \gamma_2}{\ln \gamma_1} = \frac{A_{12}}{A_{21}} \left[ \frac{x_1}{x_2} \right]^2
\]

d) Calculate the total pressure over the solution at the condition of part c). If you do not have numerical values from part c), you may assume the activity coefficient for acetone is 0.5 and that for chloroform is 0.8.
Problem 3 (30 points)
In generating expressions from $G^E/RT$ from VLE data, a convenient approach is to plot values of $G^E/RT_x_1 x_2$ vs $x_1$ and fitting the results with an appropriate function. Consider if such data were fit by the expression: $G^E/RT_x_1 x_2 = A + Bx_1^2$.

a) From the assumed expression for $G^E/RT$, provide expressions for $\ln \gamma_1$ and $\ln \gamma_2$ that are functions of $A$, $B$, $x_1$, and $x_2$.

b) For your expressions in a), relate $A$ and $B$ to the parameters $\ln \gamma_1^{\infty}$ and $\ln \gamma_2^{\infty}$ noting your approach. If you were unable to solve part a), you should still be able to provide an answer to how you would solve this problem.

c) Provide a sketch of $A + Bx_1^2$ on a graph of $G^E/RT_x_1 x_2$ vs $x_1$, noting the limiting locations of $\ln \gamma_1^{\infty}$ and $\ln \gamma_2^{\infty}$ on this graph. Provide relationships for $A$ and for $B$ to $\ln \gamma_1^{\infty}$ and $\ln \gamma_2^{\infty}$ and any other parameters needed using the plot.

Problem 4 (15 points)
A cylinder of propane (1) at 60 bar and 30 °C contains some liquid water (2). The propane is sparingly soluble in the water under these conditions. Assume that $\ln \gamma_1$ can be described by the expression $\ln \gamma_1 = Ax_2^2$. Note whether propane behaves as an ideal gas under these conditions and where conditions of an ideal solution in the gas phase apply. The saturation pressure of propane at this temperature is 10.8 bar.

a) What is the fugacity of propane in either phase?

b) Provide a value for the Henry’s law constant for propane in water at this pressure that is a function only of A. (Hint: consider how fugacities are expressed in Henry’s Law and in the modified Raoult expression.)