Please read carefully the attached article on $S_N2$-reactions that was published in *J. Am. Chem. Soc.* in July, 2004, by Ken Houk, William Jorgensen and John Brauman. Based on the article, answer the questions listed below (make sure that you understand what the questions ask before answering). NOTE: Repeating or rephrasing the questions, or pieces of text directly from the paper, is not considered as an acceptable answer.

1. Briefly state using your own words why this paper is worth publication in *J. Am. Chem. Soc.* Steric effects similar in gas phase and in solution $S_N2$ reactions.

2. Draw typical potential energy surfaces for gas-phase and solution $S_N2$-reactions and explain why they are different. Gas-phase: solvation of ion by one molecule reduces energy; solution: solvation of reactants and products increases barrier.

3. Explain why the transition states and ion-molecule complexes of the reactions discussed here are less strongly solvated in polar solvents than the reactants and the products. Delocalized charge

4. (a) Explain why Brauman needed to propose differential transition state solvation to rationalize his earlier gas-phase results. His results suggested minor steric effects without solvation.

   (b) Illustrate your answer with a potential energy surface.

5. What was found in this paper to be the major cause for the transition state energy differences for gas-phase $S_N2$-reactions involving neopentyl vs. methyl (i.e., what causes the observed steric effects)? Angle deformation

6. Consider Figure 5 and explain (by drawing the critical parts of TS:s) what it tells about the difference in geometries of the transition states for chloride exchange in ethyl and neopentyl chlorides in methanol solution. Angle deformation

7. Discuss the reasons for the slightly different C-Cl distances in the transition states of these $S_N2$-reactions in polar solution vs. gas phase. Lengthening of C-Cl bond allows better solvation of the Cl-part

8. Does solvation have a major impact on the structures of the transition states of the reactions considered here? No
9. Explain how nonstatistical behavior of the reacting system in the gas-phase reactions discussed here should produce slower rates than statistical behavior. **Recrossing of the TS slows down the reaction.**

10. Based on this paper, would you expect more significant steric effects for the discussed $S_{N2}$-reactions in solution or in the gas phase, or no difference? **No difference.**
A. Average $A = 0.934 \pm 0.013 \, (15)$

So, the std. error of the mean

$$\frac{\sigma}{\sqrt{n}} = \frac{2.5\sigma_{0.013}}{2.45} = 0.014 \, (3.1\% \, rel.)$$

$$A = E \cdot C = 0.934 = 3.540 \text{ lit.} / \text{cm} \cdot \text{cm}^{-1}$$

$$C \text{ (undiluted solution)} = 1.24 \times 10^{-5} \text{ mole} / \text{liter}$$

$$\times \text{dilution factor } 4/1 = 4.96 \times 10^{-4} \text{ mole /liter}$$

in the 1.0 ml sample.

$$Y = 0.300 \, l \text{ (total)} = 1.488 \times 10^{-4} \text{ mole} \times 4 \text{ ml} \times \frac{300 \text{ ml}}{1 \text{ liter}}$$

$$\text{pHes Cys consumed} = \Delta n = \frac{\Delta P \cdot V}{RT}$$

$$= \frac{(0.11 - 0.055) \text{ atm} \cdot 3.0 \text{ l}}{0.08206 \frac{62 \text{ atm}}{\text{mole} \cdot \text{liter}}} = 6.76 \times 10^{-3} \text{ mole Cys consumed}$$

So, yield of Alanine = \frac{1.488 \times 10^{-4} \text{ mole alanine produced}}{6.76 \times 10^{-3} \text{ mole Cys consumed}}

$$= 0.0220 = 2.20\% \, (m/m)$$

At the 95% C.I. $\alpha = 2.20 \pm (0.031 - 2.20)$

$$= 2.20 \pm 0.031 \%$$

So, Bob's confidence interval is $2.13 - 2.27\%$

This is significantly different from Miller's yield.
2) The question asked about overall uncertainty, not precision, so the uncertainties must be propagated.

We first express the calculation as:

\[
\frac{(A/EL)\cdot 40 \cdot 0.300}{(0.11-0.055) \cdot 3.0} = 0.08206 \cdot 2.98
\]

For addition and subtraction, the absolute variances (\(S^2\)) add, while for multiplication and division, the relative variances add.

The dilution factor (\(40\)) results from an addition, i.e.

\[
\frac{\sqrt{(\pm 0.05) ml + 39(\pm 0.05) ml}}{\sqrt{1(\pm 0.05) ml}} = \frac{40(\pm 0.070)}{1\pm 0.05} = 40(\pm 0.18\%) = 40(\pm 5\%)
\]

The relative uncertainty in the dilution factor 40 is thus:

\[
(0.05)^2 + (0.0018)^2)^{1/2} = 0.05
\]

For the \(\Delta n\), we have

\[
0.11(\pm 0.005) - 0.055(\pm 0.005) = 0.055 (\pm (0.005^2 + 0.005^2)^{1/2}) = 0.055 \pm 0.0071
\]

As a relative uncertainty, this is

\[
\frac{0.0071}{0.055} = 0.13 = 13\%
\]
Next we express the calculation with relative uncertainties:

\[
0.434 (± 3\%) / 35.080 (± 0.14\%) - 1 (± 0\% \text{ assumed}) .90 (± 5\%) - 300 (± 2.3\%)
\]

\[
= 0.55 (± 13\%) - 3.0 (± 0.33\%)
\]

\[
= 0.08206 - 2.95
\]

Assume no uncertainty here.

When you have one term that is 1%, this will be a good approximation.

Now, the overall fractional uncertainty is:

\[
\left(0.03\right)^2 + \left(0.001\right)^2 + \left(0.05\right)^2 + \left(0.033\right)^2 + \left(0.13\right)^2 + \left(0.033\right)^2 \right)^{\frac{1}{2}}
\]

\[
= \left(0.0009 + 0.000001 + 0.0025 + 0.00011 + 0.0169 + 0.0001\right)^{\frac{1}{2}}
\]

\[
= \sqrt{0.02}
\]

\[
= 0.14 = 14\%
\]

or, his final result should be

\[
2.20 (± 0.31\%)
\]

3) There are many... (you may come up with other valid and a key set of questions for the analyst to ask:

- Is the chemistry that makes a colored complex specific to alanine?

- Are there any other non-complexing species that could absorb at \(\lambda = 350\) nm?

These two would cause a positive error.

It is also possible that alanine could react with some other species in solution before being mixed with the reagent. This would result in a negative error.
4.) This is very important!
Bob said:
- Conduct the experiment for the same period of time but without the arc.
- Conduct the experiment for the same period of time, but without the Chy.
Simple, eh?

5.) Amino acid + amino acid → polypeptide

\[ \text{NH}_2 \]

\[ \text{CH}_3 \text{C} = \text{O} \text{H}^{+} + \text{H}_2 \text{NCH}_2 \text{COOH} \]

E.g.: CH$_3$CHOHCH$_2$COOH + H$_2$NCH$_2$COOH →

\[ \text{NH}_2 \text{O} \]

\[ \text{CH}_3 \text{C} = \text{C} \]

\[ \text{H} \]

\[ \text{NCH}_2 \text{COOH} \] (dipeptide)

If this happens in solution before you mix with reagent, you might underestimate alanine.