In the field of computational chemistry, the term “chemical accuracy” refers to the ability to calculate thermochemical quantities like enthalpies of formation to within 1 kcal/mol (or about 4 kJ/mol) of experimental values. But where does this specific 1 kcal/mol threshold come from?

The origin traces back to the pioneering work of John Pople, one of the founders of modern computational chemistry. Pople realized that for computational models to be truly useful in predicting chemical properties, they needed to match or exceed the accuracy of experimental measurements. For thermodynamic data like heats of formation or ionization potentials, he proposed a “global accuracy” target of 1 kcal/mol as an appropriate goal.

This 1 kcal/mol benchmark has a few key justifications:

1. It matches typical uncertainties in experimental thermochemical measurements. By achieving 1 kcal/mol accuracy, computational methods can effectively reproduce and predict experimental energies.
2. At room temperature, a 1.4 kcal/mol difference in free energy translates to about a 10-fold change in equilibrium or rate constants. Therefore, an accuracy of ~1 kcal/mol allows predictions to be within an order of magnitude of experiment.
3. An accuracy of 1 kcal/mol corresponds to about 0.05 eV, which would constitute good accuracy for properties like ionization energies and electron affinities.

With these motivations, Pople spearheaded the development of sophisticated composite methods like G1, G2, G3 and others aimed at reaching the coveted 1 kcal/mol “chemical accuracy” for thermochemical predictions across a wide range of molecules and properties.

So in essence, the 1 kcal/mol definition originated as a pragmatic threshold to match the accuracy limits of experiments at the time. It allowed computational chemistry to become a truly predictive tool for real chemical systems, rather than just a qualitative model. While modern methods have improved and sub-kcal/mol accuracies are possible, 1 kcal/mol remains an iconic target emblematic of the transition to reliable, quantitative computational thermochemistry.

References:

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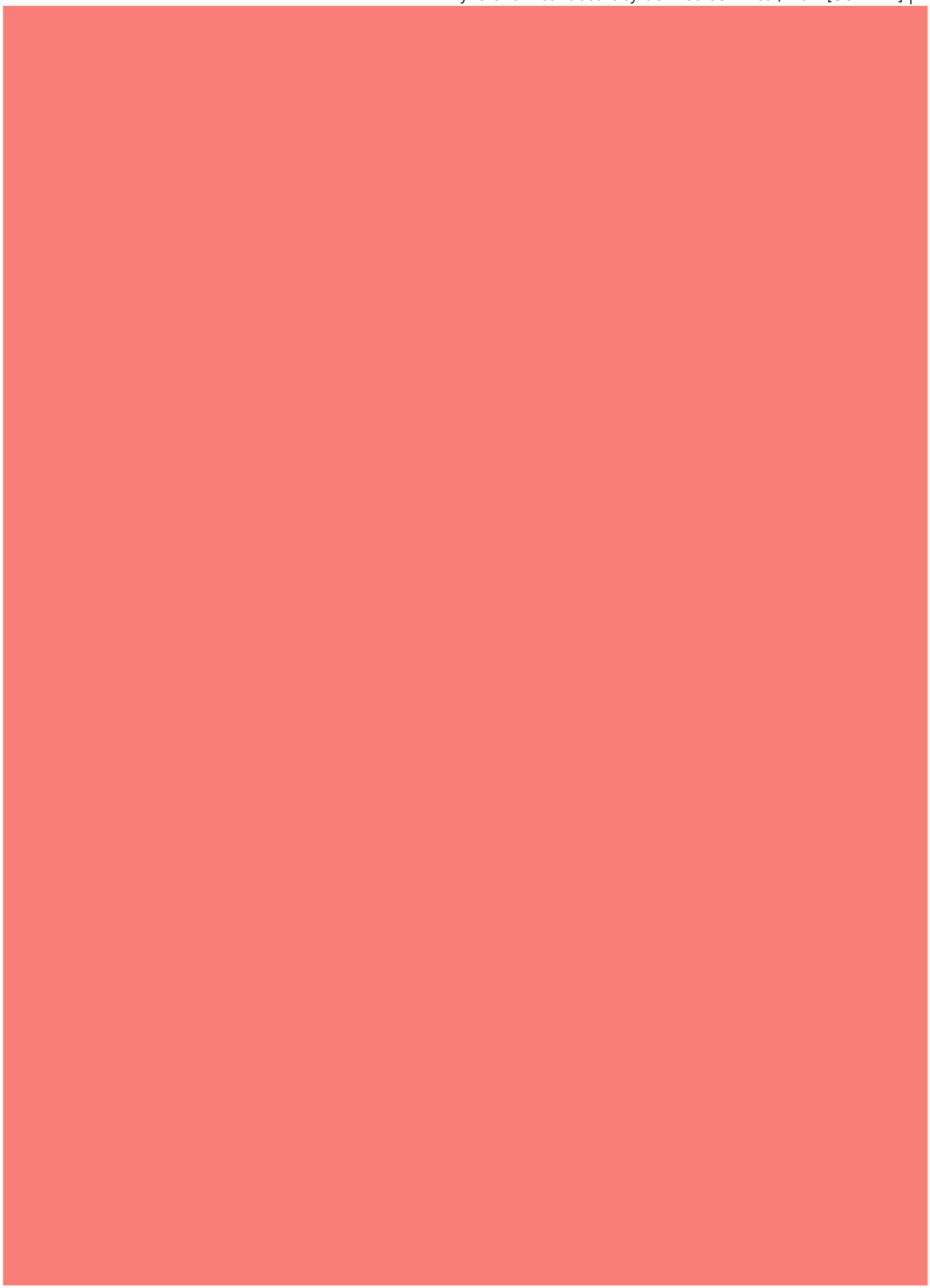

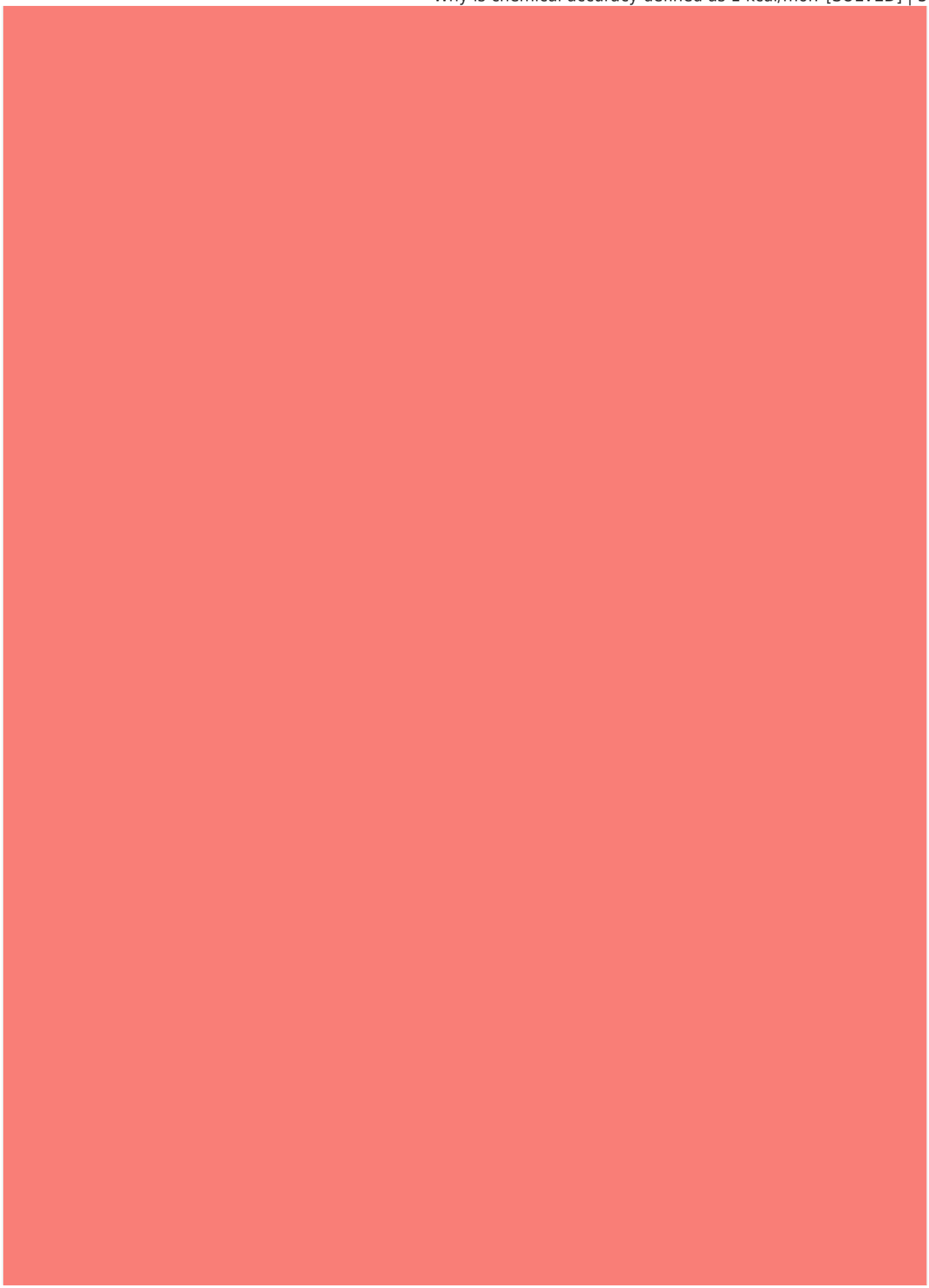

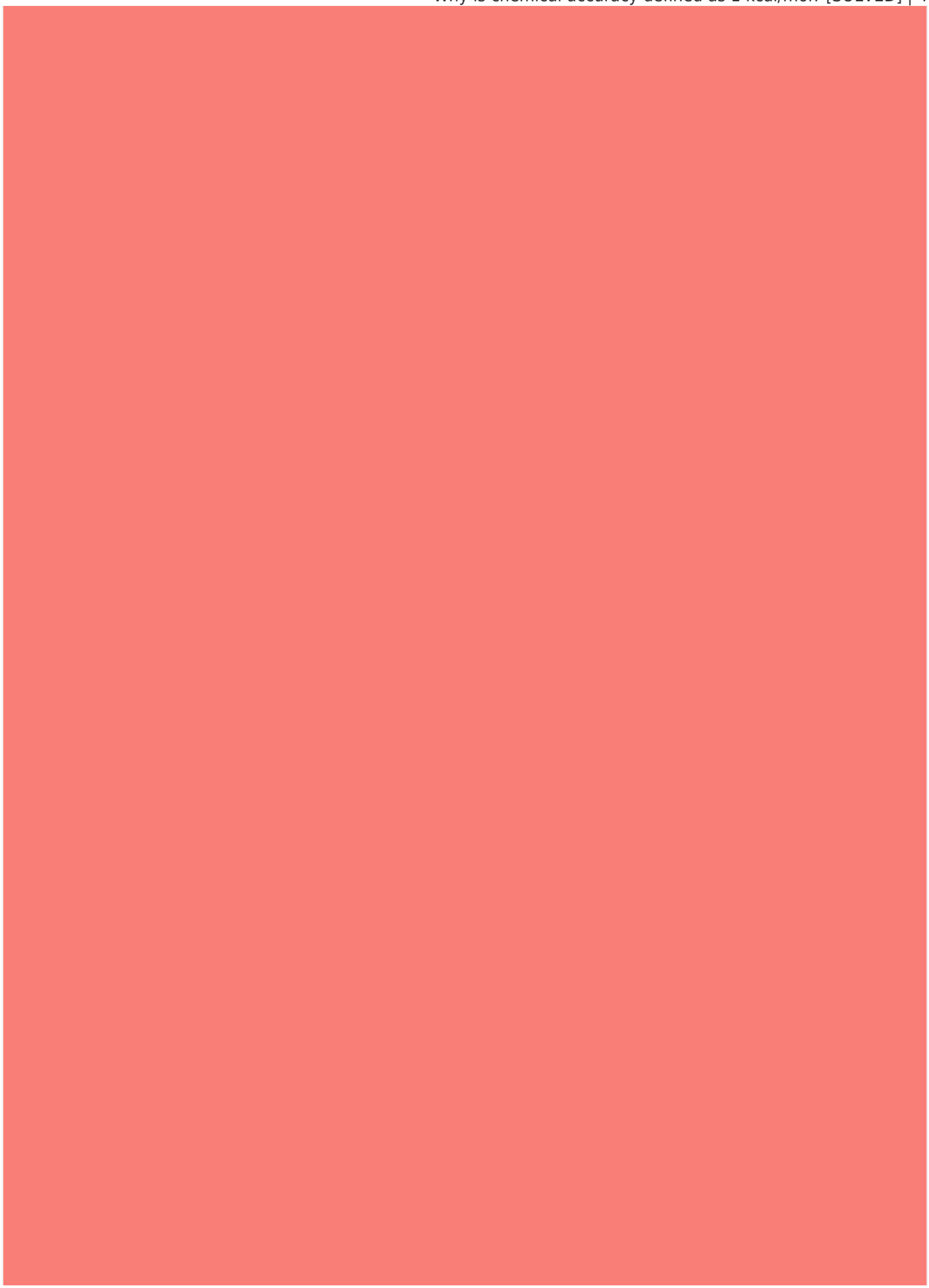

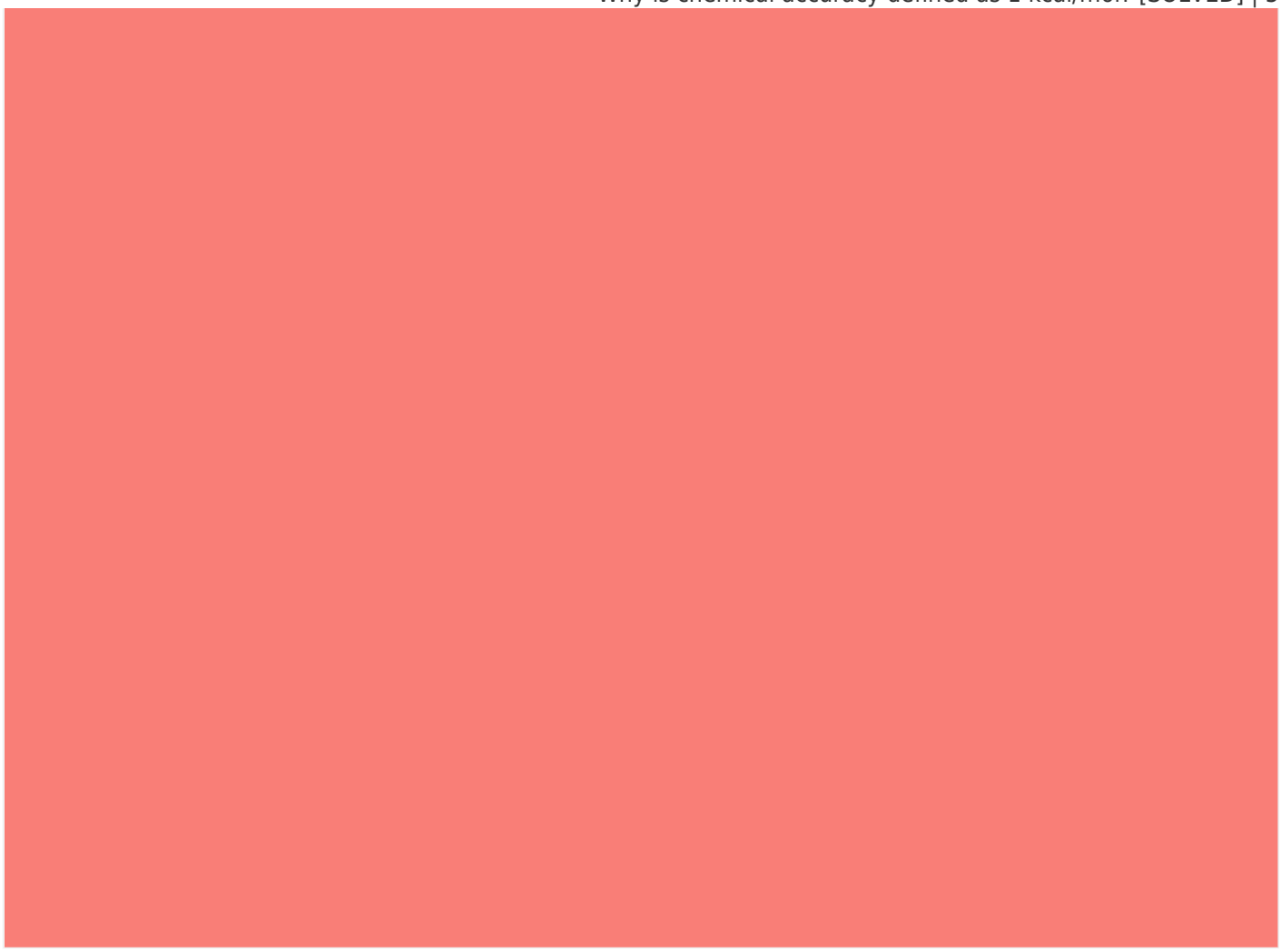

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