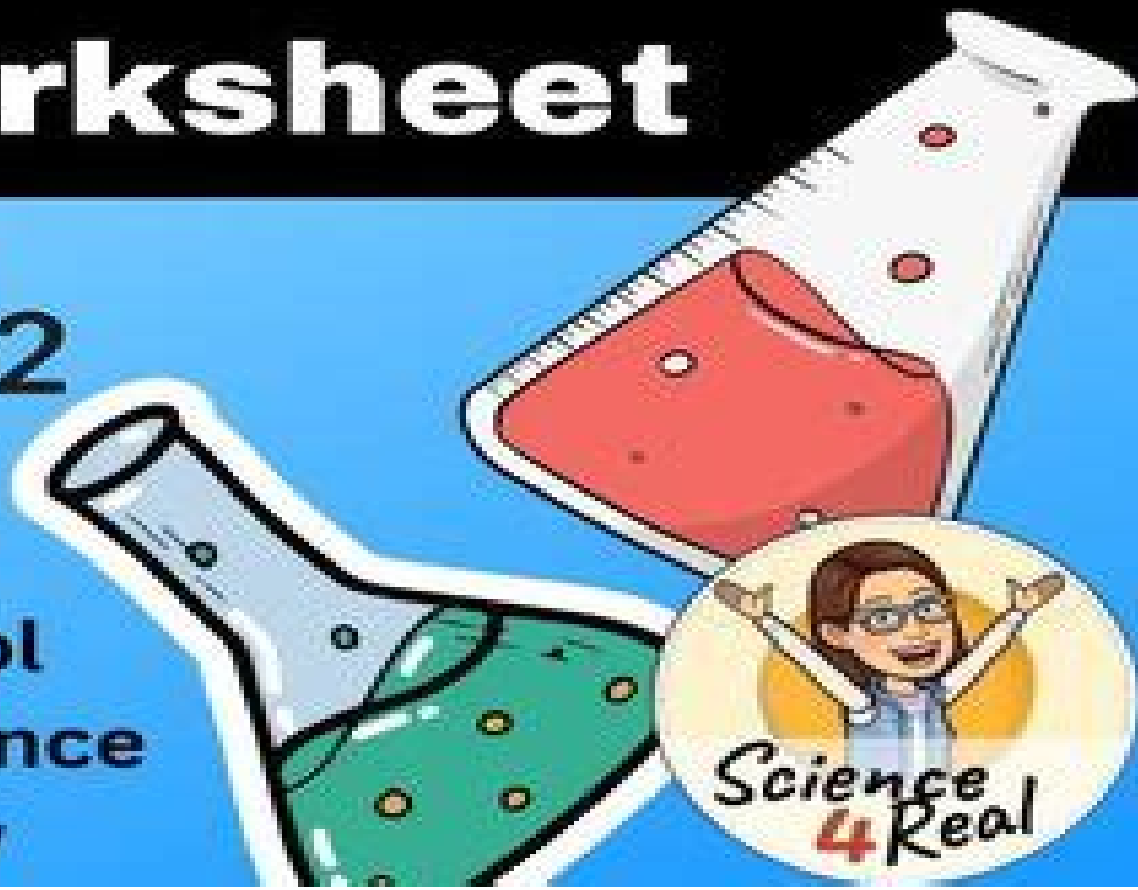


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2003, □□□ □□ □□□□□□ **Chemical Equilibria in Solution** M. J. Blandamer, 1992 The Equilibrium Assumption in the Theory of Absolute Reaction Rates Charles Francis Curtiss, 1948 The assumption that systems in the activated state are in

equilibrium with the reactant molecules has been open to question In this paper the methods of classical mechanics are used to obtain an expression for the rate constant without making this assumption The result is similar in form to that obtained by Eyring except that the average velocity of the points in configuration space is related directly to the distribution in velocities of the molecules of the gas in real space If one assumes that this distribution is Maxwellian one obtains the Eyring expression However the chemical reaction itself acts as a perturbing influence and causes the distribution in velocities to be somewhat different from Maxwellian It is this perturbation of the distribution function which leads to a different value of the rate constant and consequently to a measure of the effect of the equilibrium assumption Author

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