

Compare and contrast gas phase and surface/catalytic reactions

	Gas phase	catalytic reactions
Kinetics	<ol style="list-style-type: none"> 1. Usually simple overall rate law (first order, second order, half order) 2. Often first order 3. Usually follows Arrhenius's law or Perin's equation 	<ol style="list-style-type: none"> 4. Usually complex kinetics 5. often zero order 6. sometimes negative order 7. curved arrhenius plots 8. Individual steps follow arrhenius' law 9. Overall does not follow arrhenius's law
Mechanisms	<ol style="list-style-type: none"> 10. Initiation propagation mechanism 11. Reactive species are radicals 12. Reaction occur throughout the phase 13. Usually only single radicals 14. Initiation step - bond in reactants break 15. Propagation steps where radicals products form 16. Require a catalytic cycle 17. Require low barriers 18. $E_a < 0.15T$ for initiation 19. $E_a < 0.07 T$ for propagation 20. Usually Termination 	<ol style="list-style-type: none"> 21. Initiation propagation mechanism 22. Reactive species are radicals bound to surfaces 23. Reactions occur only near the catalyst 24. Can be di or tri-radicals 25. Initiation step - create an active site 26. Propagation steps where radicals products form 27. Require a catalytic cycle 28. Require low barriers 29. $E_a < 0.15T$ for initiation 30. $E_a < 0.07 T$ for propagation 31. No Termination needed
Relative rates	<ol style="list-style-type: none"> 32. Low rates except at high temperatures 33. Low selectivity 	<ol style="list-style-type: none"> 34. Much higher rates (10^{10} to 10^{40} higher) 35. Much higher selectivity's 36. Possible to form different products (because of di radicals)
Activation barriers	<ol style="list-style-type: none"> 37. High 38. Often determined by initiation step 39. Can estimate with Polayni equation of Blowers-Masel 40. $E_{a0}=1$ for initiation 41. $E_{a0}=12$ for atom transfer 42. $E_{a0}=45$ for ligand transfer to hydrogen 43. $E_{a0}=50$ for ligand transfer to hydrogen 	<ol style="list-style-type: none"> 44. Low 45. Usually determined by propagation steps 46. Can estimate with Blowers-Masel 47. Polayni usually does not work 48. $E_{a0}=1$ for initiation 49. $E_{a0}=12$ for atom transfer 50. $E_{a0}=45$ for ligand transfer to hydrogen 51. $E_{a0}=50$ for ligand transfer to hydrogen 52. Extra 15 kcal/mole for proximity effect.