

CONTENTS

NOTATION	xi
1. THE TRANSITION STATE METHOD	
1. The adiabatic approximation. Potential energy surfaces	1
2. Basic assumptions of the transition state method. Deduction of a formula for the rate of an elementary process	7
3. Over-barrier reflection and tunnel corrections	20
4. The quantum partition functions and symmetry numbers	23
5. The isotope effect	28
6. The principle of detailed balance and the transition state method	34
2. THE EXCHANGE OF VIBRATIONAL AND TRANSLATIONAL ENERGY IN MOLECULAR COLLISIONS	
7. General observations on the exchange of energy in molecular collisions	41
8. Model of a forced harmonic oscillator	52
9. Vibrational transitions between the lowest levels of diatomic molecules in non-degenerate electronic states	58
10. The vibrational relaxation of oxygen and nitrogen	78
11. Strong coupling of the vibrational and translational motion	83
12. Resonant exchange of vibrational energy	92
13. Exchange of energy in the collisions of polyatomic molecules	96
3. THE EXCHANGE OF ELECTRONIC, VIBRATIONAL, AND TRANSLATIONAL ENERGY IN MOLECULAR COLLISIONS	
14. The classification of nonadiabatic transitions	99
15. The linear model. The Landau-Zener formula	107
16. Generalization of the linear model	117
17. Model of non-linear terms	124
18. Nonadiabatic processes in atomic collisions	132
19. Nonadiabatic processes in the collisions of atoms with diatomic molecules	148
20. Vibrational transitions between the lowest levels of a diatomic molecule in a degenerate electronic state	166
21. Vibrational relaxation of nitric oxide	175
4. UNIMOLECULAR REACTIONS	
22. The thermal decomposition and isomerization of molecules as unimolecular reactions	179
23. Dependence of the rate constant on the pressure. The mechanism of strongly-activating collisions	181
24. The Slater model	193
25. Kassel's model	208

26. The effect of anharmonicity on the reaction rate	217
27. Nonadiabatic reactions	227
5. THE STATISTICAL THEORY OF REACTIONS	
28. The basic assumptions of the statistical theory	237
29. Harmonic model of an active molecule	244
30. An anharmonic model of an active molecule	253
31. Statistical theory with regard for the conservation of angular momentum	258
32. The isotope effect	271
33. The application of the statistical theory to thermal reactions	274
6. DIFFUSION THEORY OF REACTIONS	
34. Diffusion in phase space	283
35. Diffusion through energy states	294
36. Relaxation and the transmission of particles across a potential barrier	299
37. Tunnel transitions in a double potential well	305
38. Random walks over the discrete energy levels	310
39. Mechanism of activation and the non-equilibrium distribution function in unimolecular reactions	315
7. DISSOCIATION OF DIATOMIC MOLECULES AND THE RECOMBINATION OF ATOMS	
40. Equilibrium theory of decomposition and recombination	322
41. The contribution of various degrees of freedom of a dissociating molecule to the decomposition rate constant	328
42. Variational theory of dissociation and recombination	334
43. The vibrational relaxation of diatomic molecules	342
44. Non-equilibrium theory of dissociation and recombination	350
45. Connection between the rate constants of dissociation and recombination	360
46. Thermal dissociation of oxygen	364
8. BIMOLECULAR REACTIONS	
47. Exchange as a bimolecular reaction	367
48. The potential energy surfaces of bimolecular reactions	370
49. Equilibrium theory	386
50. The statistical theory	391
51. Theory of direct reactions	403
52. Dynamics of exchange reactions	412
53. Disturbance of the equilibrium distribution in bimolecular reactions	424
APPENDIX: PROBLEMS OF ELEMENTARY PROCESSES IN THERMAL GAS REACTIONS	434
REFERENCES	446
INDEX	469