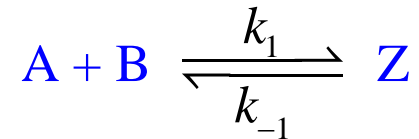


Oposing Reactions – 2nd Order Case



At equilibrium $-\frac{da}{dt} = -\frac{db}{dt} = k_1 ab - k_{-1} z = \frac{dz}{dt} = 0$ and $k_1 a_{\text{eq}} b_{\text{eq}} = k_{-1} z$

$$a(t) = a_{\text{eq}} - x(t), \quad b(t) = b_{\text{eq}} - x(t), \quad z(t) = z_{\text{eq}} + x(t), \quad \frac{dz}{dt} = \frac{dx}{dt} = -\frac{da}{dt}$$

$$-\frac{da}{dt} = k_1 (a_{\text{eq}} - x)(b_{\text{eq}} - x) - k_{-1} (z_{\text{eq}} + x) = \frac{dx}{dt}$$

$$-\frac{dx}{dt} = (k_1 a_{\text{eq}} + k_1 b_{\text{eq}} + k_{-1} - k_1 x) x$$

For $x \ll a_{\text{eq}}, b_{\text{eq}}$ the quadratic term can be ignored

\Rightarrow first-order return to equilibrium with $k_{\text{eff}} = k_1 (a_{\text{eq}} + b_{\text{eq}}) + k_{-1}$

$$R_1 - R_2 = 0$$

$$R_2 - R_3 = 0$$

$$R_4 + R_3 - R_5 = 0$$

$$R_1 - R_4 + R_5 - 2R_6 = 0$$

$$R_1 = R_2 = R_3$$

$$R_1 + R_3 - 2R_6 = 0$$

$$2R_1 - 2R_6 = 0$$

$$R_1 = R_6$$

$$R_1 = k_1 [\text{CH}_3\text{CHO}]$$

$$R_2 = k_2 [\text{CHO}]$$

$$R_3 = k_3 [\text{H}][\text{CH}_3\text{CHO}]$$

$$R_4 = k_4 [\text{CH}_3][\text{CH}_3\text{CHO}]$$

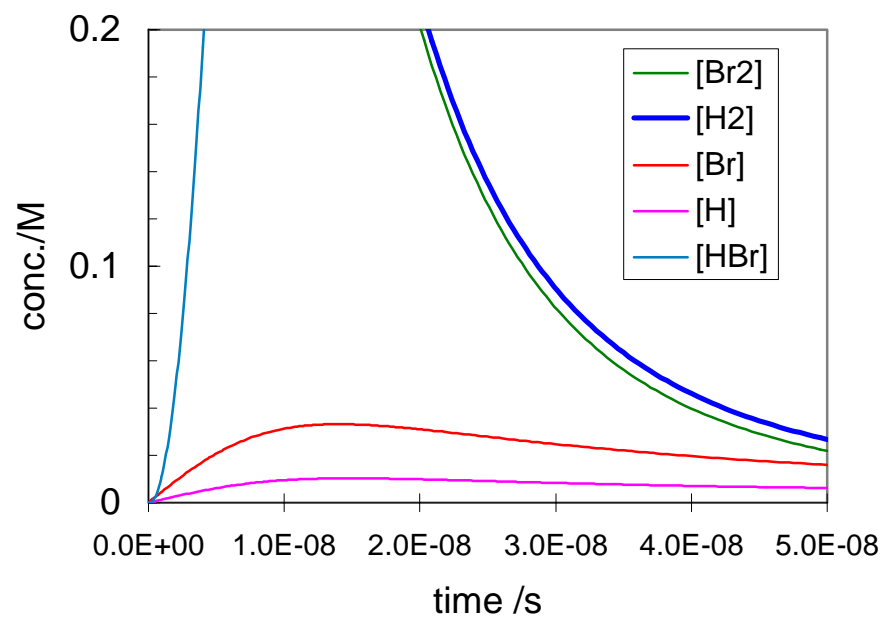
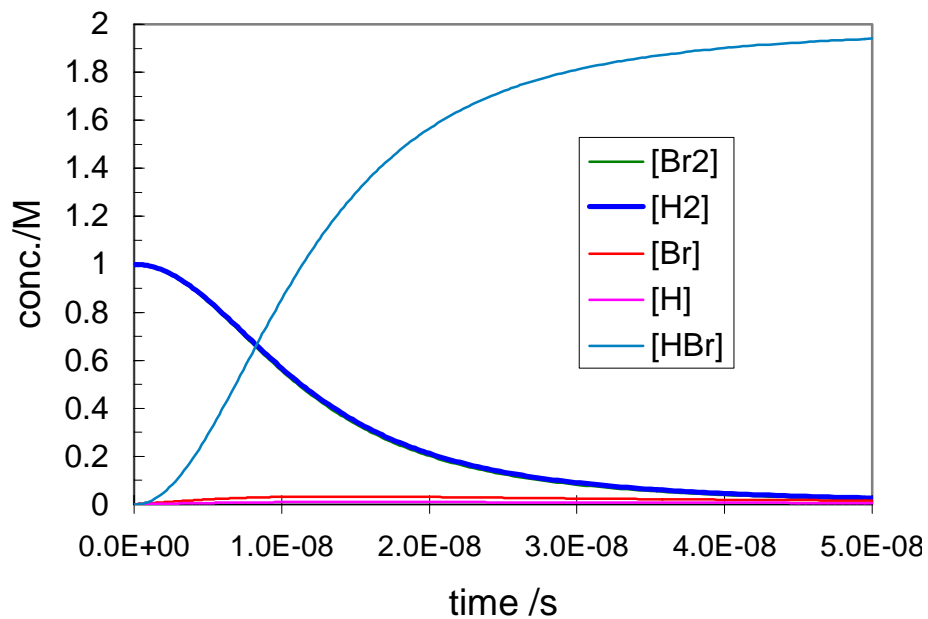
$$R_5 = k_5 [\text{CH}_3\text{CO}]$$

$$R_6 = k_6 [\text{CH}_3]^2$$

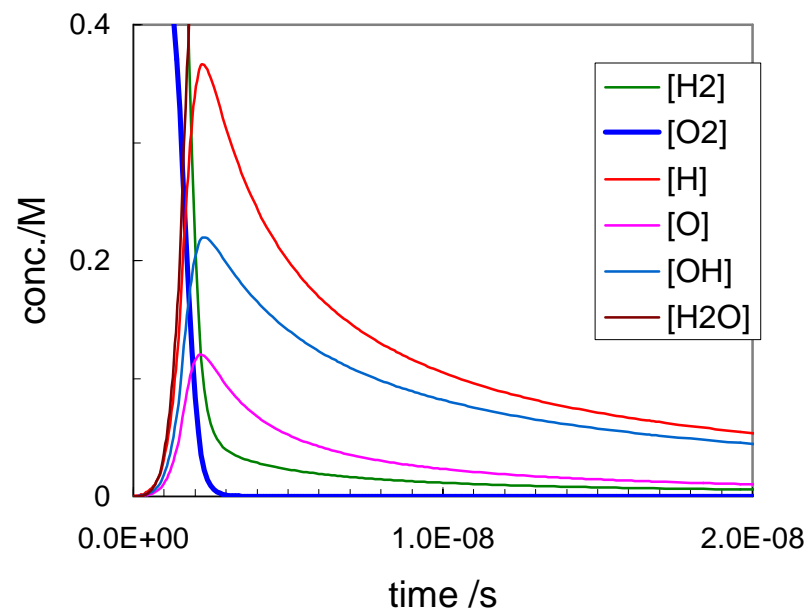
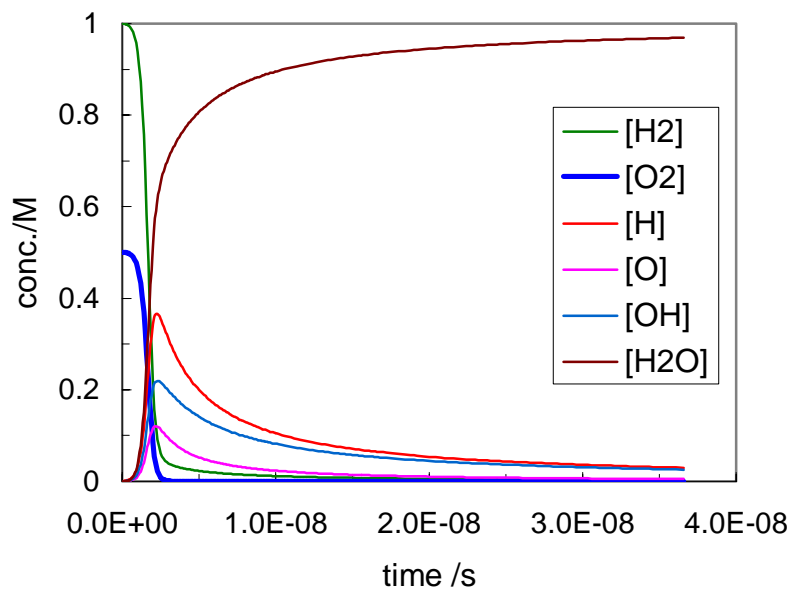
$$[\text{CH}_3]^2 = (k_1/k_6)[\text{CH}_3\text{CHO}]$$

$$\text{rate} = \frac{d}{dt}[\text{CH}_4] = R_4 = k_4 (k_1/k_6)^{1/2} [\text{CH}_3\text{CHO}]^{3/2}$$

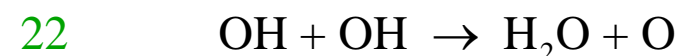
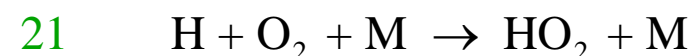
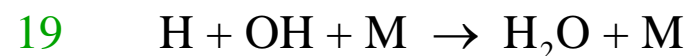
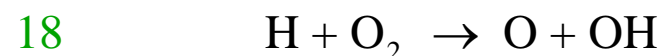
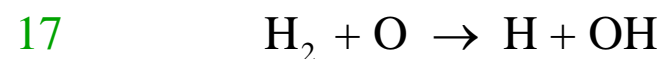
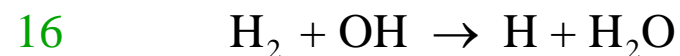
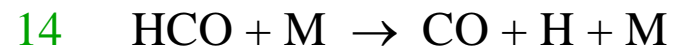
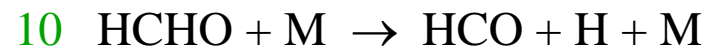
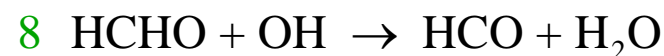
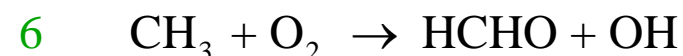
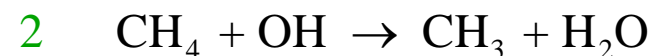
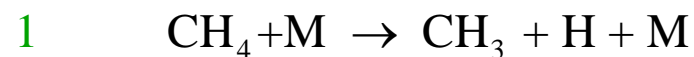
Br ₂ + H ₂ --> 2HBr										
Br ₂ --> 2Br			R1 = k1 [Br ₂]			k1 =	3.0E+06	s ⁻¹		
Br + H ₂ --> HBr + H			R2 = k2 [H ₂][Br]			k2 =	3.0E+09	M ⁻¹ s ⁻¹		
H + Br ₂ --> HBr + Br			R3 = k3 [Br ₂][H]			k3 =	1.0E+10	M ⁻¹ s ⁻¹		
2Br --> Br ₂			R4 = k4 [Br] ²			k4 =	1.0E+09	M ⁻¹ s ⁻¹		
dt /s =	1.00E-10	2.00E-10	3.00E-10	4.00E-10	5.00E-10					
[Br ₂] _o /M =	1.00		[H ₂] _o /M =	1.00		[HBr] _o /M =	0.00			
time	[Br ₂]	[H ₂]	[Br]	[H]	[HBr]	R1	R2	R3	R4	
0.0E+00	1.0000	1.0000	0.0000	0.0000	0.0000	3.00E+06	0.00E+00	0.00E+00	0.00E+00	
1.0E-10	0.9997	1.0000	0.0006	0.0000	0.0000	3.00E+06	1.80E+06	0.00E+00	3.60E+02	
2.0E-10	0.9994	0.9998	0.0010	0.0002	0.0002	3.00E+06	3.06E+06	1.80E+06	1.04E+03	
3.0E-10	0.9989	0.9995	0.0015	0.0003	0.0007	3.00E+06	4.48E+06	3.06E+06	2.23E+03	
4.0E-10	0.9983	0.9991	0.0020	0.0004	0.0014	2.99E+06	5.84E+06	4.47E+06	3.80E+03	
5.0E-10	0.9976	0.9985	0.0024	0.0006	0.0025	2.99E+06	7.22E+06	5.84E+06	5.81E+03	



2H ₂ + O ₂ --> 2H ₂ O														
H ₂ --> 2H			R1 = k1 [H ₂]		k1 = 3.0E+06 s ⁻¹									
H + O ₂ --> OH + O			R2 = k2 [O ₂][H]		k2 = 1.0E+10 M ⁻¹ s ⁻¹									
O + H ₂ --> OH + H			R3 = k3 [H ₂][O]		k3 = 1.0E+10 M ⁻¹ s ⁻¹									
OH + H ₂ --> H ₂ O + H			R4 = k4 [H ₂][OH]		k4 = 1.0E+10 M ⁻¹ s ⁻¹									
2H --> H ₂			R5 = k5 [H] ²		k5 = 1.0E+09 M ⁻¹ s ⁻¹									
dt / s =	5.00E-11	1.00E-10	2.00E-10	4.00E-10	5.00E-10									
[H ₂] ₀ /M =	1.00		[O ₂] ₀ /M =	0.50		[H ₂ O] ₀ /M =	0.00							
time	[H ₂]	[O ₂]	[H]	[O]	[OH]	[H ₂ O]	R1	R2	R3	R4	R5			
0.0E+00	1.0000	0.5000	0.0000	0.0000	0.0000	0.0000	3.00E+06	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00		
5.0E-11	0.9999	0.5000	0.0003	0.0000	0.0000	0.0000	3.00E+06	1.50E+06	0.00E+00	0.00E+00	9.00E+01			
1.0E-10	0.9997	0.4999	0.0005	0.0001	0.0001	0.0000	3.00E+06	2.62E+06	7.50E+05	7.50E+05	2.76E+02			
1.5E-10	0.9995	0.4998	0.0008	0.0002	0.0002	0.0000	3.00E+06	3.84E+06	1.69E+06	2.06E+06	5.91E+02			
2.0E-10	0.9991	0.4996	0.0011	0.0003	0.0004	0.0001	3.00E+06	5.31E+06	2.76E+06	3.79E+06	1.13E+03			
2.5E-10	0.9987	0.4993	0.0014	0.0004	0.0006	0.0003	3.00E+06	7.12E+06	4.04E+06	5.93E+06	2.03E+03			
3.0E-10	0.9980	0.4990	0.0019	0.0006	0.0009	0.0006	3.00E+06	9.37E+06	5.57E+06	8.53E+06	3.10E+03			

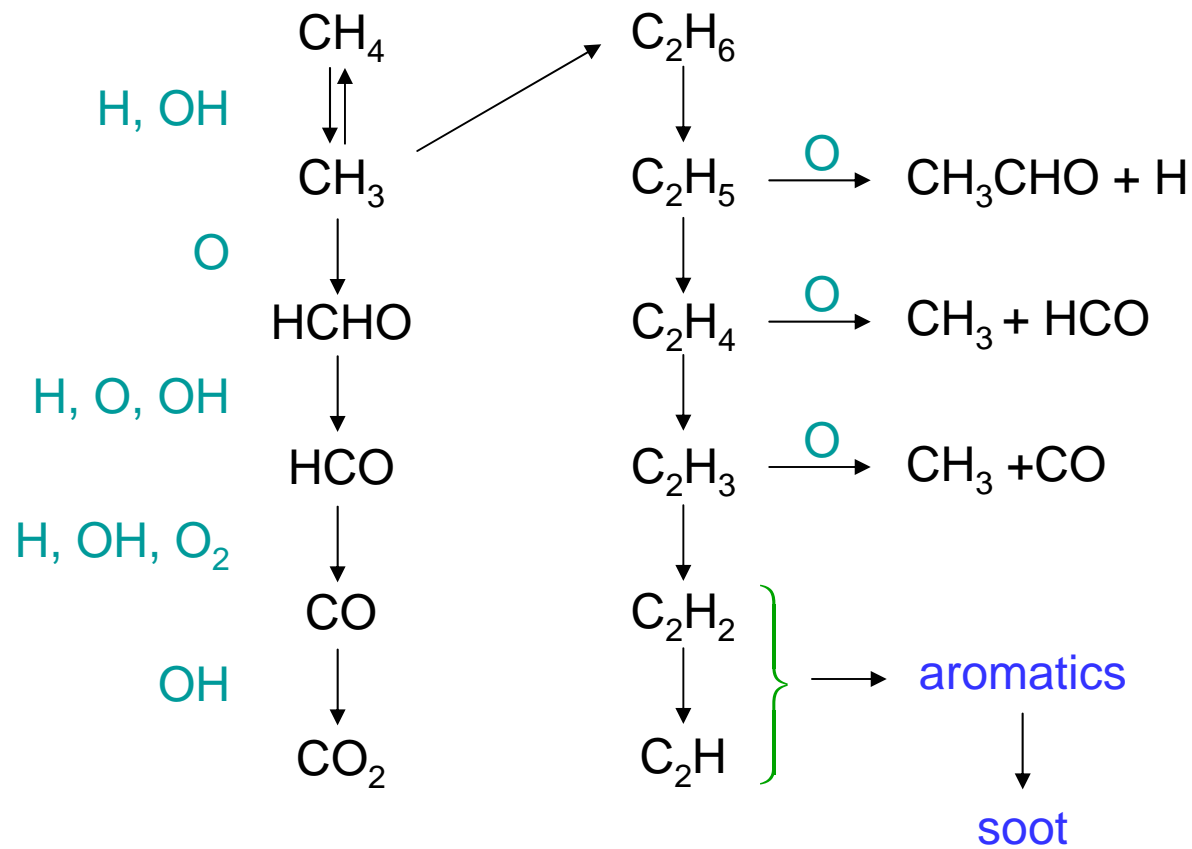


High Temperature Oxidation of Methane



At 2000 K all the rate constants are within a factor of ten of each other.

Oxidation of Methane – 2



Sensitivity Analysis

Consider a complex reaction scheme of M reactions (and thus M rate constants) involving N chemical species. The kinetics are described by a set of M coupled rate equations:

$$\frac{dy_i}{dt} = f_i(y_1, y_2, \dots, y_N, t, k_1, k_2, \dots, k_M)$$

whose solutions are $y_i = g_i(t, k_1, k_2, \dots, k_M)$

subject to the boundary conditions $y_i(t=0)$

The sensitivity of each species to small changes in each rate constant is given by

$$\Delta y_i = \sum_{j=1}^M S_{ij} \Delta k_j$$

where $S_{ij} = \frac{\partial y_i}{\partial k_j}$ are elements of the sensitivity matrix

Practical application of sensitivity analysis involves evaluating the sensitivity coefficients and identifying the lowest values. If any row (chemical species) or column (reaction) has all low values, that row/species is unimportant and can be neglected in a simpler model.