Electrochemical series

Stronger oxidizing agent

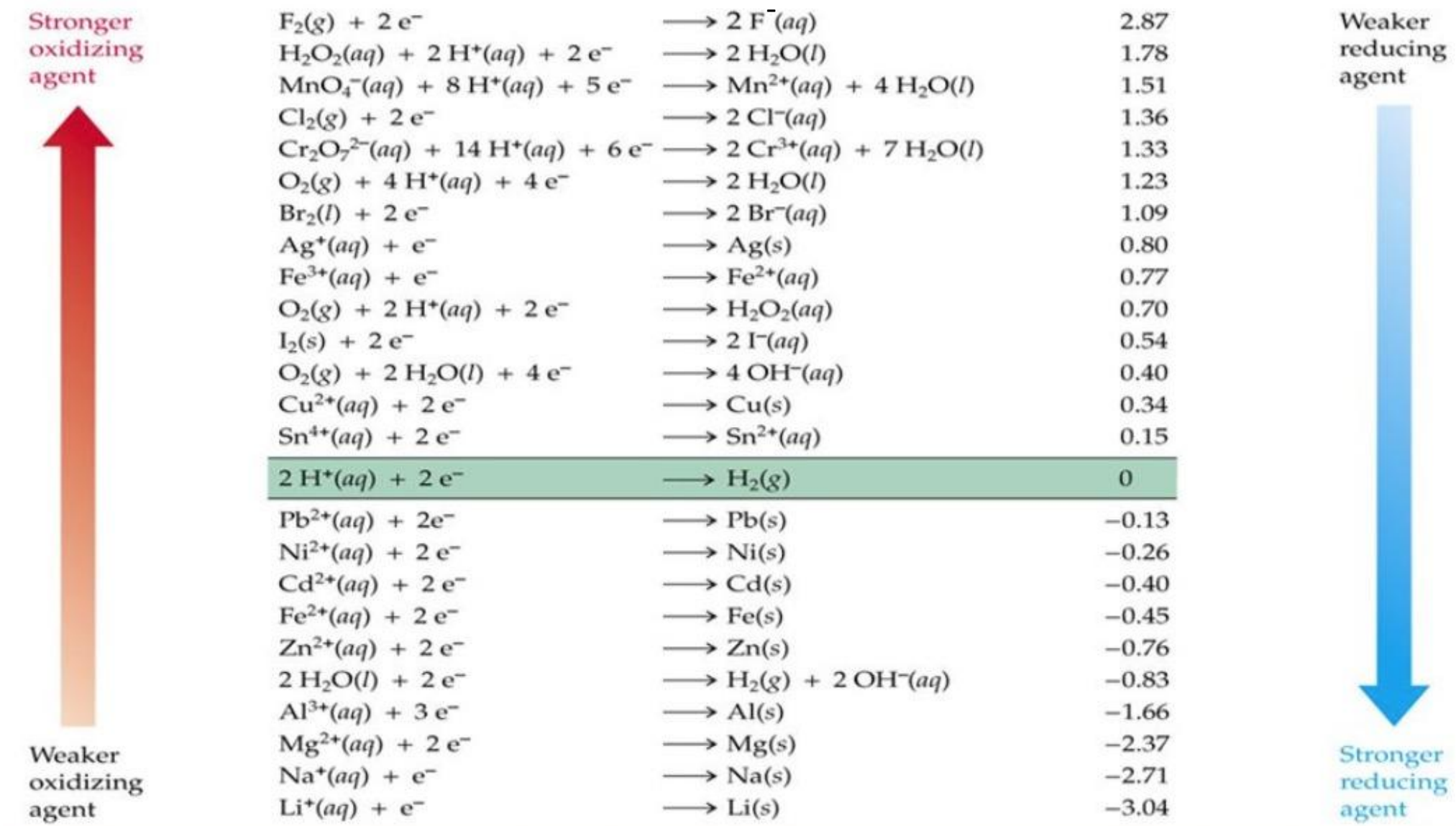
$F_2(g) + 2\,e^- \longrightarrow 2\,F^-(aq)$		2.87
$H_2O_2(aq) + 2\,H^+(aq) + 2\,e^- \longrightarrow 2\,H_2O(l)$		1.78
$MnO_4^-(aq) + 8\,H^+(aq) + 5\,e^- \longrightarrow Mn^{2+}(aq) + 4\,H_2O(l)$		1.51
$Cl_2(g) + 2\,e^- \longrightarrow 2\,Cl^-(aq)$		1.36
$Cr_2O_7^{2-}(aq) + 14\,H^+(aq) + 6\,e^- \longrightarrow 2\,Cr^{3+}(aq) + 7\,H_2O(l)$		1.33
$O_2(g) + 4\,H^+(aq) + 4\,e^- \longrightarrow 2\,H_2O(l)$		1.23
$Br_2(l) + 2\,e^- \longrightarrow 2\,Br^-(aq)$		1.09
$Ag^+(aq) + e^- \longrightarrow Ag(s)$		0.80
$Fe^{3+}(aq) + e^- \longrightarrow Fe^{2+}(aq)$		0.77
$O_2(g) + 2\,H^+(aq) + 2\,e^- \longrightarrow H_2O_2(aq)$		0.70
$I_2(s) + 2\,e^- \longrightarrow 2\,I^-(aq)$		0.54
$O_2(g) + 2\,H_2O(l) + 4\,e^- \longrightarrow 4\,OH^-(aq)$		0.40
$Cu^{2+}(aq) + 2\,e^- \longrightarrow Cu(s)$		0.34
$Sn^{4+}(aq) + 2\,e^- \longrightarrow Sn^{2+}(aq)$		0.15
$2\,H^+(aq) + 2\,e^- \longrightarrow H_2(g)$		0
$Pb^{2+}(aq) + 2e^- \longrightarrow Pb(s)$		−0.13
$Ni^{2+}(aq) + 2\,e^- \longrightarrow Ni(s)$		−0.26
$Cd^{2+}(aq) + 2\,e^- \longrightarrow Cd(s)$		−0.40
$Fe^{2+}(aq) + 2\,e^- \longrightarrow Fe(s)$		−0.45
$Zn^{2+}(aq) + 2\,e^- \longrightarrow Zn(s)$		−0.76
$2\,H_2O(l) + 2\,e^- \longrightarrow H_2(g) + 2\,OH^-(aq)$		−0.83
$Al^{3+}(aq) + 3\,e^- \longrightarrow Al(s)$		−1.66
$Mg^{2+}(aq) + 2\,e^- \longrightarrow Mg(s)$		−2.37
$Na^+(aq) + e^- \longrightarrow Na(s)$		−2.71
$Li^+(aq) + e^- \longrightarrow Li(s)$		−3.04

Stronger reducing agent

standard potentials

A a measure of the tendency of a half-reaction to occur as a reduction (gain of electrons) relative to the standard hydrogen electrode (SHE) under standard conditions (25°C, 1 atm pressure, 1 M concentration of ions).

Electrochemical series



$F_2(g) + 2\,e^- \longrightarrow 2\,F^-(aq)$		2.87
$H_2O_2(aq) + 2\,H^+(aq) + 2\,e^- \longrightarrow 2\,H_2O(l)$		1.78
$MnO_4^-(aq) + 8\,H^+(aq) + 5\,e^- \longrightarrow Mn^{2+}(aq) + 4\,H_2O(l)$		1.51
$Cl_2(g) + 2\,e^- \longrightarrow 2\,Cl^-(aq)$		1.36
$Cr_2O_7^{2-}(aq) + 14\,H^+(aq) + 6\,e^- \longrightarrow 2\,Cr^{3+}(aq) + 7\,H_2O(l)$		1.33
$O_2(g) + 4\,H^+(aq) + 4\,e^- \longrightarrow 2\,H_2O(l)$		1.23
$Br_2(l) + 2\,e^- \longrightarrow 2\,Br^-(aq)$		1.09
$Ag^+(aq) + e^- \longrightarrow Ag(s)$		0.80
$Fe^{3+}(aq) + e^- \longrightarrow Fe^{2+}(aq)$		0.77
$O_2(g) + 2\,H^+(aq) + 2\,e^- \longrightarrow H_2O_2(aq)$		0.70
$I_2(s) + 2\,e^- \longrightarrow 2\,I^-(aq)$		0.54
$O_2(g) + 2\,H_2O(l) + 4\,e^- \longrightarrow 4\,OH^-(aq)$		0.40
$Cu^{2+}(aq) + 2\,e^- \longrightarrow Cu(s)$		0.34
$Sn^{4+}(aq) + 2\,e^- \longrightarrow Sn^{2+}(aq)$		0.15
$2\,H^+(aq) + 2\,e^- \longrightarrow H_2(g)$		0
$Pb^{2+}(aq) + 2e^- \longrightarrow Pb(s)$		−0.13
$Ni^{2+}(aq) + 2\,e^- \longrightarrow Ni(s)$		−0.26
$Cd^{2+}(aq) + 2\,e^- \longrightarrow Cd(s)$		−0.40
$Fe^{2+}(aq) + 2\,e^- \longrightarrow Fe(s)$		−0.45
$Zn^{2+}(aq) + 2\,e^- \longrightarrow Zn(s)$		−0.76
$2\,H_2O(l) + 2\,e^- \longrightarrow H_2(g) + 2\,OH^-(aq)$		−0.83
$Al^{3+}(aq) + 3\,e^- \longrightarrow Al(s)$		−1.66
$Mg^{2+}(aq) + 2\,e^- \longrightarrow Mg(s)$		−2.37
$Na^+(aq) + e^- \longrightarrow Na(s)$		−2.71
$Li^+(aq) + e^- \longrightarrow Li(s)$		−3.04

Equilibrium constant calculation

Equilibrium constant calculation

cell reaction $2\,Cu^{+}(aq) \rightarrow Cu(s) + Cu^{2+}(aq)$

A *disproportionation reaction*

Equilibrium constant calculation

cell reaction $2\,Cu^{+}(aq) \rightarrow Cu(s) + Cu^{2+}(aq)$ A *disproportionation reaction*

R: $Cu(s)|Cu^{+}(aq)$ $Cu^{+}(aq) + e^{-} \rightarrow Cu(s)$ $E^{\ominus}(R) = +0.52\,V$

L: $Pt(s)|Cu^{2+}(aq),Cu^{+}(aq)$ $Cu^{2+}(aq) + e^{-} \rightarrow Cu^{+}(aq)$ $E^{\ominus}(L) = +0.16\,V$

Equilibrium constant calculation

cell reaction $2\,Cu^{+}(aq) \rightarrow Cu(s) + Cu^{2+}(aq)$ A *disproportionation reaction*

R: $Cu(s)\|Cu^{+}(aq)$	$Cu^{+}(aq) + e^{-} \rightarrow Cu(s)$	$E^{\ominus}(R) = +0.52\,V$
L: $Pt(s)\|Cu^{2+}(aq),Cu^{+}(aq)$	$Cu^{2+}(aq) + e^{-} \rightarrow Cu^{+}(aq)$	$E^{\ominus}(L) = +0.16\,V$

$$E^{\ominus}_{cell} = 0.52\,V - 0.16\,V = +0.36\,V$$

Equilibrium constant calculation

cell reaction $2\,Cu^{+}(aq) \rightarrow Cu(s) + Cu^{2+}(aq)$ A *disproportionation reaction*

R: $Cu(s)|Cu^{+}(aq)$ $Cu^{+}(aq) + e^{-} \rightarrow Cu(s)$ $E^{\ominus}(R) = +0.52\,V$

L: $Pt(s)|Cu^{2+}(aq),Cu^{+}(aq)$ $Cu^{2+}(aq) + e^{-} \rightarrow Cu^{+}(aq)$ $E^{\ominus}(L) = +0.16\,V$

$$E^{\ominus}_{cell} = 0.52\,V - 0.16\,V = +0.36\,V$$

$$E_{cell} = E^{\ominus}_{cell} - \frac{RT}{\nu F}\ln Q$$

$$E^{\ominus}_{cell} = \frac{RT}{\nu F}\ln K$$

Equilibrium constant calculation

cell reaction $2\,Cu^{+}(aq) \rightarrow Cu(s) + Cu^{2+}(aq)$ A *disproportionation reaction*

R: $Cu(s)\vert Cu^{+}(aq)$	$Cu^{+}(aq) + e^{-} \rightarrow Cu(s)$	$E^{\ominus}(R) = +0.52\,V$
L: $Pt(s)\vert Cu^{2+}(aq),Cu^{+}(aq)$	$Cu^{2+}(aq) + e^{-} \rightarrow Cu^{+}(aq)$	$E^{\ominus}(L) = +0.16\,V$

$$E^{\ominus}_{cell} = 0.52\,V - 0.16\,V = +0.36\,V$$

$$E_{cell} = E^{\ominus}_{cell} - \frac{RT}{\nu F}\ln Q$$

$$E^{\ominus}_{cell} = \frac{RT}{\nu F}\ln K$$

$$RT/F = 0.025\,693\,V$$

Equilibrium constant calculation

cell reaction $2\,Cu^{+}(aq) \rightarrow Cu(s) + Cu^{2+}(aq)$ A *disproportionation reaction*

R: $Cu(s)|Cu^{+}(aq)$ $Cu^{+}(aq) + e^{-} \rightarrow Cu(s)$ $E^{\ominus}(R) = +0.52\,V$

L: $Pt(s)|Cu^{2+}(aq),Cu^{+}(aq)$ $Cu^{2+}(aq) + e^{-} \rightarrow Cu^{+}(aq)$ $E^{\ominus}(L) = +0.16\,V$

$$E^{\ominus}_{cell} = 0.52\,V - 0.16\,V = +0.36\,V$$

$$E_{cell} = E^{\ominus}_{cell} - \frac{RT}{\nu F}\ln Q$$

$$E^{\ominus}_{cell} = \frac{RT}{\nu F}\ln K$$

$$\nu = 1$$

$$RT/F = 0.025\,693\,V$$

Equilibrium constant calculation

cell reaction $2\,Cu^+(aq) \rightarrow Cu(s) + Cu^{2+}(aq)$ A *disproportionation reaction*

R: $Cu(s)|Cu^+(aq)$ $Cu^+(aq) + e^- \rightarrow Cu(s)$ $E^\ominus(R) = +0.52\,V$

L: $Pt(s)|Cu^{2+}(aq),Cu^+(aq)$ $Cu^{2+}(aq) + e^- \rightarrow Cu^+(aq)$ $E^\ominus(L) = +0.16\,V$

$$E^\ominus_{cell} = 0.52\,V - 0.16\,V = +0.36\,V$$

$$\ln K = \frac{0.36\,V}{0.025\,693\,V} = 14.0\ldots$$

$$K = 1.2 \times 10^6.$$

$$E_{cell} = E^\ominus_{cell} - \frac{RT}{\nu F}\ln Q$$

$$E^\ominus_{cell} = \frac{RT}{\nu F}\ln K$$

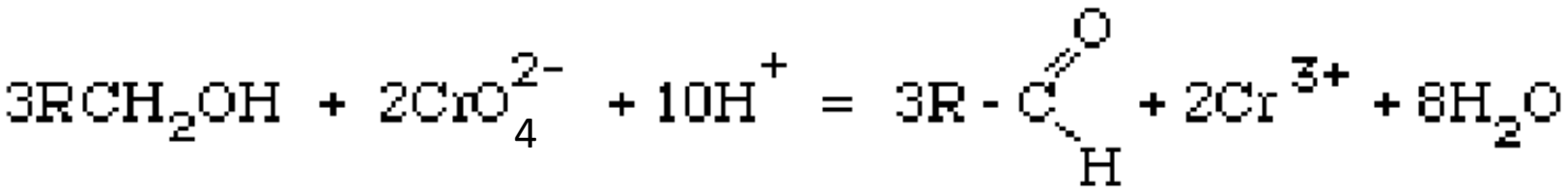
$\nu = 1$

$RT/F = 0.025\,693\,V$

Focus 17: Chemical Kinetics

- The rates of chemical reactions
- Integrated rate laws
- Reactions approaching equilibrium
- The Arrhenius equation
- Reaction mechanisms
- Photochemistry

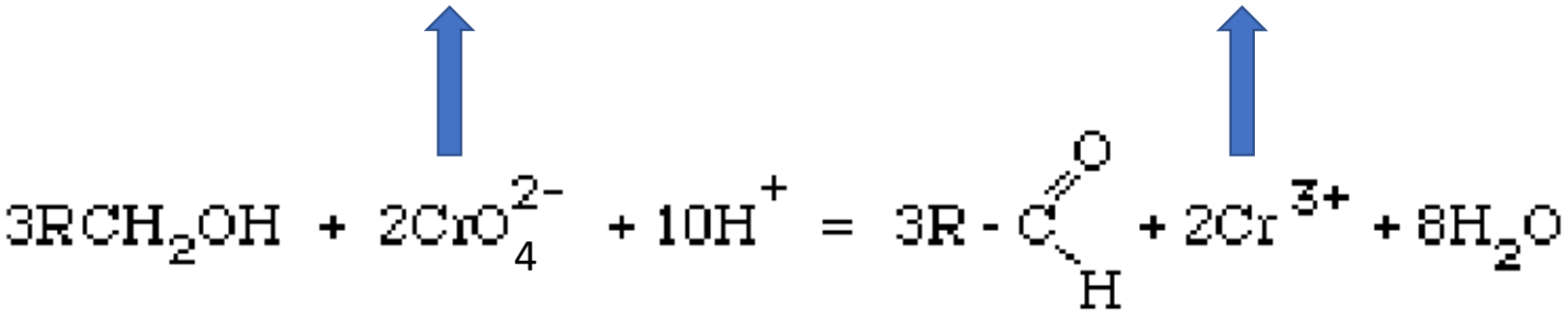
Monitoring a chemical reaction



$$R = [CH_3 - O - CH_2-]$$

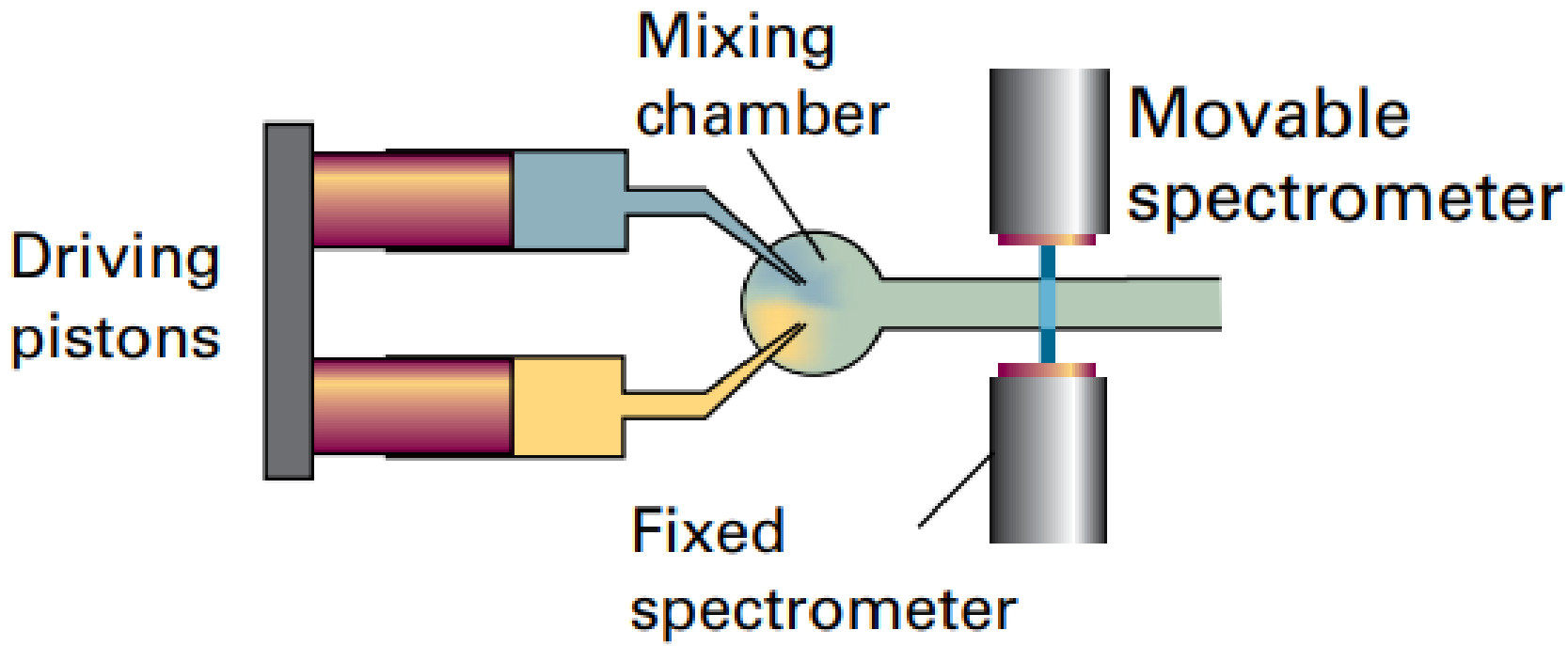
Monitoring a chemical reaction

monitor using UV-VIS as a function of time



$R = [CH_3 - O - CH_2-]$

Flow method


Mixing
chamber
Movable
spectrometer
Driving
pistons
Fixed
spectrometer

Monitoring very fast chemical reactions

Kinetics of the Reaction, $CN + C_2H_6 \longrightarrow HCN + C_2H_5$

Monitoring very fast chemical reactions

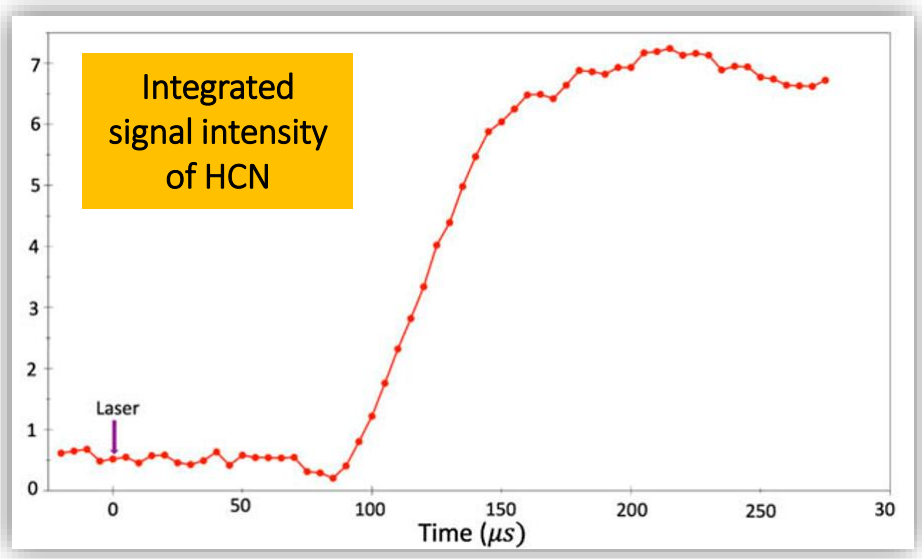
Kinetics of the Reaction, $CN + C_2H_6 \longrightarrow HCN + C_2H_5$ (at 50 K)

- CN radical was produced by 193 nm photodissociation of BrCN.

Monitoring very fast chemical reactions

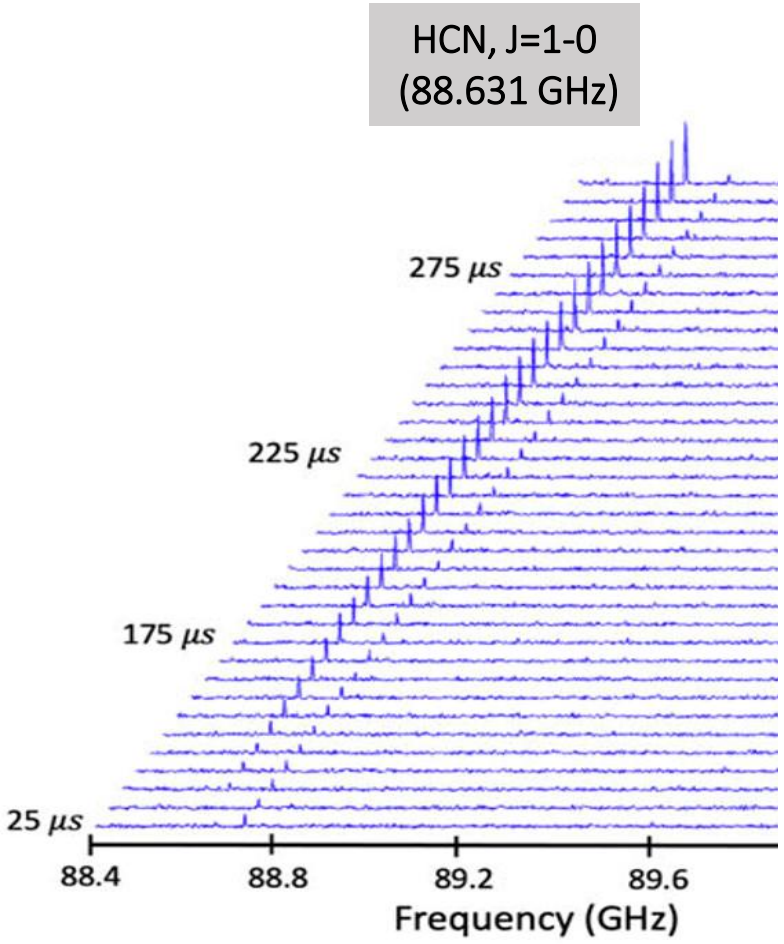
Kinetics of the Reaction, $CN + C_2H_6 \longrightarrow HCN + C_2H_5$ (at 50 K)

- CN radical was produced by 193 nm photodissociation of BrCN.
- HCN was quantitated using the integrated signal intensity

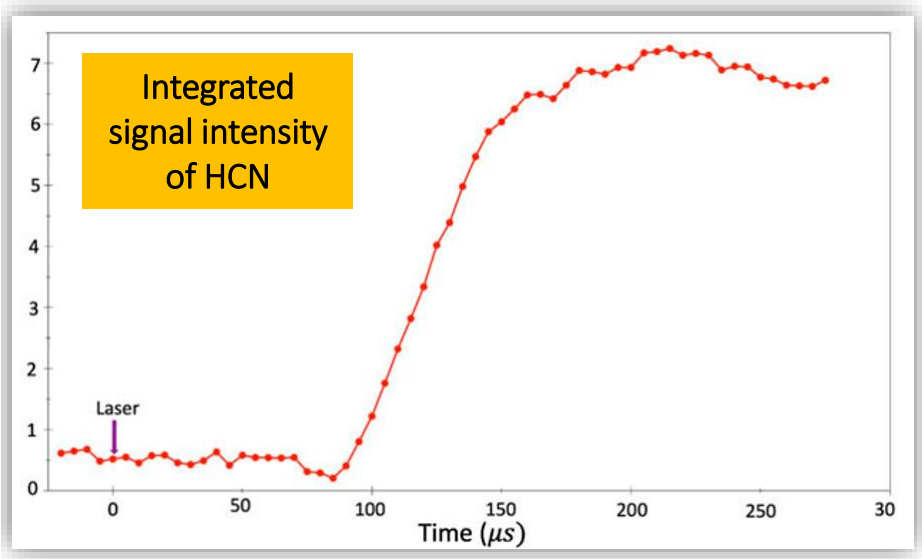


Monitoring very fast chemical reactions

Kinetics of the Reaction, $CN + C_2H_6 \longrightarrow HCN + C_2H_5$ (at 50 K)

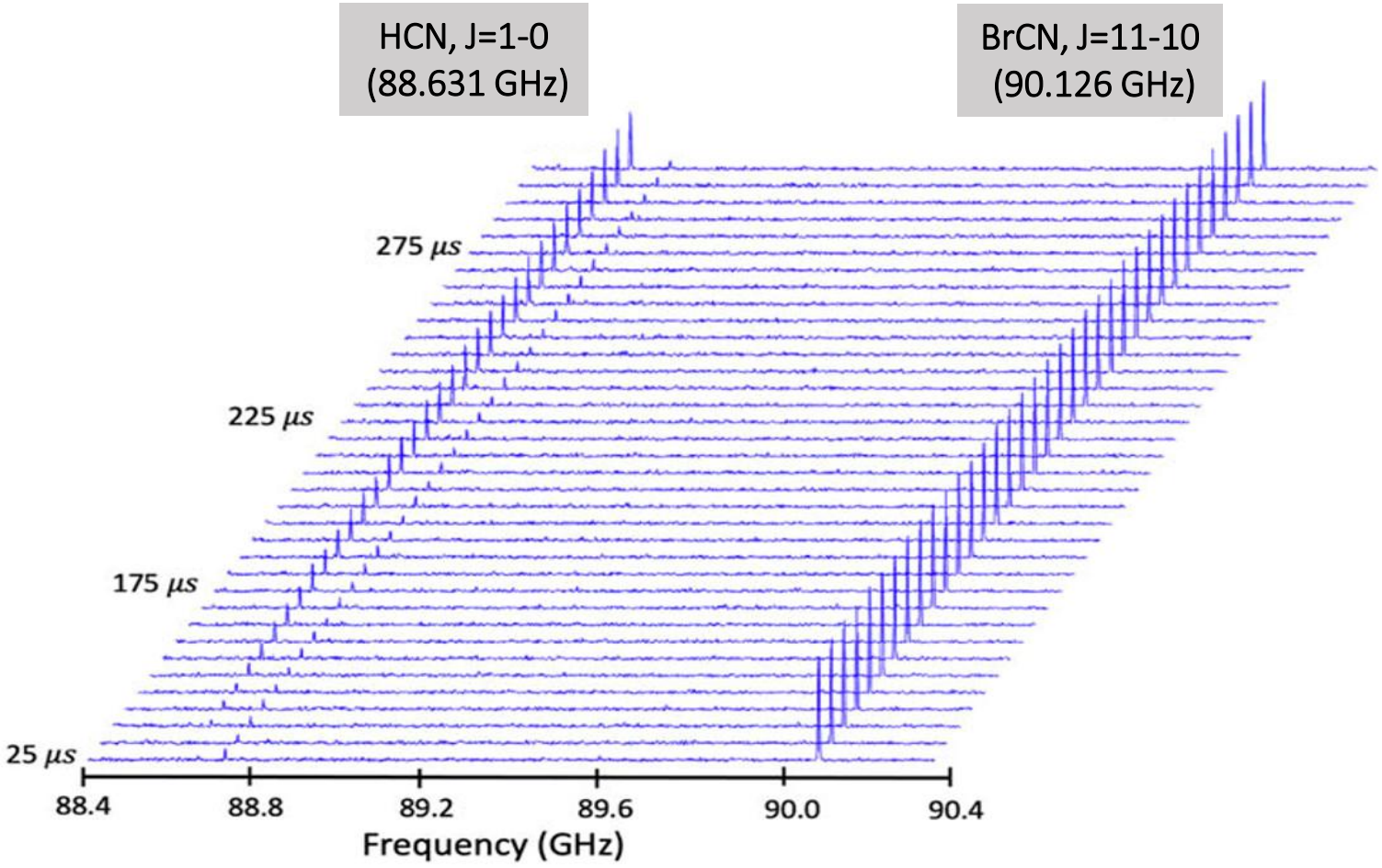


- CN radical was produced by 193 nm photodissociation of BrCN.
- HCN was quantitated using the integrated signal intensity

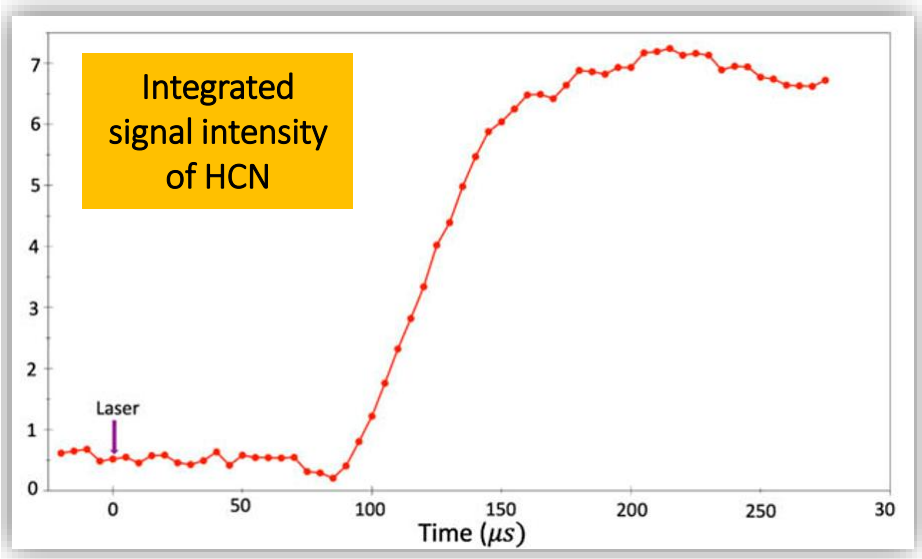


Monitoring very fast chemical reactions

Kinetics of the Reaction, $CN + C_2H_6 \longrightarrow HCN + C_2H_5$ (at 50 K)



- CN radical was produced by 193 nm photodissociation of BrCN.
- HCN was quantitated using the integrated signal intensity



Monitoring very fast chemical reactions

Kinetics Data Fitting

Performed 7 kinetics runs at CN limited conditions (pseudo 1st order)

Kinetic run	C_2H_6 flow rate (SCCM)	C_2H_6 (%)	$[C_2H_6]/10^{13}$ (molecules cm^{-3})
1	10.0	0.074	7.4
2	20.0	0.15	14
3	30.0	0.22	22
4	40.0	0.30	29
5	50.0	0.37	37
6	60.0	0.44	44
7	70.0	0.52	51

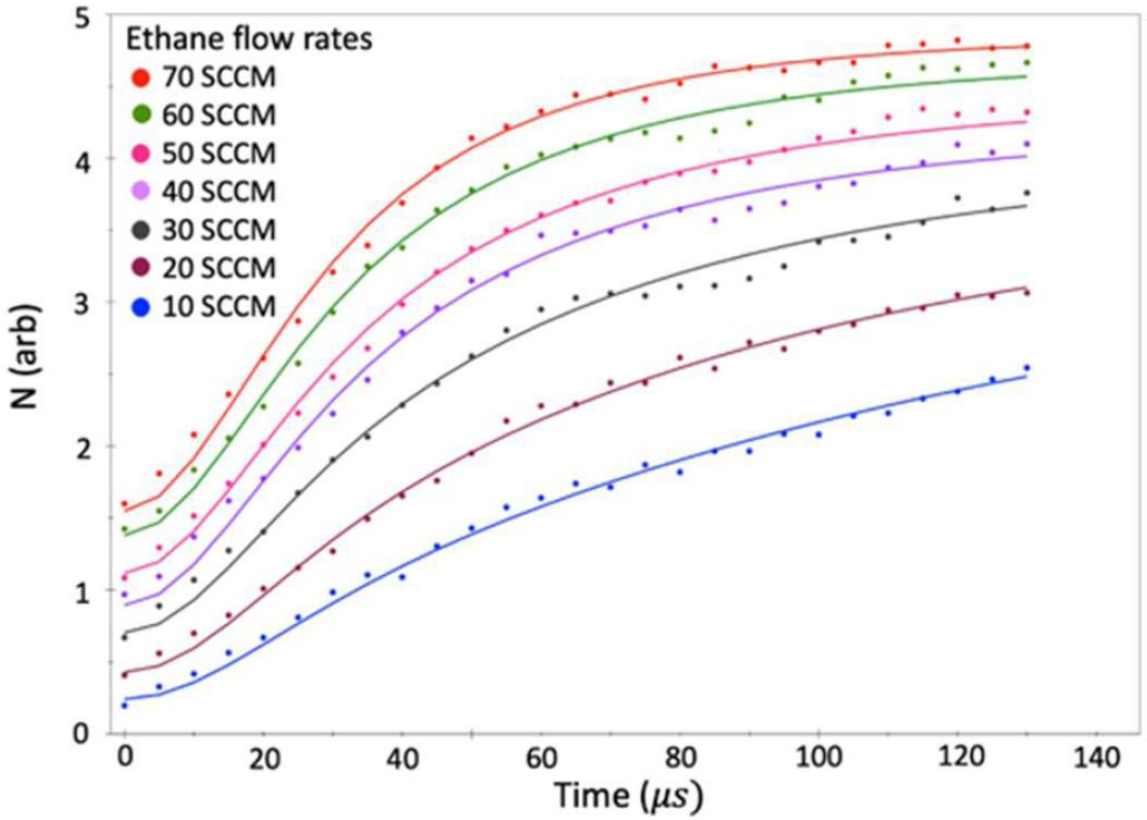
Monitoring very fast chemical reactions

Kinetics Data Fitting

Performed 7 kinetics runs at CN limited conditions (pseudo 1st order)

Kinetic run	C_2H_6 flow rate (SCCM)	C_2H_6 (%)	$[C_2H_6]/10^{13}$ (molecules cm^{-3})
1	10.0	0.074	7.4
2	20.0	0.15	14
3	30.0	0.22	22
4	40.0	0.30	29
5	50.0	0.37	37
6	60.0	0.44	44
7	70.0	0.52	51

Best-fit curves and experimental data points



Monitoring very fast chemical reactions

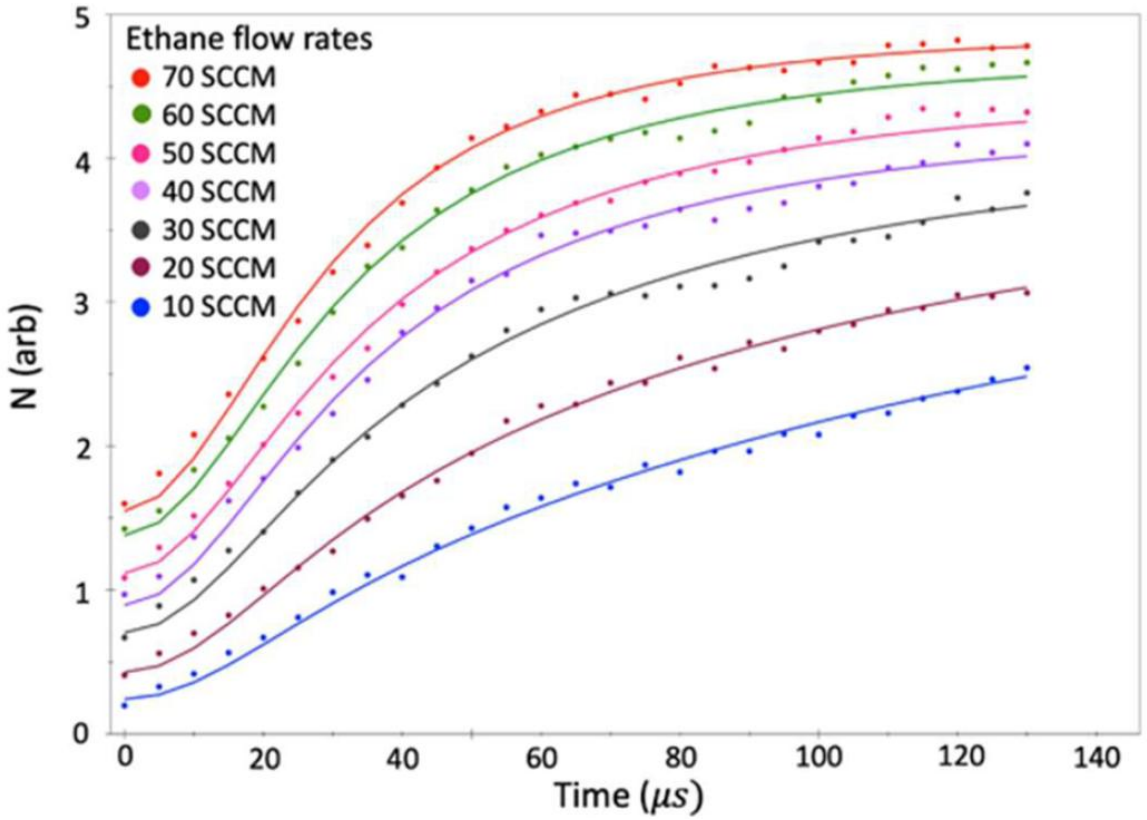
Kinetics Data Fitting

Performed 7 kinetics runs at CN limited conditions (pseudo 1st order)

Kinetic run	C_2H_6 flow rate (SCCM)	C_2H_6 (%)	$[C_2H_6]/10^{13}$ (molecules cm^{-3})	$k/10^3$ (s^{-1})
1	10.0	0.074	7.4	8.82
2	20.0	0.15	14	12.9
3	30.0	0.22	22	17.9
4	40.0	0.30	29	22.9
5	50.0	0.37	37	23.7
6	60.0	0.44	44	26.9
7	70.0	0.52	51	30.8

Pseudo 1st order rate constants

Best-fit curves and experimental data points

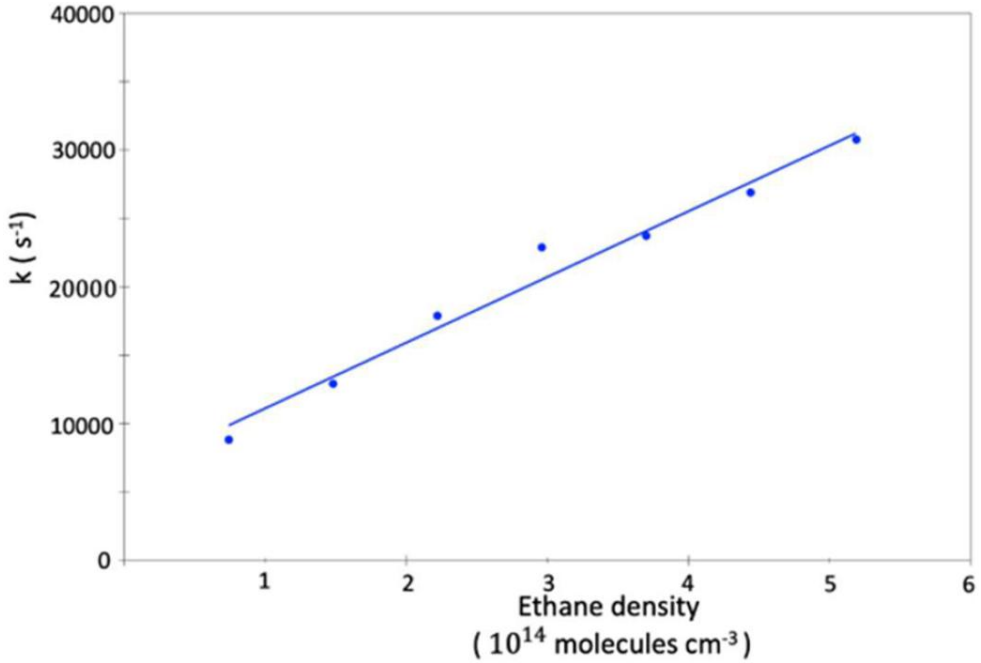


Monitoring very fast chemical reactions

Bimolecular Rate Constant

Kinetic run	C_2H_6 flow rate (SCCM)	C_2H_6 (%)	$[C_2H_6]/10^{13}$ (molecules cm^{-3})	$k/10^3$ (s^{-1})
1	10.0	0.074	7.4	8.82
2	20.0	0.15	14	12.9
3	30.0	0.22	22	17.9
4	40.0	0.30	29	22.9
5	50.0	0.37	37	23.7
6	60.0	0.44	44	26.9
7	70.0	0.52	51	30.8

1st-order rate constants vs ethane densities

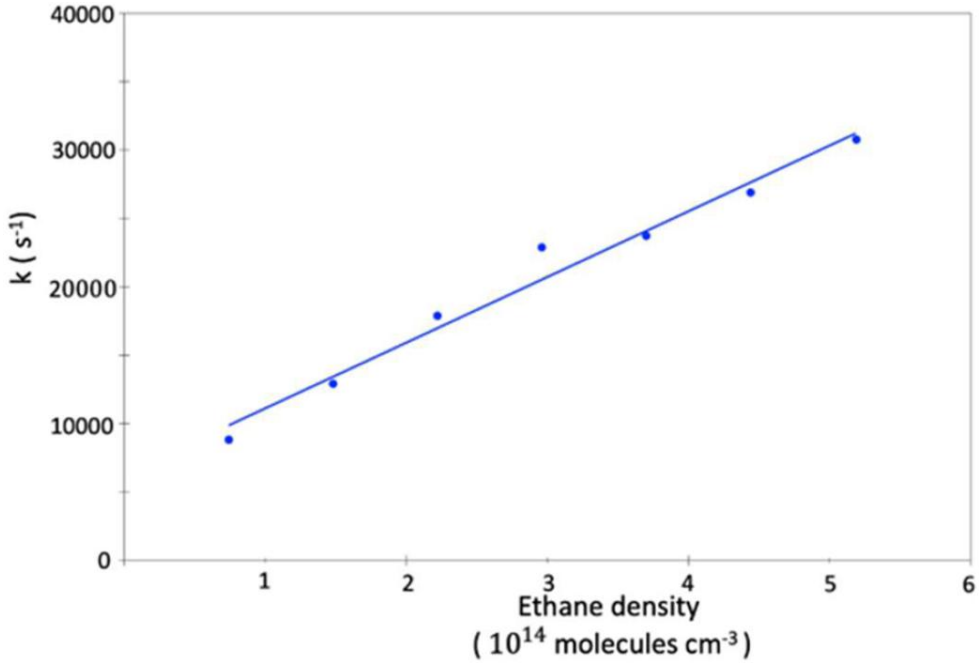


Monitoring very fast chemical reactions

Bimolecular Rate Constant

Kinetic run	C_2H_6 flow rate (SCCM)	C_2H_6 (%)	$[C_2H_6]/10^{13}$ (molecules cm^{-3})	$k/10^3$ (s^{-1})
1	10.0	0.074	7.4	8.82
2	20.0	0.15	14	12.9
3	30.0	0.22	22	17.9
4	40.0	0.30	29	22.9
5	50.0	0.37	37	23.7
6	60.0	0.44	44	26.9
7	70.0	0.52	51	30.8

1st-order rate constants vs ethane densities



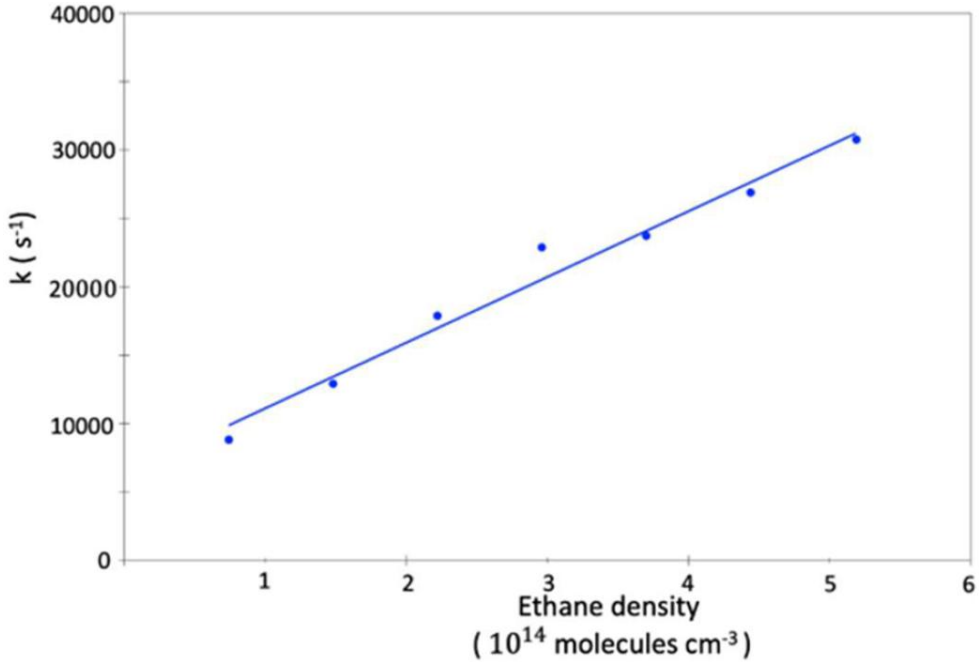
This work (50 K)
mmW rotational spectroscopy
$4.80 \pm 0.82 \times 10^{-11}$ cm^3 $molecule^{-1}$ s^{-1}

Monitoring very fast chemical reactions

Bimolecular Rate Constant

Kinetic run	C_2H_6 flow rate (SCCM)	C_2H_6 (%)	$[C_2H_6]/10^{13}$ (molecules cm^{-3})	$k/10^3$ (s^{-1})
1	10.0	0.074	7.4	8.82
2	20.0	0.15	14	12.9
3	30.0	0.22	22	17.9
4	40.0	0.30	29	22.9
5	50.0	0.37	37	23.7
6	60.0	0.44	44	26.9
7	70.0	0.52	51	30.8

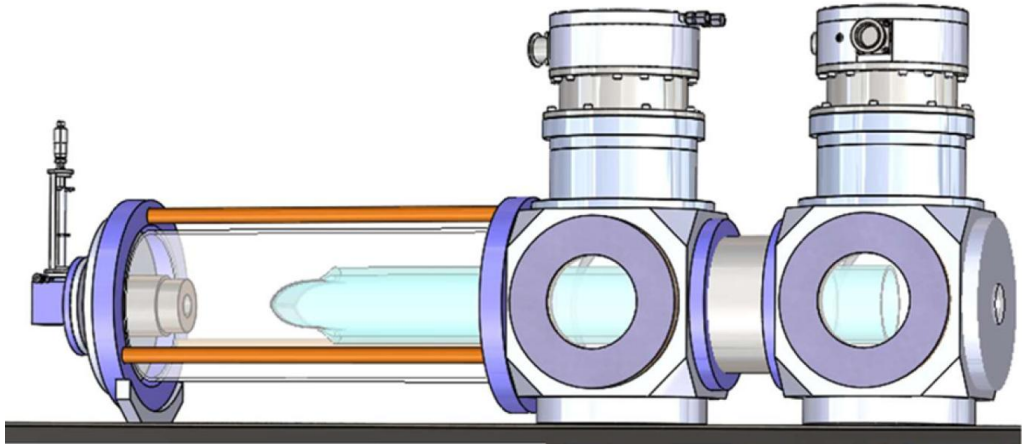
1st-order rate constants vs ethane densities



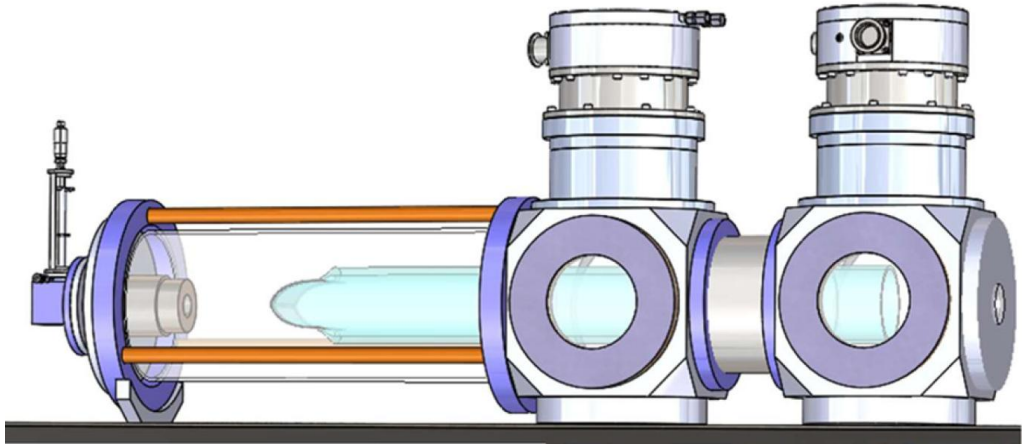
This work (50 K)	Sims et al. (49 K)[1]
mmW rotational spectroscopy	Laser induced fluorescence (LIF)
$4.80 \pm 0.82 \times 10^{-11}$ cm^3 $molecule^{-1}$ s^{-1}	4.81×10^{-11} cm^3 $molecule^{-1}$ s^{-1}

Reference 1: I. R. Sims, J.-L. Queffelec, D. Travers, B. R. Rowe, L. B. Herbert, J. Karthäuser, and I. W. M. Smith, Chem. Phys. Lett. 211, 461 (1993)

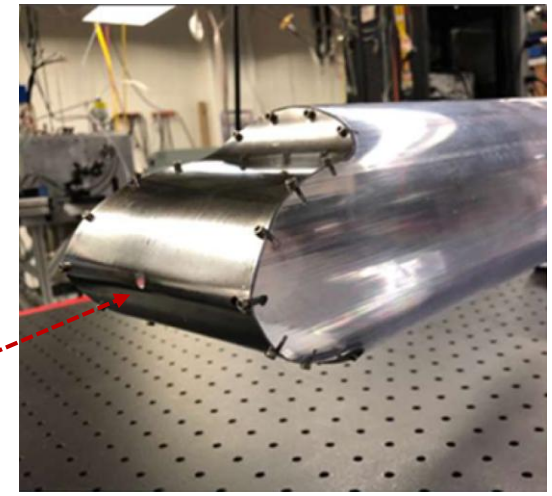
New “airfoil” equipped CPUF design



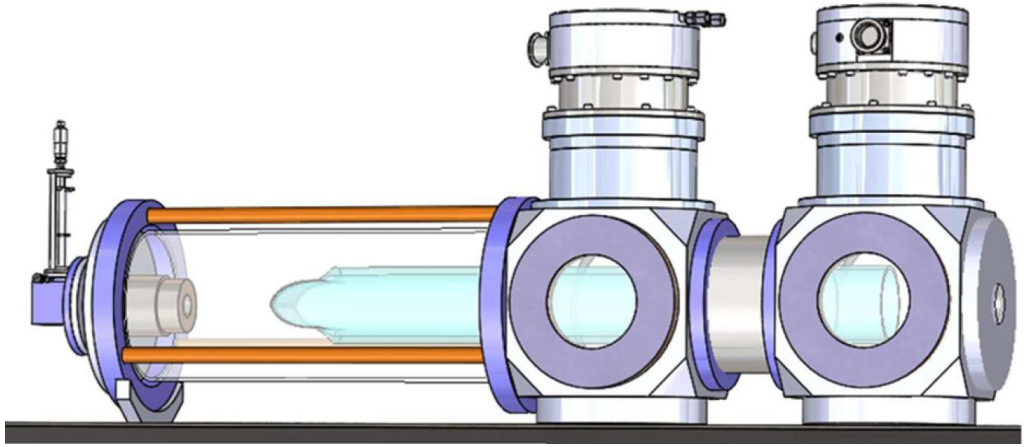
New “airfoil” equipped CPUF design



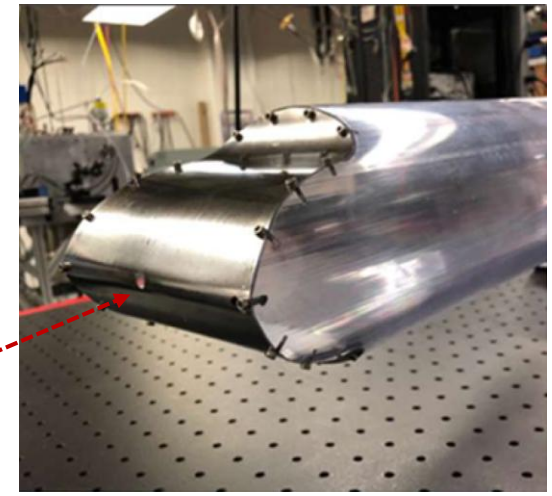
Airfoil-shaped sampling chamber



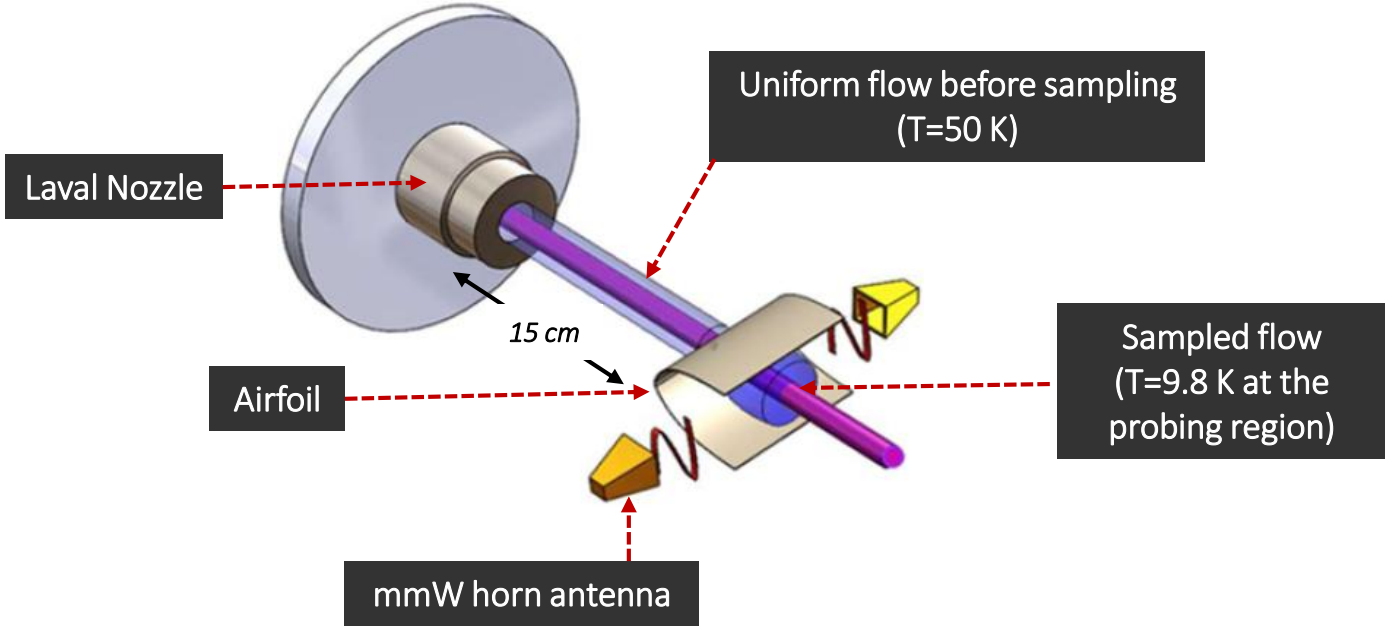
New “airfoil” equipped CPUF design



Airfoil-shaped sampling chamber



Airfoil aperture, 5 mm diameter



The Journal of Chemical Physics

Uniform supersonic flow sampling for detection by chirped-pulse rotational spectroscopy

Cite as: J. Chem. Phys. **156**, 014202 (2022); https://doi.org/10.1063/5.0073527
Submitted: 30 September 2021 • Accepted: 07 December 2021 • Accepted Manuscript Online: 09 December 2021 • Published Online: 04 January 2022

Ranil M. Gurusinghe, Nureshan Dias, Ritter Krueger, et al.

No Access • Submitted: 30 September 2021 • Accepted: 07 December 2021 • Accepted Manuscript Online: 09 December 2021 • Published Online: 04 January 2022

Uniform supersonic flow sampling for detection by chirped-pulse rotational spectroscopy

J. Chem. Phys. 156, 014202 (2022); https://doi.org/10.1063/5.0073527

Ranil M. Gurusinghe, Nureshan Dias, Ritter Krueger, *and* Arthur G. Suits[a)]

View Affiliations View Contributors

ABSTRACT

Chirped-pulse Fourier transform microwave (CP-FTMW) spectroscopy is a powerful near-universal detection method finding application in many areas. We have previously coupled it with supersonic flows (CPUF) to obtain product branching in reaction and photodissociation. Because chirped-pulse microwave detection requires monitoring the free induction decay on the timescale of microseconds, it cannot be employed with good sensitivity at the high densities achieved in some uniform supersonic flows. For application to low-temperature kinetics studies, a truly uniform flow is required to obtain reliable rate measurements and enjoy all the advantages that CP-FTMW has to offer. To this end, we present a new setup that combines sampling of uniform supersonic flows using an airfoil-shaped sampling device with chirped-pulse mmW detection. Density and temperature variations in the airfoil-sampled uniform flow were revealed using time-dependent rotational spectroscopy of pyridine and vinyl cyanide photoproducts, highlighting the use of UV photodissociation as a sensitive diagnostic tool for uniform flows. The performance of the new airfoil-equipped CPUF rotational spectrometer was validated using kinetics measurements of the CN + C_2H_6 reaction at 50 K with detection of the HCN product. Issues relating to product detection by rotational spectroscopy and airfoil sampling are discussed. We show that airfoil sampling enables direct measurements of low temperature reaction kinetics on a microsecond timescale, while rotational spectroscopic detection enables highly specific simultaneous detection of reactants and products.

Rates of reactions

$$A + 2B \rightarrow 3C + D$$

Rates of reactions

$$A + 2B \rightarrow 3C + D$$

$$\text{rate of reaction, } v, \quad = \quad \frac{d[D]}{dt}$$

Rates of reactions

$$A + 2B \rightarrow 3C + D$$

$$\text{rate of reaction, } v, \quad = \quad \frac{d[D]}{dt} = \frac{1}{3}\frac{d[C]}{dt}$$

Rates of reactions

$$A + 2B \rightarrow 3C + D$$

$$\textbf{rate of reaction, } v, \quad = \quad \frac{d[D]}{dt} = \frac{1}{3}\frac{d[C]}{dt} = -\frac{d[A]}{dt}$$

Rates of reactions

$$A + 2B \rightarrow 3C + D$$

$$\textbf{rate of reaction, } v, = \frac{d[D]}{dt} = \frac{1}{3}\frac{d[C]}{dt} = -\frac{d[A]}{dt} = -\frac{1}{2}\frac{d[B]}{dt}$$

Rates of reactions

$$A + 2B \rightarrow 3C + D$$

$$\textbf{rate of reaction, } v, = \frac{d[D]}{dt} = \frac{1}{3}\frac{d[C]}{dt} = -\frac{d[A]}{dt} = -\frac{1}{2}\frac{d[B]}{dt}$$

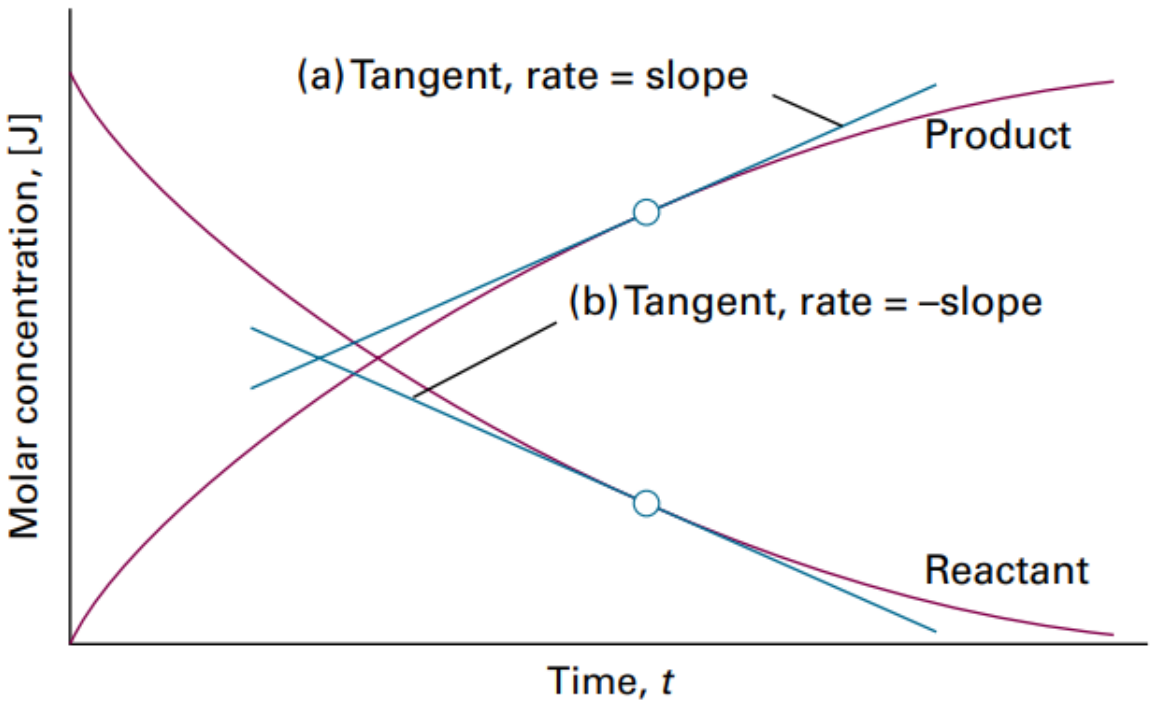
$$v = \frac{1}{\nu_J}\frac{d[J]}{dt}$$

Rates of reactions

$$A + 2B \rightarrow 3C + D$$

$$\textbf{rate of reaction, } v, = \frac{d[D]}{dt} = \frac{1}{3}\frac{d[C]}{dt} = -\frac{d[A]}{dt} = -\frac{1}{2}\frac{d[B]}{dt}$$

$$v = \frac{1}{\nu_J}\frac{d[J]}{dt}$$



Rates of reactions

$$A + 2B \rightarrow 3C + D$$

$$\textbf{rate of reaction, } v, = \frac{d[D]}{dt} = \frac{1}{3}\frac{d[C]}{dt} = -\frac{d[A]}{dt} = -\frac{1}{2}\frac{d[B]}{dt}$$

$$v = \frac{1}{\nu_J}\frac{d[J]}{dt}$$

rate of reaction, v,

For solution phase reactions $(\text{mol dm}^{-3}\,\text{s}^{-1})$

Rates of reactions

$$A + 2B \rightarrow 3C + D$$

rate of reaction, v, $= \dfrac{d[D]}{dt} = \frac{1}{3}\dfrac{d[C]}{dt} = -\dfrac{d[A]}{dt} = -\frac{1}{2}\dfrac{d[B]}{dt}$

$$v = \frac{1}{\nu_J}\frac{d[J]}{dt}$$

rate of reaction, v,

For solution phase reactions $(\text{mol dm}^{-3}\,\text{s}^{-1})$

For gas phase reactions $(\text{molecules cm}^{-3}\,\text{s}^{-1})$

Rates of reactions

$$A + 2B \rightarrow 3C + D$$

$$\textbf{rate of reaction, } v, = \frac{d[D]}{dt} = \frac{1}{3}\frac{d[C]}{dt} = -\frac{d[A]}{dt} = -\frac{1}{2}\frac{d[B]}{dt}$$

$$v = \frac{1}{\nu_J}\frac{d[J]}{dt}$$

rate of reaction, v,

For solution phase reactions $(\text{mol dm}^{-3}\text{ s}^{-1})$

For gas phase reactions $(\text{molecules cm}^{-3}\text{ s}^{-1})$

For heterogeneous reactions $(\text{mol m}^{-2}\text{ s}^{-1})$

Example

The rate of formation of NO, d[NO]/dt, in the reaction $2\,NOBr(g) \rightarrow 2\,NO(g) + Br_2(g)$ is reported as $0.16\,mmol\,dm^{-3}\,s^{-1}$.

Example

The rate of formation of NO, d[NO]/dt, in the reaction $2\,NOBr(g) \rightarrow 2\,NO(g) + Br_2(g)$ is reported as $0.16\,mmol\,dm^{-3}\,s^{-1}$.

$$v = \frac{1}{\nu_J}\frac{d[J]}{dt}$$

Example

The rate of formation of NO, d[NO]/dt, in the reaction $2\,NOBr(g) \rightarrow 2\,NO(g) + Br_2(g)$ is reported as $0.16\,mmol\,dm^{-3}\,s^{-1}$.

$$v = \frac{1}{\nu_J}\frac{d[J]}{dt}$$

$$v = \tfrac{1}{2}d[NO]/dt = 0.080\,mmol\,dm^{-3}\,s^{-1}$$

Rate Laws

Mathematical expressions that describe the rate of a chemical reaction as a function of the concentrations of reactants or products.

Rate Laws

$$v = k_r[\mathrm{A}][\mathrm{B}]$$

Rate Laws

$$v = k_r[\mathrm{A}][\mathrm{B}]$$

rate constant

Independent of concentration

Rate Laws

$$v = k_r[\mathrm{A}][\mathrm{B}]$$

rate constant

Independent of concentration

$$v = f([\mathrm{A}],[\mathrm{B}],\ldots)$$

$$v = f(p_\mathrm{A},p_\mathrm{B},\ldots)$$

Rate Laws

$$v = k_r[\mathrm{A}][\mathrm{B}]$$

$$v = f([\mathrm{A}],[\mathrm{B}],\ldots)$$

$$v = f(p_\mathrm{A},p_\mathrm{B},\ldots)$$

rate constant

Independent of concentration

$$\mathrm{H_2(g) + Br_2(g) \rightarrow 2\,HBr(g)}$$

Rate Laws

$$v = k_r[A][B]$$

rate constant

$$v = f([A],[B],\ldots)$$

$$v = f(p_A,p_B,\ldots)$$

Independent of concentration

$$H_2(g) + Br_2(g) \rightarrow 2\,HBr(g)$$

$$v = \frac{k_a[H_2][Br_2]^{3/2}}{[Br_2] + k_b[HBr]}$$

A complicated rate law!

Reaction order

Reaction order

$$v = k_r[A]^a[B]^b \ldots$$

The power to which the concentration of a species is raised in a rate law of this kind is the order of the reaction with respect to that species

Reaction order

$$v = k_r[A]^a[B]^b \ldots$$

The power to which the concentration of a species is raised in a rate law of this kind is the order of the reaction with respect to that species

$$\textbf{overall order} = a + b + \cdots$$

Reaction order

$$v = k_r[\mathrm{A}]^a[\mathrm{B}]^b \ldots$$

The power to which the concentration of a species is raised in a rate law of this kind is the order of the reaction with respect to that species

$$\textbf{overall order} = a + b + \cdots$$

$$v = k_r[\mathrm{A}][\mathrm{B}]$$

First order in A and first order in B.
Overall order = 1+1 = 2
“second-order”

Reaction order

$$v = k_r[A]^a[B]^b \ldots$$

The power to which the concentration of a species is raised in a rate law of this kind is the order of the reaction with respect to that species

$$\textbf{overall order} = a + b + \cdots$$

$$v = k_r[A][B]$$

First order in A and first order in B.
Overall order = 1+1 = 2
“second-order”

$$v = k_r$$

Zeroth order

Reaction order

$$v = k_r[A]^a[B]^b \ldots$$

The power to which the concentration of a species is raised in a rate law of this kind is the order of the reaction with respect to that species

overall order $= a + b + \cdots$

$$v = k_r[A][B]$$

First order in A and first order in B.
Overall order = 1+1 = 2
"second-order"

$$v = k_r$$

Zeroth order

$$v = k_r[A]^{1/2}[B]$$

is half order in A, first order in B, and three-halves order overall.

Reaction order

$$H_2(g) + Br_2(g) \rightarrow 2\,HBr(g)$$

$$v = \frac{k_a[H_2][Br_2]^{3/2}}{[Br_2] + k_b[HBr]}$$

Reaction order

$$H_2(g) + Br_2(g) \rightarrow 2\,HBr(g)$$

$$v = \frac{k_a[H_2][Br_2]^{3/2}}{[Br_2] + k_b[HBr]}$$

Reaction is first order in H_2

Reaction order

$$H_2(g) + Br_2(g) \rightarrow 2\,HBr(g)$$

$$v = \frac{k_a[H_2][Br_2]^{3/2}}{[Br_2] + k_b[HBr]}$$

Reaction is first order in H_2

Reaction has an indefinite order with respect to both Br_2 and HBr

Reaction order

$$H_2(g) + Br_2(g) \rightarrow 2\,HBr(g)$$

$$v = \frac{k_a[H_2][Br_2]^{3/2}}{[Br_2] + k_b[HBr]}$$

Reaction is first order in H_2

Reaction has an indefinite order with respect to both Br_2 and HBr

Reaction has an indefinite order overall

Determination of rate law

$$v = k_r[\mathrm{A}][\mathrm{B}]^2$$

rate law

Determination of rate law

effective rate constant

$$k_{r,eff} = k_r[B]_0^2$$

$$v = k_r[A][B]^2$$

rate law

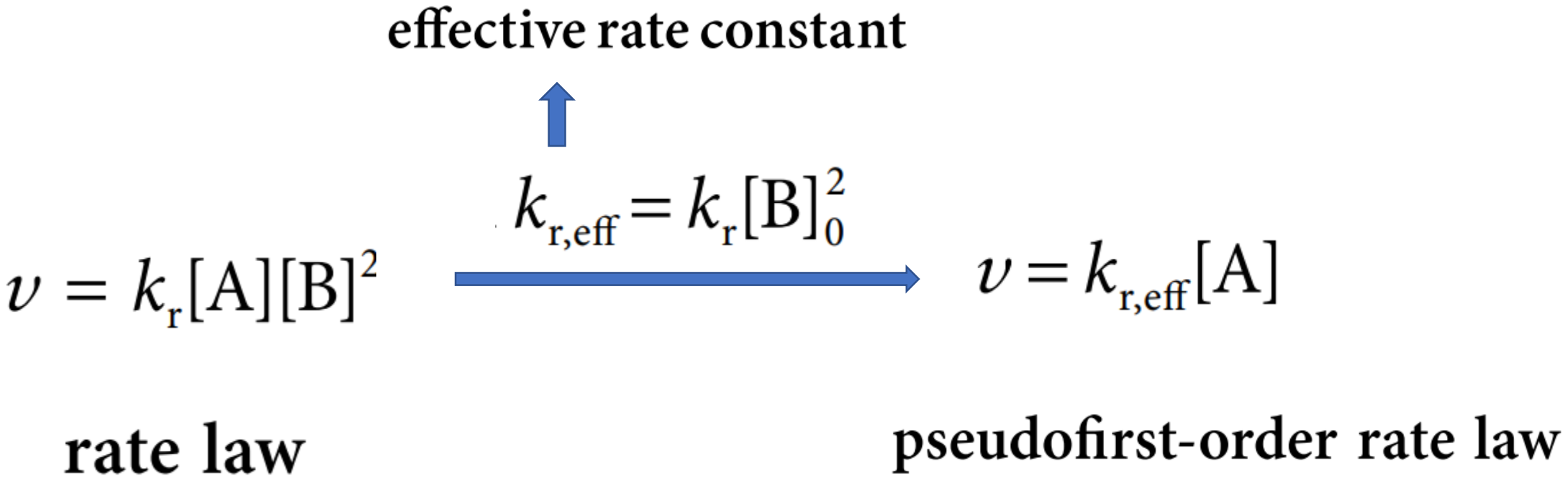
Determination of rate law

effective rate constant

$$v = k_r[A][B]^2 \xrightarrow{k_{r,eff} = k_r[B]_0^2} v = k_{r,eff}[A]$$

rate law

Determination of rate law



Method of initial rates

The instantaneous rate is measured at the beginning of the reaction for several different initial concentrations of the isolated reactant

Gen Chem 2 – Read!

Method of initial rates

The instantaneous rate is measured at the beginning of the reaction for several different initial concentrations of the isolated reactant

Suppose the rate law for a reaction with A isolated is $v = k_r[\mathrm{A}]^a$

Method of initial rates

The instantaneous rate is measured at the beginning of the reaction for several different initial concentrations of the isolated reactant

Suppose the rate law for a reaction with A isolated is $v = k_r[A]^a$

initial conditions $v_0 = k_{r,eff}[A]_0^a$

Method of initial rates

The instantaneous rate is measured at the beginning of the reaction for several different initial concentrations of the isolated reactant

Suppose the rate law for a reaction with A isolated is $v = k_r[\mathrm{A}]^a$

initial conditions

$$v_0 = k_{r,\mathrm{eff}}[\mathrm{A}]_0^a$$

$$\log v_0 = \log\left(k_{r,\mathrm{eff}}[\mathrm{A}]_0^a\right)$$

$$\log v_0 = \log k_{r,\mathrm{eff}} + a \log [\mathrm{A}]_0$$

Method of initial rates

Find the orders of reaction with respect to I and Ar, and the rate constant

$$2\,I(g) + Ar(g) \rightarrow I_2(g) + Ar(g)$$

$[I]_0/(10^{-5}\,mol\,dm^{-3})$		1.0	2.0	4.0	6.0	Ar concentrations
$v_0/(mol\,dm^{-3}\,s^{-1})$	(a)	8.70×10^{-4}	3.48×10^{-3}	1.39×10^{-2}	3.13×10^{-2}	$1.0 \times 10^{-3}\,mol\,dm^{-3}$
	(b)	4.35×10^{-3}	1.74×10^{-2}	6.96×10^{-2}	1.57×10^{-1}	$5.0 \times 10^{-3}\,mol\,dm^{-3}$
	(c)	8.69×10^{-3}	3.47×10^{-2}	1.38×10^{-1}	3.13×10^{-1}	$1.0 \times 10^{-2}\,mol\,dm^{-3}$

Method of initial rates

Find the orders of reaction with respect to I and Ar, and the rate constant

$$2\,I(g) + Ar(g) \rightarrow I_2(g) + Ar(g)$$

			Ar concentrations
$[I]_0/(10^{-5}\,mol\,dm^{-3})$		1.0	2.0
$v_0/(mol\,dm^{-3}\,s^{-1})$	(a)	8.70×10^{-4}	3.48×10^{-3}
			$1.0 \times 10^{-3}\,mol\,dm^{-3}$

Method of initial rates

Find the orders of reaction with respect to I and Ar, and the rate constant

$$2\,I(g) + Ar(g) \rightarrow I_2(g) + Ar(g)$$

				Ar concentrations
$[I]_0/(10^{-5}\,mol\,dm^{-3})$		1.0	2.0	
$v_0/(mol\,dm^{-3}\,s^{-1})$	(a)	8.70×10^{-4}	3.48×10^{-3}	$1.0 \times 10^{-3}\,mol\,dm^{-3}$

$$v = k_r[I]_0^2[Ar]_0^n$$

Method of initial rates

Find the orders of reaction with respect to I and Ar, and the rate constant

$$2\,I(g) + Ar(g) \rightarrow I_2(g) + Ar(g)$$

$[I]_0/(10^{-5}\,mol\,dm^{-3})$		1.0
$v_0/(mol\,dm^{-3}\,s^{-1})$	(a)	8.70×10^{-4}
	(b)	4.35×10^{-3}

Ar concentrations
$1.0 \times 10^{-3}\,mol\,dm^{-3}$
$5.0 \times 10^{-3}\,mol\,dm^{-3}$

Method of initial rates

Find the orders of reaction with respect to I and Ar, and the rate constant

$$2\,I(g) + Ar(g) \rightarrow I_2(g) + Ar(g)$$

$[I]_0/(10^{-5}\,mol\,dm^{-3})$		1.0	Ar concentrations
$v_0/(mol\,dm^{-3}\,s^{-1})$	(a)	8.70×10^{-4}	$1.0 \times 10^{-3}\,mol\,dm^{-3}$
	(b)	4.35×10^{-3}	$5.0 \times 10^{-3}\,mol\,dm^{-3}$

$$v = k_r[I]_0^2[Ar]_0$$

Method of initial rates

$$\log v_0 = \log k_{r,\text{eff}} + a \log [\text{I}]_0$$

$[\text{I}]_0/(10^{-5}\,\text{mol dm}^{-3})$		1.0	2.0	4.0	6.0
$v_0/(\text{mol dm}^{-3}\,\text{s}^{-1})$	(a)	8.70×10^{-4}	3.48×10^{-3}	1.39×10^{-2}	3.13×10^{-2}
	(b)	4.35×10^{-3}	1.74×10^{-2}	6.96×10^{-2}	1.57×10^{-1}
	(c)	8.69×10^{-3}	3.47×10^{-2}	1.38×10^{-1}	3.13×10^{-1}

Method of initial rates

$$\log v_0 = \log k_{r,\text{eff}} + a \log [\mathrm{I}]_0$$

$[\mathrm{I}]_0/(10^{-5}\,\mathrm{mol\,dm^{-3}})$		1.0	2.0	4.0	6.0
$v_0/(\mathrm{mol\,dm^{-3}\,s^{-1}})$	(a)	8.70×10^{-4}	3.48×10^{-3}	1.39×10^{-2}	3.13×10^{-2}
	(b)	4.35×10^{-3}	1.74×10^{-2}	6.96×10^{-2}	1.57×10^{-1}
	(c)	8.69×10^{-3}	3.47×10^{-2}	1.38×10^{-1}	3.13×10^{-1}

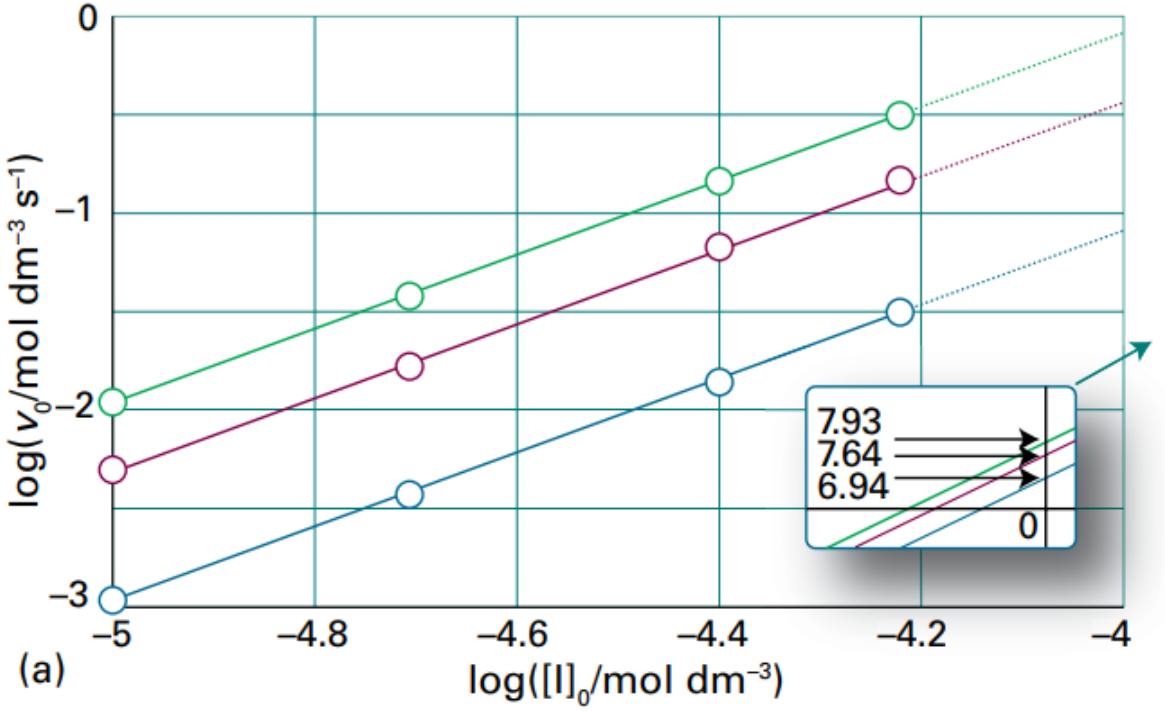
$\log([\mathrm{I}]_0/\mathrm{mol\,dm^{-3}})$		−5.00	−4.70	−4.40	−4.22
$\log(v_0/\mathrm{mol\,dm^{-3}\,s^{-1}})$	(a)	−3.060	−2.458	−1.857	−1.504
	(b)	−2.362	−1.759	−1.157	−0.804
	(c)	−2.061	−1.460	−0.860	−0.504

Method of initial rates

$$\log v_0 = \log k_{r,\text{eff}} + a \log [\mathrm{I}]_0$$

$[\mathrm{I}]_0/(10^{-5}\,\mathrm{mol\,dm^{-3}})$		1.0	2.0	4.0	6.0
$v_0/(\mathrm{mol\,dm^{-3}\,s^{-1}})$	(a)	8.70×10^{-4}	3.48×10^{-3}	1.39×10^{-2}	3.13×10^{-2}
	(b)	4.35×10^{-3}	1.74×10^{-2}	6.96×10^{-2}	1.57×10^{-1}
	(c)	8.69×10^{-3}	3.47×10^{-2}	1.38×10^{-1}	3.13×10^{-1}

$\log([\mathrm{I}]_0/\mathrm{mol\,dm^{-3}})$		−5.00	−4.70	−4.40	−4.22
$\log(v_0/\mathrm{mol\,dm^{-3}\,s^{-1}})$	(a)	−3.060	−2.458	−1.857	−1.504
	(b)	−2.362	−1.759	−1.157	−0.804
	(c)	−2.061	−1.460	−0.860	−0.504



Method of initial rates

$[\mathrm{I}]_0/(10^{-5}\,\mathrm{mol\,dm^{-3}})$		1.0	2.0	4.0	6.0
$v_0/(\mathrm{mol\,dm^{-3}\,s^{-1}})$	(a)	8.70×10^{-4}	3.48×10^{-3}	1.39×10^{-2}	3.13×10^{-2}
	(b)	4.35×10^{-3}	1.74×10^{-2}	6.96×10^{-2}	1.57×10^{-1}
	(c)	8.69×10^{-3}	3.47×10^{-2}	1.38×10^{-1}	3.13×10^{-1}

$$\log v_0 = \log k_{\mathrm{r,eff}} + a \log [\mathrm{I}]_0$$

$$k_{\mathrm{r,eff}} = k_{\mathrm{r}}[\mathrm{Ar}]_0^b$$

Method of initial rates

$[\mathrm{I}]_0/(10^{-5}\,\mathrm{mol\,dm^{-3}})$		1.0	2.0	4.0	6.0
$v_0/(\mathrm{mol\,dm^{-3}\,s^{-1}})$	(a)	8.70×10^{-4}	3.48×10^{-3}	1.39×10^{-2}	3.13×10^{-2}
	(b)	4.35×10^{-3}	1.74×10^{-2}	6.96×10^{-2}	1.57×10^{-1}
	(c)	8.69×10^{-3}	3.47×10^{-2}	1.38×10^{-1}	3.13×10^{-1}

$$\log v_0 = \log k_{\mathrm{r,eff}} + a\log\,[\,\mathrm{I}\,]_0$$

$$k_{\mathrm{r,eff}} = k_{\mathrm{r}}[\mathrm{Ar}]_0^b$$

$$\log k_{\mathrm{r,eff}} = \log k_{\mathrm{r}} + b\log[\mathrm{Ar}]_0$$

Method of initial rates

$[\mathrm{I}]_0/(10^{-5}\,\mathrm{mol\,dm^{-3}})$		1.0	2.0	4.0	6.0
$v_0/(\mathrm{mol\,dm^{-3}\,s^{-1}})$	(a)	8.70×10^{-4}	3.48×10^{-3}	1.39×10^{-2}	3.13×10^{-2}
	(b)	4.35×10^{-3}	1.74×10^{-2}	6.96×10^{-2}	1.57×10^{-1}
	(c)	8.69×10^{-3}	3.47×10^{-2}	1.38×10^{-1}	3.13×10^{-1}

$$\log v_0 = \log k_{\mathrm{r,eff}} + a\log\,[\mathrm{I}]_0$$

$$k_{\mathrm{r,eff}} = k_{\mathrm{r}}[\mathrm{Ar}]_0^b$$

$$\log k_{\mathrm{r,eff}} = \log k_{\mathrm{r}} + b\log[\mathrm{Ar}]_0$$

$[\mathrm{Ar}]_0/(\mathrm{mol\,dm^{-3}})$	1.0×10^{-3}	5.0×10^{-3}	1.0×10^{-2}
$\log([\mathrm{Ar}]_0/\mathrm{mol\,dm^{-3}})$	−3.00	−2.30	−2.00
$\log(k_{\mathrm{r,eff}}/\mathrm{dm^3\,mol^{-1}\,s^{-1}})$	6.94	7.64	7.93

Method of initial rates

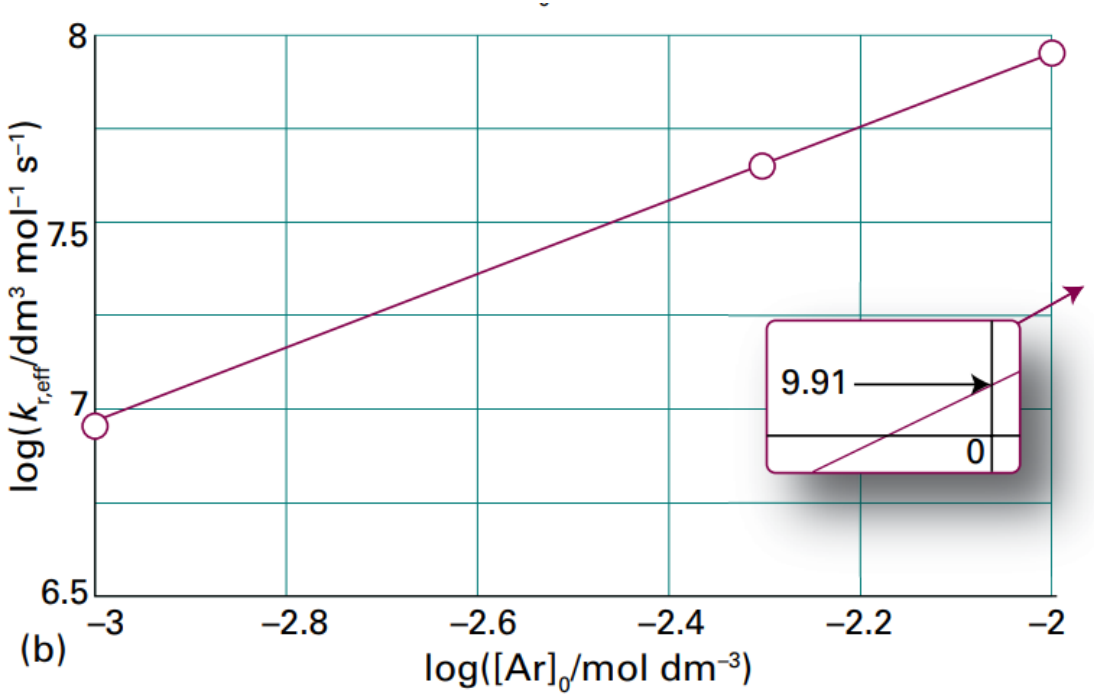
$[\mathrm{I}]_0/(10^{-5}\,\mathrm{mol\,dm^{-3}})$		1.0	2.0	4.0	6.0
$v_0/(\mathrm{mol\,dm^{-3}\,s^{-1}})$	(a)	8.70×10^{-4}	3.48×10^{-3}	1.39×10^{-2}	3.13×10^{-2}
	(b)	4.35×10^{-3}	1.74×10^{-2}	6.96×10^{-2}	1.57×10^{-1}
	(c)	8.69×10^{-3}	3.47×10^{-2}	1.38×10^{-1}	3.13×10^{-1}

$$\log v_0 = \log k_{\mathrm{r,eff}} + a\log[\mathrm{I}]_0$$

$$k_{\mathrm{r,eff}} = k_{\mathrm{r}}[\mathrm{Ar}]_0^b$$

$$\log k_{\mathrm{r,eff}} = \log k_{\mathrm{r}} + b\log[\mathrm{Ar}]_0$$

$[\mathrm{Ar}]_0/(\mathrm{mol\,dm^{-3}})$	1.0×10^{-3}	5.0×10^{-3}	1.0×10^{-2}
$\log([\mathrm{Ar}]_0/\mathrm{mol\,dm^{-3}})$	−3.00	−2.30	−2.00
$\log(k_{\mathrm{r,eff}}/\mathrm{dm^3\,mol^{-1}\,s^{-1}})$	6.94	7.64	7.93



Method of initial rates

$[\mathrm{I}]_0/(10^{-5}\,\mathrm{mol\,dm^{-3}})$		1.0	2.0	4.0	6.0
$v_0/(\mathrm{mol\,dm^{-3}\,s^{-1}})$	(a)	8.70×10^{-4}	3.48×10^{-3}	1.39×10^{-2}	3.13×10^{-2}
	(b)	4.35×10^{-3}	1.74×10^{-2}	6.96×10^{-2}	1.57×10^{-1}
	(c)	8.69×10^{-3}	3.47×10^{-2}	1.38×10^{-1}	3.13×10^{-1}

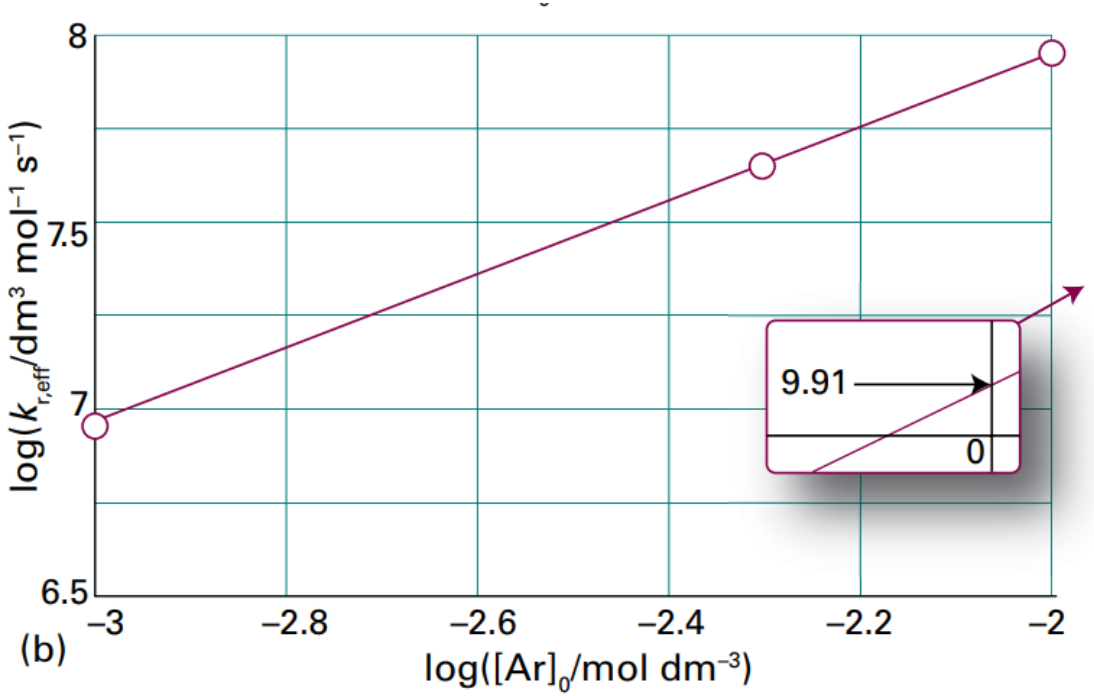
$$\log v_0 = \log k_{\mathrm{r,eff}} + a\log\,[\mathrm{I}]_0$$

$$k_{\mathrm{r,eff}} = k_{\mathrm{r}}[\mathrm{Ar}]_0^b$$

$$\log k_{\mathrm{r,eff}} = \log k_{\mathrm{r}} + b\log[\mathrm{Ar}]_0$$

$[\mathrm{Ar}]_0/(\mathrm{mol\,dm^{-3}})$	1.0×10^{-3}	5.0×10^{-3}	1.0×10^{-2}
$\log([\mathrm{Ar}]_0/\mathrm{mol\,dm^{-3}})$	−3.00	−2.30	−2.00
$\log(k_{\mathrm{r,eff}}/\mathrm{dm^3\,mol^{-1}\,s^{-1}})$	6.94	7.64	7.93

$$\log\{k_{\mathrm{r,eff}}/(\mathrm{dm^3\,mol^{-1}\,s^{-1}})\} = 9.94$$



Method of initial rates

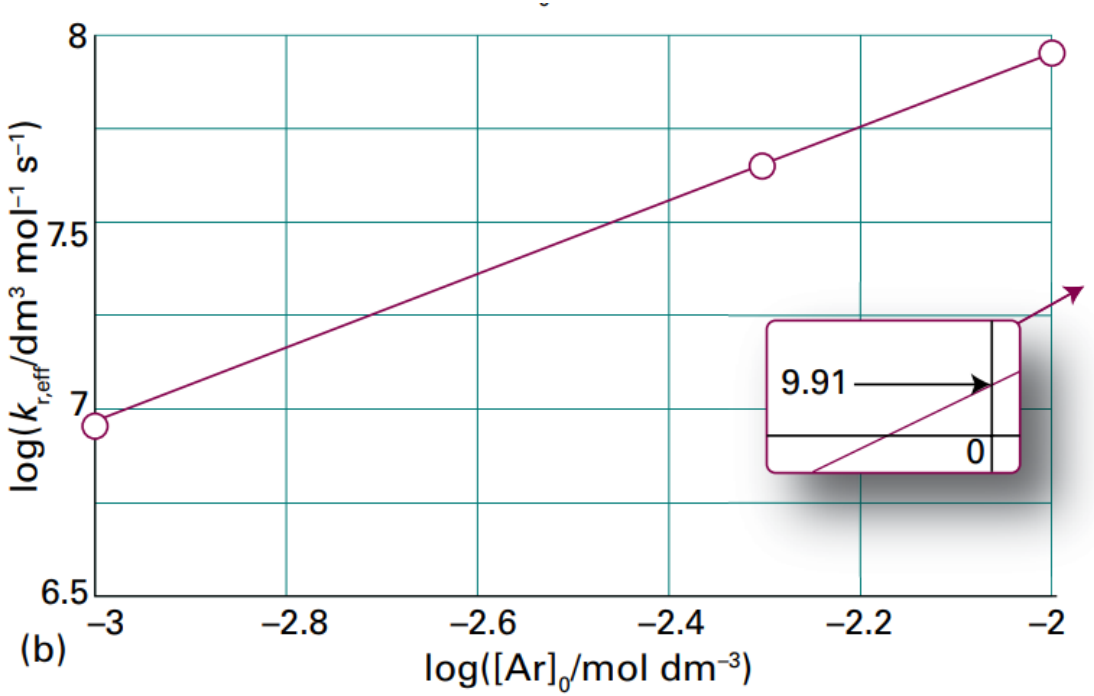
$[\mathrm{I}]_0/(10^{-5}\,\mathrm{mol\,dm^{-3}})$		1.0	2.0	4.0	6.0
$v_0/(\mathrm{mol\,dm^{-3}\,s^{-1}})$	(a)	8.70×10^{-4}	3.48×10^{-3}	1.39×10^{-2}	3.13×10^{-2}
	(b)	4.35×10^{-3}	1.74×10^{-2}	6.96×10^{-2}	1.57×10^{-1}
	(c)	8.69×10^{-3}	3.47×10^{-2}	1.38×10^{-1}	3.13×10^{-1}

$$\log v_0 = \log k_{\mathrm{r,eff}} + a\log[\mathrm{I}]_0$$

$$k_{\mathrm{r,eff}} = k_{\mathrm{r}}[\mathrm{Ar}]_0^b$$

$$\log k_{\mathrm{r,eff}} = \log k_{\mathrm{r}} + b\log[\mathrm{Ar}]_0$$

$[\mathrm{Ar}]_0/(\mathrm{mol\,dm^{-3}})$	1.0×10^{-3}	5.0×10^{-3}	1.0×10^{-2}
$\log([\mathrm{Ar}]_0/\mathrm{mol\,dm^{-3}})$	−3.00	−2.30	−2.00
$\log(k_{\mathrm{r,eff}}/\mathrm{dm^3\,mol^{-1}\,s^{-1}})$	6.94	7.64	7.93



$$\log\{k_{\mathrm{r,eff}}/(\mathrm{dm^3\,mol^{-1}\,s^{-1}})\} = 9.94$$

$$k_{\mathrm{r}} = 8.7\times10^{9}\,\mathrm{dm^6\,mol^{-2}\,s^{-1}}$$

Method of initial rates

$[\mathrm{I}]_0/(10^{-5}\,\mathrm{mol\,dm^{-3}})$		1.0	2.0	4.0	6.0
$v_0/(\mathrm{mol\,dm^{-3}\,s^{-1}})$	(a)	8.70×10^{-4}	3.48×10^{-3}	1.39×10^{-2}	3.13×10^{-2}
	(b)	4.35×10^{-3}	1.74×10^{-2}	6.96×10^{-2}	1.57×10^{-1}
	(c)	8.69×10^{-3}	3.47×10^{-2}	1.38×10^{-1}	3.13×10^{-1}

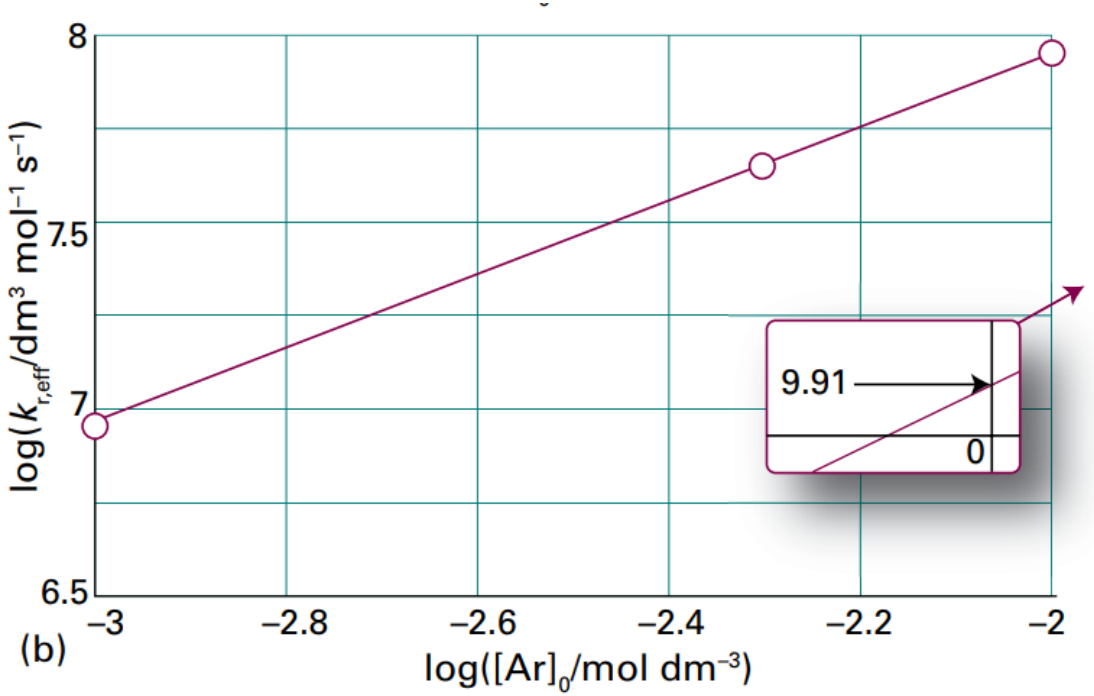
$$\log v_0 = \log k_{\mathrm{r,eff}} + a\log[\mathrm{I}]_0$$

$$v = k_{\mathrm{r}}[\mathrm{I}]_0^2[\mathrm{Ar}]_0$$

$$k_{\mathrm{r,eff}} = k_{\mathrm{r}}[\mathrm{Ar}]_0^b$$

$$\log k_{\mathrm{r,eff}} = \log k_{\mathrm{r}} + b\log[\mathrm{Ar}]_0$$

$[\mathrm{Ar}]_0/(\mathrm{mol\,dm^{-3}})$	1.0×10^{-3}	5.0×10^{-3}	1.0×10^{-2}
$\log([\mathrm{Ar}]_0/\mathrm{mol\,dm^{-3}})$	−3.00	−2.30	−2.00
$\log(k_{\mathrm{r,eff}}/\mathrm{dm^3\,mol^{-1}\,s^{-1}})$	6.94	7.64	7.93



$$\log\{k_{\mathrm{r,eff}}/(\mathrm{dm^3\,mol^{-1}\,s^{-1}})\} = 9.94$$

$$k_{\mathrm{r}} = 8.7\times10^{9}\,\mathrm{dm^6\,mol^{-2}\,s^{-1}}$$

Method of initial rates

However, products could participate in the reaction!

Method of initial rates

However, products could participate in the reaction!

H_2 (g) + Br_2 (g) --------> 2 HBr (g)

$$v = \frac{k_a[H_2][Br_2]^{3/2}}{[Br_2] + k_b[HBr]}$$

Focus 17: Chemical Kinetics

The rates of chemical reactions

Integrated rate laws

Reactions approaching equilibrium

The Arrhenius equation

Reaction mechanisms

Photochemistry