# Statistics II

Treatment and assessment of errors

33

Answers to additional problems

33.1 We first convert from V to mV. We then write, signal-to-noise ratio $= \dfrac{340}{10} = \dfrac{34}{1}$. which is acceptable. We might cite this ratio as 34 : 1.

33.2 The innate error will be half the minimum increment measurable on the watch dial. In this case, the innate error is 0.5 s since the minimum increment is 1 s.

33.3 From eqn. (33.2), the signal-to-noise ratio is $\dfrac{3.2}{0.7} = 4.6 : 1$ which is acceptable.

33.4 To linearize the data, we plot $1/[A]_t$ (as x) against time t (as y). The graph has the following appearance,
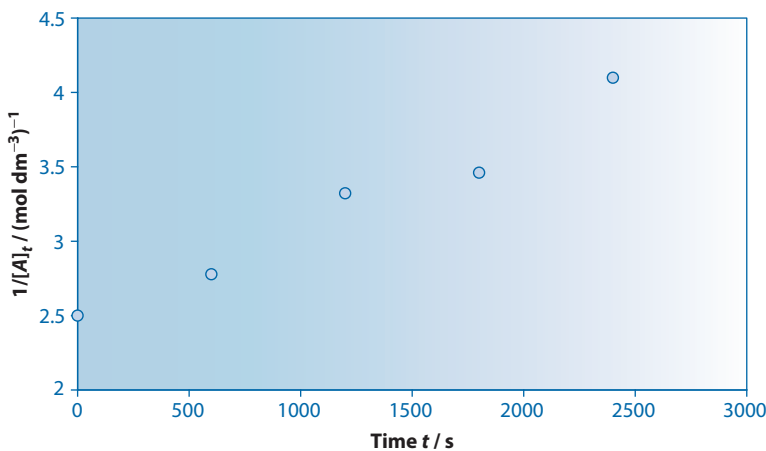
The graph clearly shows some scatter. The value of $r^2 = 0.969$.

33.5 From eqn. (33.3), the minimum error $= \left(\dfrac{0.001}{0.670} \right) = 1.49 \times 10^{-3}$, or 0.15%.

33.6 Inserting values into eqn. (33.4),

$$(\text{minimum error})^2 = \underbrace{\left(\frac{0.005}{10} \right)^2}_{\text{Pipette}} + \underbrace{\left(\frac{0.001}{0.104} \right)^2}_{\text{Concentration}} + \underbrace{\left(\frac{15}{600} \right)^2}_{\text{Time}}$$

The reading for time is 600 s because the chemist removes a sample every 10 minutes so 10×60 s

Performing the calculations yields,

$$(\text{minimum error})^2 = (5 \times 10^{-4})^2 + (9.62 \times 10^{-3})^2 + (0.025)^2$$

$$(\text{minimum error})^2 = 2.5 \times 10^{-7} + 9.25 \times 10^{-5} + 6.25 \times 10^{-4}$$
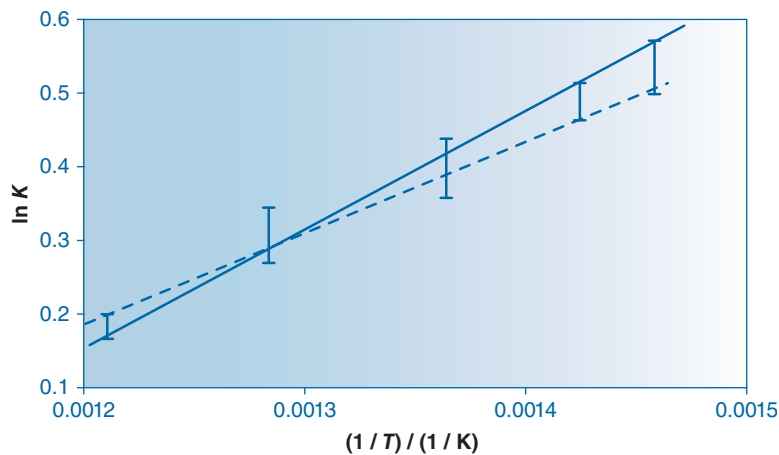
$$(\text{minimum error})^2 = 7.18 \times 10^{-4}$$

so   minimum error $= \sqrt{7.18\times10^{-4}} = 0.0268$

The error is 2.7%. Most of this error comes from the measurement of time.

33.7   It is best to start by computing the data necessary for the isochore plot.

T/K	686	702	733	779	826
$1/T \div 10^{-3}\,\text{K}^{-1}$	1.458	1.425	1.364	1.284	1.211
K_{max}	1.77	1.67	1.55	1.41	1.22
$\ln K_{max}$	0.571	0.513	0.438	0.344	0.199
K_{min}	1.67	1.59	1.43	1.31	1.18
$\ln K_{min}$	0.513	0.464	0.358	0.270	0.166

A graph is then drawn of $\ln K$ (as y), against $1/T$ (as x) for both sets of data.

The maximum gradient (line ——) is 1626 K^{-1}
The minimum gradient (line - - - -) is 1259 K^{-1}

33.8   Inserting values into eqn. (33.4),

$$(\text{minimum error})^2 = \left(\frac{1}{28.3}\right)^2 + \left(\frac{1\times10^{-5}}{4.4\times10^{-3}}\right)^2$$
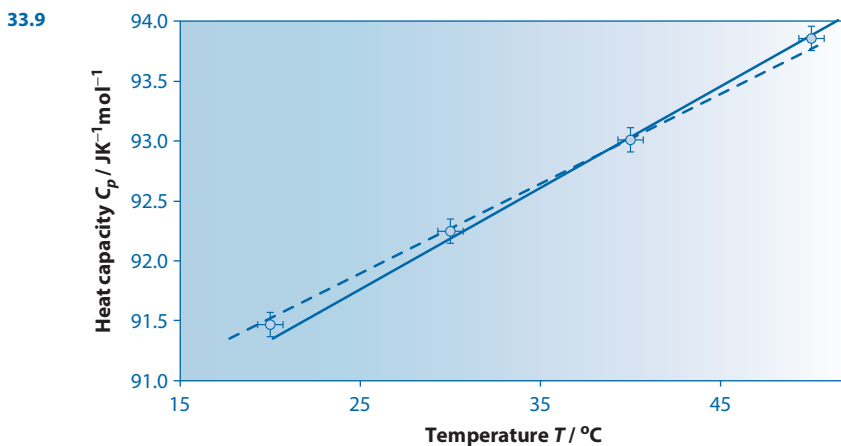
Voltmeter   Concentration

$(\text{minimum error})^2 = (0.035\,3)^2 + (0.002\,27)^2$

$(\text{minimum error})^2 = (1.246 \times 10^{-3}) + (5.165 \times 10^{-6}) = 1.251 \times 10^{-3}$

minimum error $= \sqrt{1.251\times10^{-3}} = 0.0354$

So the error is slightly over 3.5 per cent. The measurement of *emf* is the major error within this measurement.

33.9

The maximum gradient (line – – – –) has a gradient of $8.72 \times 10^{-2}\,J\,mol^{-1}$
The minimum gradient (line ——) has a gradient of $7.48 \times 10^{-2}\,J\,mol^{-1}$
The maximum gradient is 17 per cent higher than the minimum gradient.

33.10   Rearranging the equation yields, $k = \dfrac{1}{t}\ln\left(\dfrac{c_0}{c_t}\right)$ and hence $k = -\dfrac{1}{t}\ln\left(\dfrac{c_t}{c_0}\right)$

so, $\sigma_k = -\dfrac{1}{t}\left(\dfrac{\sigma_{c_t}}{c_t}\right)$

In our context here,

- The factor before the logarithm $= -1/t = -1/10$ so a in eqn. (33.8) $= -1/10$.
- The $1/c_0$ term, which is b in eqn. (33.8), disappears due to cancellation.
- The reactant concentration, c_t, is the observed variable x.
- In the question, the concentration c_t is expressed with the innate error of ± 0.005 mol dm^{-3} so we use this number as σ_{c_t}

If k had been a *linear* function of concentration as found for a zero-order reaction
($k = -c_t/t$), then we would calculate k to be $0.06 / 10 = 0.006$ mol $dm^{-3}\,s^{-1}$ and σ_k would equal,

$$\sigma_k = k\left(\dfrac{\sigma_{c_t}}{c_t}\right) = 0.006 \times \dfrac{0.005}{0.06} = 5 \times 10^{-4} = 0.05\%.$$

As it is a logarithmic function, we insert terms into eqn. (33.5),

$$\sigma_k = \left|-\dfrac{1}{10}\right| \times \left(\dfrac{0.005}{0.06}\right) = 8.33\dot{3} \times 10^{-3} = 0.83\%.$$
$$a \;(\sigma_c \div c)\; \sigma_k$$

This error is seventeen times larger than if the rate constant k had been a linear function of concentration c (cf. eqn. (33.5)).