Mean and standard deviation

1.   (a) From air: mean 2.310035 g, standard dev 0.000134 g, standard error 0.000067 g
      From NO: mean 2.300078 g, standard dev 0.001819 g, standard error 0.000910 g

      (b) The difference in mean is 0.009958 g and assuming independence the standard error of the difference is estimated to be 0.000912 g, so the difference is over 10 standard errors. There is therefore a systematic difference.

      The most likely reason for the difference is that air with the oxygen, water and CO_2 removed still contains a small amount of inert gases, mainly argon, which will be absent from nitrogen produced from NO. This was how Ar was discovered.

2.   The relevant sums rounded to 6 figures are

      $$\sum_{i=1}^{N} X_i = 793.067 \text{, hence } m = 79.3067 \text{ and } m^2 = 6289.55$$

      $$\sum_{i=1}^{N} X_i^2 = 62895.5 \text{, so } s^2 = \frac{1}{N-1}\left(\sum_{i=1}^{N} X_i^2 - Nm^2\right) = 0 \text{ and } s = 0.$$

      $$\sum_{i=1}^{N}(X_i - m)^2 = 0.00098044 \text{ so } s^2 = \frac{1}{N-1}\sum_{i=1}^{N}(X_i - m)^2 = 0.000108938 \text{ and } s =$$

      0.0104373. The first formula relies on the difference between two large numbers, which 6 figure precision is not capable of resolving.

3. $$\text{mean} = E\sum_{i} X_i = \sum_{i} EX_i = N\mu$$

      $$\text{variance} = E\left(\sum_{i} X_i - N\mu\right)^2 = E\left(\sum_{i} X_i\right)^2 - N^2\mu^2 = E\left(\sum_{i,j} X_i X_j\right) - N^2\mu^2$$

      now $EX_i X_j = \begin{cases} \mu^2 & (i \neq j) \\ \sigma^2 + \mu^2 & (i = j) \end{cases}$ and the double sum contains N terms where $i = j$ and

      $N(N-1)$ terms where $i \neq j$, hence

      $\text{variance} = N(N-1)\mu^2 + N(\mu^2 + \sigma^2) - N^2\mu^2 = N\sigma^2$ as required

      hence the sample mean has mean μ and standard error $\sigma/\sqrt{N}$.

Expectations

1. $\mu = EX = \int_0^1 x\,dx = \dfrac{1}{2}$ and $EX^2 = \int_0^1 x^2\,dx = \dfrac{1}{3}$ so $\sigma^2 = EX^2 - \mu^2 = \dfrac{1}{3} - \dfrac{1}{4} = \dfrac{1}{12}$ and

$\sigma = \dfrac{1}{\sqrt{12}} = \dfrac{\sqrt{3}}{6}$

2. (a) $\mu = ET = \omega \int_0^\infty t \exp(-\omega t)\,dt = \dfrac{1}{\omega}$

$ET^2 = \omega \int_0^\infty t^2 \exp(-\omega t)\,dt = \dfrac{2}{\omega^2}$ so $\sigma^2 = ET^2 - \mu^2 = \dfrac{1}{\omega^2}$

(b) $g(s) = E\exp(sT) = \omega \int_0^\infty \exp((s-\omega)t)\,dt = \dfrac{\omega}{\omega - s}$ $\quad (s < \omega)$

3. (a) $g(0) = E\left(\exp(0)\right) = E(1) = \int p(t)\,dt = 1$ where the integral covers the whole space.

(b) $\dfrac{dg}{ds}\Big|_{s=0} = \dfrac{d}{ds}E(\exp(sT))\Big|_{s=0} = E\dfrac{d}{ds}\exp(sT)\Big|_{s=0} = E\left(T\exp(sT)\right)\big|_{s=0} = E(T)$ or alternatively

$\dfrac{dg}{ds}\Big|_{s=0} = \dfrac{d}{ds}\int p(t)\exp(st)\,dt\Big|_{s=0} = \int p(t)\dfrac{d}{ds}\exp(st)\,dt\Big|_{s=0} = \int p(t)t\exp(st)\,dt\Big|_{s=0} = E(T)$

(c) $\dfrac{d^2g}{ds^2}\Big|_{s=0} = \dfrac{d^2}{ds^2}E(\exp(sT))\Big|_{s=0} = E\dfrac{d^2}{ds^2}\exp(sT)\Big|_{s=0} = E\left(T^2\exp(sT)\right)\big|_{s=0} = E(T^2)$

4. (a) If the random variables are independent their joint density is of the form
$p(x,y) = p_1(x)p_2(y)$, hence the mgf of $X+Y$ is

$E(\exp(s(X+Y))) = \iint p_1(x)p_2(y)\exp(s(x+y))\,dx\,dy$.

Since the domain of integration is a rectangle, i.e. the limits on x and y are constants, the integral is separable, $E(\exp(s(X+Y))) = \int p_1(x)\exp(sx)\,dx \int p_2(y)\exp(sy)\,dy = f(s)g(s)$

(b) The mgf of the time to the second collision is $f(s)g(s) = \dfrac{\omega^2}{(\omega - s)^2}$ $\quad (s < \omega)$.

The mean time to the second collision is $\dfrac{d}{ds}\dfrac{\omega^2}{(\omega - s)^2}\Big|_{s=0} = \dfrac{2\omega^2}{(\omega - s)^3}\Big|_{s=0} = \dfrac{2}{\omega}$

The mean square time to the second collision is $\dfrac{d^2}{ds^2}\dfrac{\omega^2}{(\omega - s)^2}\Big|_{s=0} = \dfrac{6\omega^2}{(\omega - s)^4}\Big|_{s=0} = \dfrac{6}{\omega^2}$

hence the variance of the time is $\dfrac{6}{\omega^2} - \dfrac{4}{\omega^2} = \dfrac{2}{\omega^2}$.

(c) Using the result of (a) the mgf of the sum is $g(s) = \exp\left(s(\mu_1 + \mu_2) + \tfrac{1}{2}s^2(\sigma_1^2 + \sigma_2^2)\right)$,

which is the mgf of a normal distribution with mean $(\mu_1 + \mu_2)$ and variance $(\sigma_1^2 + \sigma_2^2)$.

Propagation of errors

1. (a) $X = x + \varepsilon_x$ and $y = f(x)$ so the experimental value is

$Y = f(X) = f(x + \varepsilon_x) = y + f'(x)\varepsilon_x + o(\varepsilon_x)$, hence $\varepsilon_y = f'(x)\varepsilon_x + o(\varepsilon_x)$ and to first order

$\sigma_y^2 = E\varepsilon_y^2 = \left(f'(x)\right)^2 E\varepsilon_x^2 = \left(f'(x)\right)^2 \sigma_x^2$, or equivalently $\sigma_y = \left|f'(x)\right|\sigma_x$.

(b) $\Delta G° = 4009$ J mol^{-1} and $\sigma_{\Delta G°} = \left|-\dfrac{RT}{K}\right|\sigma_K = 13$ J mol^{-1}.

2. (a) Mean 0.19521, standard error 0.00035.

(b) $K = \dfrac{p_{H_2}^{1/2} p_{I_2}^{1/2}}{p_{HI}} = \dfrac{\alpha}{2(1-\alpha)}$ and $\dfrac{dK}{d\alpha} = \dfrac{1}{2(1-\alpha)^2}$, hence the estimated mean is 0.12128

and the standard deviation is 0.00027.

3. (a) The concentration is $c = n/V = 0.1000$ M so we need to use the propagation of errors for two variables.

$\sigma_c^2 = \left(\dfrac{1}{V}\right)^2 \sigma_n^2 + \left(\dfrac{-n}{V^2}\right)^2 \sigma_V^2$ assuming independence, so $\sigma_c = 0.00056$ M.

(b) $k = A\exp(-E/RT)$, and $\sigma_k = \left|\dfrac{dk}{dT}\right|\sigma_T$. Hence $\sigma_k = \left|\dfrac{kE}{RT^2}\right|\sigma_T$. We cannot calculate σ_k

without knowing k, but we can calculate the relative error $\dfrac{\sigma_k}{k} = \dfrac{E}{RT}\dfrac{\sigma_T}{T} = 0.062$.

(c) $c = 10^{-pH} = \exp(-pH \times \ln 10)$, hence $\sigma_c = \left|\dfrac{dc}{dpH}\right|\sigma_{pH} = c\ln 10 \sigma_{pH}$.

$c = 47.9$ μM and $\sigma_c = 5.5$ μM.

4. $\sigma_\kappa^2 = \left(\dfrac{\partial \kappa}{\partial G}\right)^2 \sigma_G^2 + \left(\dfrac{\partial \kappa}{\partial q}\right)^2 \sigma_q^2 + 2\left(\dfrac{\partial \kappa}{\partial G}\right)\left(\dfrac{\partial \kappa}{\partial q}\right)\sigma_{Gq}^2 = q^2\sigma_G^2 + G^2\sigma_q^2$, assuming independence,

or equivalently $\dfrac{\sigma_\kappa^2}{\kappa^2} = \dfrac{\sigma_G^2}{G^2} + \dfrac{\sigma_q^2}{q^2}$, so $\kappa = 1.06$ S m^{-1} with an estimated standard deviation of 1.5%.

$\sigma_\Lambda^2 = \left(\dfrac{\partial \Lambda}{\partial \kappa}\right)^2 \sigma_\kappa^2 + \left(\dfrac{\partial \Lambda}{\partial c}\right)^2 \sigma_c^2 + 2\left(\dfrac{\partial \Lambda}{\partial \kappa}\right)\left(\dfrac{\partial \Lambda}{\partial c}\right)\sigma_{\kappa c}^2 = \dfrac{\sigma_\kappa^2}{c^2} + \dfrac{\kappa^2}{c^4}\sigma_c^2$, assuming independence,

or equivalently $\dfrac{\sigma_\Lambda^2}{\Lambda^2} = \dfrac{\sigma_\kappa^2}{\kappa^2} + \dfrac{\sigma_c^2}{c^2}$, so $\Lambda = 10.1$ mS m^2 with an estimated standard deviation of 1.65%. (Note the standard A level method of handling errors, i.e. adding relative errors for multiplication and division would give an estimate of 2.7%, which is safe but over-conservative). The assumption that errors in κ and c are independent is questionable, as errors in making up the solution will lead to errors in conductivity, however these errors are likely to be in the same direction and so cancel out. Introducing a correlation coefficient r for this error would give

$$\sigma_\Lambda^2 = \frac{\sigma_\kappa^2}{c^2} + \frac{\kappa^2}{c^4}\sigma_c^2 - 2r\frac{\kappa}{c^3}\sigma_\kappa\sigma_c \quad \text{or equivalently} \quad \frac{\sigma_\Lambda^2}{\Lambda^2} = \frac{\sigma_\kappa^2}{\kappa^2} + \frac{\sigma_c^2}{c^2} - 2r\frac{\sigma_\kappa}{\kappa}\frac{\sigma_c}{c},$$ so that with a

correlation coefficient of 1 would give a reduced error of 0.9%.

5. From the Beer Lambert law $c = A/\varepsilon\ell$. Hence

$$\sigma_c^2 = \left(\frac{\partial c}{\partial A}\right)^2\sigma_A^2 + \left(\frac{\partial c}{\partial\varepsilon}\right)^2\sigma_\varepsilon^2 + 2\left(\frac{\partial c}{\partial A}\right)\left(\frac{\partial c}{\partial\varepsilon}\right)\sigma_{A\varepsilon}^2 = \frac{\sigma_A^2}{\varepsilon^2\ell^2} + \frac{A^2}{\varepsilon^4\ell^2}\sigma_\varepsilon^2,$$ assuming

independence, or equivalently $\frac{\sigma_c^2}{c^2} = \frac{\sigma_A^2}{A^2} + \frac{\sigma_\varepsilon^2}{\varepsilon^2}$. Hence $c = 0.719$ mM and

$\sigma_c/c = 4.8\%$ so $\sigma_c = 35\ \mu\text{M}$.

6. (i) The fundamental transition is from $V = 0$ to 1 and has wavenumber
$\tilde\omega_{1\leftarrow0} = \tilde\omega_e - 2\tilde\omega_e x_e$ and the first overtone is from 0 to 2 and therefore has
wavenumber $\tilde\omega_{2\leftarrow0} = 2\tilde\omega_e - 6\tilde\omega_e x_e$. We can therefore calculate the two required
constants by solving simultaneous equations giving from $3\tilde\omega_{1\leftarrow0} - \tilde\omega_{2\leftarrow0} = \tilde\omega_e$ and
$\tilde\omega_{1\leftarrow0} - \frac{1}{2}\tilde\omega_{2\leftarrow0} = \tilde\omega_e x_e$..
Assuming the errors to be independent we have

$$\sigma_e^2 = \left(\frac{\partial\tilde\omega_e}{\partial\tilde\omega_{10}}\right)^2\sigma_{10}^2 + \left(\frac{\partial\tilde\omega_e}{\partial\tilde\omega_{20}}\right)^2\sigma_{20}^2 = 9\sigma_{10}^2 + \sigma_{20}^2 \quad\text{and}$$

$$\sigma_{wx}^2 = \left(\frac{\partial\tilde\omega_e x_e}{\partial\tilde\omega_{10}}\right)^2\sigma_{10}^2 + \left(\frac{\partial\tilde\omega_e x_e}{\partial\tilde\omega_{20}}\right)^2\sigma_{20}^2 = \sigma_{10}^2 + \frac{\sigma_{20}^2}{4}$$

Hence $\tilde\omega_e = 2987.0$ cm^{-1} with an error of 0.3 cm^{-1}, and $\tilde\omega_e x_e = 51.0$ cm^{-1} with an
error of 0.1 cm^{-1}.
(ii) The dissociation wavenumber of a Morse oscillator is given by

$$D_e = \frac{\tilde\omega_e^2}{4\tilde\omega_e x_e},\text{ and expressing this in terms of the data } D_e = \frac{\left(3\tilde\omega_{10} - \tilde\omega_{20}\right)^2}{\left(4\tilde\omega_{10} - 2\tilde\omega_{20}\right)}$$

$$\sigma_D^2 = \left(\frac{\partial}{\partial\tilde\omega_{10}}\frac{\left(3\tilde\omega_{10} - \tilde\omega_{20}\right)^2}{\left(4\tilde\omega_{10} - 2\tilde\omega_{20}\right)}\right)^2\sigma_{10}^2 + \left(\frac{\partial}{\partial\tilde\omega_{20}}\frac{\left(3\tilde\omega_{10} - \tilde\omega_{20}\right)^2}{\left(4\tilde\omega_{10} - 2\tilde\omega_{20}\right)}\right)^2\sigma_{20}^2 =$$

$$= \left(\frac{6\left(3\tilde\omega_{10} - \tilde\omega_{20}\right)}{\left(4\tilde\omega_{10} - 2\tilde\omega_{20}\right)} - \frac{4\left(3\tilde\omega_{10} - \tilde\omega_{20}\right)^2}{\left(4\tilde\omega_{10} - 2\tilde\omega_{20}\right)^2}\right)^2\sigma_{10}^2 + \left(\frac{-2\left(3\tilde\omega_{10} - \tilde\omega_{20}\right)}{\left(4\tilde\omega_{10} - 2\tilde\omega_{20}\right)} + \frac{2\left(3\tilde\omega_{10} - \tilde\omega_{20}\right)^2}{\left(4\tilde\omega_{10} - 2\tilde\omega_{20}\right)^2}\right)^2\sigma_{20}^2$$

$$= \left(\frac{\left(3\tilde\omega_{10} - 2\tilde\omega_{20}\right)\left(3\tilde\omega_{10} - \tilde\omega_{20}\right)}{\left(2\tilde\omega_{10} - \tilde\omega_{20}\right)^2}\right)^2\sigma_{10}^2 + \left(\frac{\left(-\tilde\omega_{10} + \tilde\omega_{20}\right)\left(3\tilde\omega_{10} - \tilde\omega_{20}\right)}{2\left(2\tilde\omega_{10} - \tilde\omega_{20}\right)^2}\right)^2\sigma_{20}^2$$

i.e. D_e = 43736 cm^{-1} with an error of 87 cm^{-1}.
This is likely to be an underestimate because the Morse formula will not be accurate
all the way from the lowest levels to the dissociation limit. We can only estimate
statistical (random) errors by this method, not systematic errors inherent in the
method.

7. (a) $\sigma_{1/K} = \left| \dfrac{d(1/K)}{K} \right| \sigma_K = \dfrac{\sigma_K}{K^2}$. Hence $\dfrac{\sigma_{1/K}}{1/K} = K\sigma_{1/K} = \dfrac{\sigma_K}{K}$, which was to be shown.

(b) The data come from an undergraduate experiment. The concentration of complex can be obtained from the Beer Lambert law as $c = A/\varepsilon\ell$. From this the concentration of unbound iron and salicylate can be determined, e.g.

$[S^-]_{\text{free}} = [S^-]_{\text{tot}} - A/\varepsilon\ell$. Following the hint and denoting $[S^-]_{\text{tot}} \equiv S$ and $[Fe^{3+}]_{\text{tot}} = F$

we get $\dfrac{1}{K} = \dfrac{[S^-]_{\text{free}}[Fe^{3+}]_{\text{free}}}{[FeS^{2+}]} = \dfrac{(S - A/\varepsilon\ell)(F - A/\varepsilon\ell)}{A/\varepsilon\ell} = SF\dfrac{\varepsilon\ell}{A} - (S+F) + \dfrac{A}{\varepsilon\ell}$

Hence $\sigma_{1/K}^2 = \left(\dfrac{\partial(1/K)}{\partial S} \right)^2 \sigma_S^2 + \left(\dfrac{\partial(1/K)}{\partial F} \right)^2 \sigma_F^2 + \left(\dfrac{\partial(1/K)}{\partial A} \right)^2 \sigma_A^2 + \left(\dfrac{\partial(1/K)}{\partial\varepsilon} \right)^2 \sigma_\varepsilon^2$

$\sigma_{1/K}^2 = \left(F\dfrac{\varepsilon\ell}{A} - 1 \right)^2 \sigma_S^2 + \left(S\dfrac{\varepsilon\ell}{A} - 1 \right)^2 \sigma_F^2 + \left(-SF\dfrac{\varepsilon\ell}{A^2} + \dfrac{1}{\varepsilon\ell} \right)^2 \sigma_A^2 + \left(SF\dfrac{\ell}{A} - \dfrac{A}{\varepsilon^2\ell} \right)^2 \sigma_\varepsilon^2$ in terms

of relative errors, and denoting $A/\varepsilon\ell \equiv X$ and $SF/X = Y$ this simplifies to

$\sigma_{1/K}^2 = (Y - S)^2 \dfrac{\sigma_S^2}{S^2} + (Y - F)^2 \dfrac{\sigma_F^2}{F^2} + (Y - X)^2 \left(\dfrac{\sigma_A^2}{A^2} + \dfrac{\sigma_\varepsilon^2}{\varepsilon^2} \right)$.

For the three experiments the results are as follows

$[Fe^{3+}]_{\text{tot}} / 10^{-4}$ M	7.5	5.0	2.5
$[S^-]_{\text{tot}} / 10^{-4}$ M	2.5	5.0	7.5
A	0.37	0.65	0.40
$[FeS^{2+}]_{\text{tot}} / 10^{-4}$ M	2.18	3.82	2.35
$[Fe^{3+}]_{\text{free}} / 10^{-4}$ M	5.32	1.18	0.15
$[S^-]_{\text{free}} / 10^{-4}$ M	0.32	1.18	5.15
$K / 10^4$ M^{-1}	1.3	2.8	3.1
$1/K / 10^{-5}$ M	7.9	3.6	3.2
$\sigma_{1/K} / 10^{-5}$ M	3.5	1.5	3.1
σ_K / K	45%	41%	96%
$\sigma_K / 10^4$ M^{-1}	0.6	1.1	3.0

The errors are obviously too large to use the propagation of errors formula, the result is very sensitive to the concentration of the most dilute ingredient because it has to be calculated by subtraction.

8 (a) The first equation simply follows from a Taylor expansion of κ.

The variance is $\sigma_\kappa^2 = E(\delta_m\kappa + \delta_c\kappa)^2 = \sigma_{m,\kappa}^2 + \sigma_{c,\kappa}^2 = \sigma_{m,\kappa}^2 + \left(\dfrac{d\kappa}{dc} \right)^2 \sigma_c^2$ because the two sources of error are independent.

The covariance is $\sigma_{\kappa c}^2 = E(\delta_m\kappa\delta c + \delta_c\kappa\delta c) = 0 + \left(\dfrac{d\kappa}{dc} \right)\sigma_c^2$

The correlation coefficient is $r = \dfrac{\sigma_{\kappa c}^2}{\sigma_\kappa\sigma_c} = \dfrac{\left(\dfrac{d\kappa}{dc} \right)}{\sqrt{\dfrac{\sigma_{m,\kappa}^2}{\sigma_c^2} + \left(\dfrac{d\kappa}{dc} \right)^2}}$

(b) (i) $K_a = \dfrac{\alpha^2 c}{1-\alpha}$ and so $K_a = \dfrac{\kappa^2}{\Lambda_0 (c\Lambda_0 - \kappa)}$

(ii) $\dfrac{1}{K_a} = \dfrac{c\Lambda_0^2}{\kappa^2} - \dfrac{\Lambda_0}{\kappa}$, so $\sigma_{1/K}^2 = \left(\dfrac{\partial(1/K)}{\partial\kappa}\right)^2 \sigma_\kappa^2 + \left(\dfrac{\partial(1/K)}{\partial c}\right)^2 \sigma_c^2 + 2\left(\dfrac{\partial(1/K)}{\partial\kappa}\right)\left(\dfrac{\partial(1/K)}{\partial c}\right)\sigma_{\kappa c}^2$

i.e. $\sigma_{1/K}^2 = \left(\dfrac{-2c\Lambda_0^2}{\kappa^3} + \dfrac{\Lambda_0}{\kappa^2}\right)^2 \sigma_\kappa^2 + \left(\dfrac{\Lambda_0^2}{\kappa^2}\right)^2 \sigma_c^2 + 2\left(\dfrac{-2c\Lambda_0^2}{\kappa^3} + \dfrac{\Lambda_0}{\kappa^2}\right)\left(\dfrac{\Lambda_0^2}{\kappa^2}\right)\sigma_{\kappa c}^2$

because of the frequent occurrence of the ratio $\dfrac{\Lambda_0}{\kappa}$ in this equation it is convenient to use the degree of dissociation, which contains this ratio, and the relative errors:

$$\sigma_{1/K}^2 = \dfrac{1}{\alpha^2 c^2}\left[\left(1 - \dfrac{2}{\alpha}\right)^2 \dfrac{\sigma_\kappa^2}{\kappa^2} + \left(\dfrac{1}{\alpha^2}\right)\dfrac{\sigma_c^2}{c^2} + \dfrac{2}{\alpha}\left(1 - \dfrac{2}{\alpha}\right)\dfrac{\sigma_{\kappa c}^2}{c\kappa}\right]$$

Substituting for the variance and covariance,

$$\sigma_{1/K}^2 = \dfrac{1}{\alpha^2 c^2}\left[\left(1 - \dfrac{2}{\alpha}\right)^2 \dfrac{\sigma_{m,\kappa}^2}{\kappa^2} + \left(1 - \dfrac{2}{\alpha}\right)^2\left(\dfrac{d\kappa}{dc}\right)^2 \dfrac{\sigma_c^2}{\kappa^2} + \left(\dfrac{1}{\alpha^2}\right)\dfrac{\sigma_c^2}{c^2} + \dfrac{2}{\alpha}\left(1 - \dfrac{2}{\alpha}\right)\left(\dfrac{d\kappa}{dc}\right)\dfrac{\sigma_c^2}{c\kappa}\right]$$

To find $\dfrac{d\kappa}{dc}$ we need to solve for the degree of dissociation $\alpha = \dfrac{K_a}{2c}\left(\sqrt{1 + 4c/K_a} - 1\right)$, from which $\kappa = \dfrac{K_a\Lambda_0}{2}\left(\sqrt{1 + 4c/K_a} - 1\right)$ and finally $\dfrac{d\kappa}{dc} = \dfrac{\Lambda_0}{\sqrt{1 + 4c/K_a}}$ and after a lot of simplification this becomes

$$\sigma_{1/K}^2 = \dfrac{1}{\alpha^2 c^2}\left[\left(1 - \dfrac{2}{\alpha}\right)^2 \dfrac{\sigma_{m,\kappa}^2}{\kappa^2} + \left(1 + \left(1 - \dfrac{2}{\alpha}\right)\left(\dfrac{1}{\sqrt{1 + 4c/K_a}}\right)\right)^2 \dfrac{1}{\alpha^2}\dfrac{\sigma_c^2}{c^2}\right]$$

(iii) Using the method outlined above the acid dissociation constant is 1.78×10^{-5} with a standard deviation of 1.5×10^{-6}. The correlation coefficient is 0.26, i.e. κ and c are positively correlated, as expected.