

# 1 Constants

## 1.1 Molar mass

H: 1.00794, He: 4.002602, C: 12.0107, O: 15.9994, Al: 26.98154, Si: 28.0855, K: 39.0983, Ar: 39.948, Ca: 40.078, Rb: 85.4678, Sr: 87.62, I: 126.904, Xe: 131.293, Nd: 144.242, Sm: 150.36, Eu: 151.964, Lu: 174.967, Hf: 178.49, W: 183.84, Re: 186.207, Os: 190.23, Pb: 207.2, Th: 232.04, U: 238.04

## 1.2 Isotopic ratios

K:  $^{40}\text{K}/\text{K} = 0.01167\%$   
 Ar:  $^{40}\text{Ar}/^{36}\text{Ar} (\text{atm}) = 298.5$ ;  $^{38}\text{Ar}/^{36}\text{Ar} = 0.187$   
 Rb:  $^{85}\text{Rb}/^{87}\text{Rb} = 2.59337$   
 Sr:  $^{84}\text{Sr}/^{86}\text{Sr} = 0.056584$ ;  $^{86}\text{Sr}/^{88}\text{Sr} = 0.1194$   
 Sm:  $^{147}\text{Sm}/\text{Sm} = 14.99\%$   
 U:  $^{238}\text{U}/^{235}\text{U} = 137.818$ ;  
 $\text{A}(^{234}\text{U})/\text{A}(^{238}\text{U})[\text{modern ocean}] \approx 1.15$ .

## 1.3 Half-lives and decay constants

C:  $t_{1/2}(^{14}\text{C}) = 5730 \text{ yr}$   
 K:  $\lambda_{\beta^-} = 4.962 \times 10^{-10} \text{ yr}^{-1}$ ;  $\lambda_e = 0.581 \times 10^{-10} \text{ yr}^{-1}$ ;  
 $t_{1/2}(e + \beta^-) = 1.248 \text{ Gyr}$   
 Rb:  $t_{1/2}(^{87}\text{Rb}) = 48.8 \text{ Gyr}$   
 Sm:  $t_{1/2}(^{147}\text{Sm}) = 106 \text{ Gyr}$   
 U:  $t_{1/2}(^{238}\text{U}) = 4.468 \text{ Gyr}$ ;  $t_{1/2}(^{235}\text{U}) = 703.8 \text{ Myr}$ ;  
 $t_{1/2}(^{234}\text{U}) = 245.5 \text{ kyr}$ ;  $\lambda_f = 8.46 \times 10^{-17} \text{ yr}^{-1}$   
 Th:  $t_{1/2}(^{232}\text{Th}) = 14.05 \text{ Gyr}$ ;  $t_{1/2}(^{230}\text{Th}) = 75.38 \text{ kyr}$

# 2 Basic notions

## 2.1 Radioactivity

The decay equation:

$$\frac{dP}{dt} = -\lambda P$$

Its solution:

$$P = P_0 e^{-\lambda t}$$

The fundamental age equation:

$$t = \frac{1}{\lambda} \ln \left( \frac{D^*}{P} + 1 \right)$$

where  $D^*$  marks the radiogenic daughter component. Half-life vs. decay constant:

$$\frac{P_0}{2} = P_0 e^{-\lambda t_{1/2}} \Rightarrow t_{1/2} = \frac{\ln(2)}{\lambda} \quad (4)$$

## 2.2 Decay series

$$\text{for } P: dP/dt = -\lambda_P P \quad (5)$$

$$\text{for } D_1: dD_1/dt = \lambda_P P - \lambda_1 D_1 \quad (6)$$

$$\text{for } D_*: dD_*/dt = \lambda_1 D_1 \quad (7)$$

Assuming that  $D_1 = 0$  at  $t = 0$ :

$$D_1 = \frac{\lambda_P}{\lambda_1 - \lambda_P} P_0 [e^{-\lambda_P t} - e^{-\lambda_1 t}] \quad (8)$$

Secular equilibrium:

$$D_1 \lambda_1 = P \lambda_P \quad (9)$$

or, equivalently:

$$\frac{P}{D_1} = \frac{t_{1/2}(P)}{t_{1/2}(D_1)} \quad (10)$$

# 3 Analytical techniques

## 3.1 Mass spectrometry

Kinetic energy of single-charged ion of  $m$  a.m.u. in a mass spectrometer:

$$E = eV = \frac{mv^2}{2} \quad (11)$$

With  $e = 1.60219 \times 10^{-19} \text{ C}$  and  $1 \text{ a.m.u.} = 1.660538 \times 10^{-27} \text{ kg}$ . The mass analyser deflects the ions according to the following equation:

$$Hev = \frac{mv^2}{r} \quad (12)$$

(1) from which it follows that:

$$r = \frac{1}{H} \sqrt{\frac{2mV}{e}} \quad (13)$$

## 3.2 Isotope dilution

(3) Will not be part of the exam.

## 3.3 Sample-standard bracketing

Will not be part of the exam.

# 4 Simple parent-daughter pairs

## 4.1 $^{14}\text{C}$ dating

$$\frac{d^{14}\text{C}}{dt} = -\lambda_{14} \times ^{14}\text{C} \quad (14)$$

where  $\lambda_{14} = 0.120968 \text{ kyr}^{-1}$ .

$$t = -\frac{1}{\lambda_{14}} \ln \left[ \frac{d^{14}\text{C}/dt}{(d^{14}\text{C}/dt)_0} \right] \quad (15)$$

## 4.2 The Rb-Sr method

Ingrowth equation:

$$^{87}\text{Sr} = ^{87}\text{Sr}_0 + ^{87}\text{Rb}(e^{\lambda_{87}t} - 1) \quad (16)$$

where  $^{87}\text{Sr}_0$  is the initial  $^{87}\text{Sr}$  content.  $^{87}\text{Rb}/^{86}\text{Sr}$ -ratio is calculated as:

$$\frac{^{87}\text{Rb}}{^{86}\text{Sr}} = \frac{\text{Rb}}{\text{Sr}} \frac{Ab(^{87}\text{Rb})M(\text{Sr})}{Ab(^{86}\text{Sr})M(\text{Rb})} \quad (17)$$

where  $Ab(\cdot)$  signifies ‘abundance’.

## 4.3 Isochrons

The universal isochron equation:

$$\frac{D}{d} = \left( \frac{D}{d} \right)_0 + \frac{P}{d} (e^{\lambda_P t} - 1) \quad (18)$$

where  $P$  = the parent isotope,  $D$  = the daughter isotope,  $d$  = a non-radiogenic sister isotope of the radiogenic daughter. For the Rb-Sr method:

$$\frac{^{87}\text{Sr}}{^{86}\text{Sr}} = \left( \frac{^{87}\text{Sr}}{^{86}\text{Sr}} \right)_0 + \frac{^{87}\text{Rb}}{^{86}\text{Sr}} (e^{\lambda_{87}t} - 1) \quad (19)$$

## 4.4 The Sm-Nd method

The age equation:

$$^{143}\text{Nd} = ^{143}\text{Nd}_o + ^{147}\text{Sm}(e^{\lambda_{147}t} - 1) \quad (20)$$

Isochron equation:

$$\frac{^{143}\text{Nd}}{^{144}\text{Nd}} = \left( \frac{^{143}\text{Nd}}{^{144}\text{Nd}} \right)_o + \frac{^{147}\text{Sm}}{^{144}\text{Nd}} (e^{\lambda_{147}t} - 1) \quad (21)$$

## 5 The U-Pb system

$$\begin{aligned} ^{238}\text{U} &\rightarrow ^{206}\text{Pb} + 8\alpha + 6\beta + 47\text{MeV} \\ ^{235}\text{U} &\rightarrow ^{207}\text{Pb} + 7\alpha + 4\beta + 45\text{MeV} \\ ^{232}\text{Th} &\rightarrow ^{208}\text{Pb} + 6\alpha + 4\beta + 40\text{MeV} \end{aligned}$$

## 6 The U-(Th-)Pb method

Ingrowth equations:

$$\begin{aligned} ^{206}\text{Pb}^* &= ^{238}\text{U}(e^{\lambda_{238}t} - 1) \\ ^{207}\text{Pb}^* &= ^{235}\text{U}(e^{\lambda_{235}t} - 1) \\ ^{208}\text{Pb}^* &= ^{232}\text{Th}(e^{\lambda_{232}t} - 1) \end{aligned} \quad (23)$$

where  $^{20x}\text{Pb}^*$  is the radiogenic  $^{20x}\text{Pb}$  component ( $^{20x}\text{Pb} = ^{20x}\text{Pb}^* + ^{20x}\text{Pb}_o$ ). The corresponding age equations are:

$$\begin{aligned} t_{206} &= \frac{1}{\lambda_{238}} \ln \left( \frac{^{206}\text{Pb}^*}{^{238}\text{U}} + 1 \right) \\ t_{207} &= \frac{1}{\lambda_{235}} \ln \left( \frac{^{207}\text{Pb}^*}{^{235}\text{U}} + 1 \right) \\ t_{208} &= \frac{1}{\lambda_{232}} \ln \left( \frac{^{208}\text{Pb}^*}{^{232}\text{Th}} + 1 \right) \end{aligned} \quad (24)$$

with common Pb correction:

$$\begin{aligned} t_{206} &= \frac{1}{\lambda_{238}} \ln \left( \frac{\left( \frac{^{206}\text{Pb}}{^{204}\text{Pb}} \right) - \left( \frac{^{206}\text{Pb}}{^{204}\text{Pb}} \right)_o}{\frac{^{238}\text{U}}{^{204}\text{Pb}}} + 1 \right) \\ t_{207} &= \frac{1}{\lambda_{235}} \ln \left( \frac{\left( \frac{^{207}\text{Pb}}{^{204}\text{Pb}} \right) - \left( \frac{^{207}\text{Pb}}{^{204}\text{Pb}} \right)_o}{\frac{^{235}\text{U}}{^{204}\text{Pb}}} + 1 \right) \\ t_{208} &= \frac{1}{\lambda_{232}} \ln \left( \frac{\left( \frac{^{208}\text{Pb}}{^{204}\text{Pb}} \right) - \left( \frac{^{208}\text{Pb}}{^{204}\text{Pb}} \right)_o}{\frac{^{232}\text{Th}}{^{204}\text{Pb}}} + 1 \right) \end{aligned} \quad (25)$$

## 6.1 The Pb-Pb method

Age equation:

$$\frac{^{207}\text{Pb}^*}{^{206}\text{Pb}^*} = \frac{\left( \frac{^{207}\text{Pb}}{^{204}\text{Pb}} \right) - \left( \frac{^{207}\text{Pb}}{^{204}\text{Pb}} \right)_o}{\left( \frac{^{206}\text{Pb}}{^{204}\text{Pb}} \right) - \left( \frac{^{206}\text{Pb}}{^{204}\text{Pb}} \right)_o} = \frac{1}{137.818} \frac{e^{\lambda_{235}t} - 1}{e^{\lambda_{238}t} - 1} \quad (26)$$

where  $^{238}\text{U}/^{235}\text{U} = 137.818$ . For modern samples:

$$\left( \frac{^{207}\text{Pb}}{^{206}\text{Pb}} \right)_p^* = \frac{\lambda_{235}}{137.818\lambda_{238}} = 0.04607 \quad (27)$$

## 7 The K-Ar system

(22) Ingrowth equation:

$$\begin{aligned} ^{40}\text{Ar} &= ^{40}\text{Ar}_o + ^{40}\text{Ar}^* \\ \text{where } ^{40}\text{Ar}^* &= \frac{\lambda_e}{\lambda} ^{40}\text{K}(e^{\lambda t} - 1) \end{aligned} \quad (28)$$

### 7.1 K-Ar dating

Age equation:

$$t = \frac{1}{\lambda} \ln \left[ 1 + \frac{\lambda}{\lambda_e} \left( \frac{^{40}\text{Ar}^*}{^{40}\text{K}} \right) \right] \quad (29)$$

Isochron equation:

$$\frac{^{40}\text{Ar}}{^{36}\text{Ar}} = \left( \frac{^{40}\text{Ar}}{^{36}\text{Ar}} \right)_o + \frac{\lambda_e}{\lambda} \frac{^{40}\text{K}}{^{36}\text{Ar}} (e^{\lambda t} - 1) \quad (30)$$

### 7.2 $^{40}\text{Ar}/^{39}\text{Ar}$ dating

Sample:

$$t_x = \frac{1}{\lambda} \ln \left[ 1 + J \left( \frac{^{40}\text{Ar}^*}{^{39}\text{Ar}} \right)_x \right] \quad (31)$$

Standard:

$$t_s = \frac{1}{\lambda} \ln \left[ 1 + J \left( \frac{^{40}\text{Ar}^*}{^{39}\text{Ar}} \right)_s \right] \quad (32)$$

Age equation:

$$\frac{^{40}\text{Ar}}{^{36}\text{Ar}} = \left( \frac{^{40}\text{Ar}}{^{36}\text{Ar}} \right)_o + \frac{^{39}\text{Ar}}{^{36}\text{Ar}} \frac{e^{\lambda t} - 1}{J} \quad (33)$$

## 8 Thermochronology

### 8.1 The U-Th-He method

Ingrowth equation:

$$[^4\text{He}] = 8(e^{\lambda_{238}t} - 1)[^{238}\text{U}] + 7(e^{\lambda_{235}t} - 1)[^{235}\text{U}] + 6(e^{\lambda_{232}t} - 1)[^{232}\text{Th}] + (e^{\lambda_{147}t} - 1)[^{147}\text{Sm}] \quad (34)$$

where  $[^4\text{He}]$ ,  $[^{238}\text{U}]$ ,  $[^{235}\text{U}]$ ,  $[^{232}\text{Th}]$  and  $[^{147}\text{Sm}]$  are concentrations in atoms or moles per unit mass or volume.

Fick's Law:

$$\frac{\partial C}{\partial t} = D \left( \frac{\partial^2 C}{\partial x^2} + \frac{\partial^2 C}{\partial y^2} + \frac{\partial^2 C}{\partial z^2} \right) \quad (35)$$

Arrhenius equation:

$$\ln(D) = \ln(D_o) - \frac{E_a}{RT} \quad (36)$$

where  $R = 8.3144621 \text{ J/mol.K}$ .

Closure temperature (assuming that  $t \propto 1/T$ ):

$$\frac{E_a}{RT_c} = \ln \left( \frac{ART_c^2 D_o / r^2}{E_a dT/dt} \right) \quad (37)$$

where  $A = 55$  for a sphere, 27 for a cylinder and 8.7 for a plane sheet.

### 8.2 Fission tracks

The volume density  $n_s$  (in  $\text{cm}^{-3}$ ) of fission tracks:

$$n_s = \frac{\lambda_f}{\lambda} [^{238}\text{U}] (e^{\lambda t} - 1) \quad (38)$$

The surface density  $\rho$  (in  $\text{cm}^{-2}$ ):

$$\rho = gLn_s \quad (39)$$

Where  $g=1$  for internal and  $g=1/2$  for external surfaces, and  $L \sim 15\mu\text{m}$  for apatite. Age equation:

$$t = \frac{1}{\lambda} \ln \left( \frac{\lambda}{\lambda_f} \frac{\rho_s}{[^{238}\text{U}]g_s L} + 1 \right) \quad (40)$$

External detector method:

$$t = \frac{1}{\lambda} \ln \left( 1 + \frac{g_i}{g_s} \lambda \zeta \rho_d \frac{N_s}{N_i} \right) \quad (41)$$

where  $N_s$  and  $N_i$  are the spontaneous and induced track counts. Arrhenius relationship for fading fission tracks:

$$\ln(t) = \frac{E_A}{kT} + \ln \left[ \ln \left( \frac{\rho_o}{\rho} \right) \right] - \ln(C) \quad (42)$$

where  $k = 8.616 \times 10^{-5} \text{ eV/K}$ .

## 9 Cosmogenic nuclides

Will not be part of the exam.

## 10 U-series disequilibrium

### 10.1 The $^{234}\text{U}$ - $^{238}\text{U}$ method

Age equation:

$$\frac{A(^{234}\text{U})}{A(^{238}\text{U})} = 1 + [\gamma_o - 1] e^{-\lambda_{234}t} \quad (43)$$

### 10.2 The $^{230}\text{Th}$ method

Ingrowth equation:

$$A(^{230}\text{Th}) = A(^{230}\text{Th})_o e^{-\lambda_{230}t} + A(^{238}\text{U})(1 - e^{-\lambda_{230}t}) \quad (44)$$

Isochron equation:

$$\frac{A(^{230}\text{Th})}{A(^{232}\text{Th})} = \frac{A(^{230}\text{Th})_o}{A(^{232}\text{Th})} e^{-\lambda_{230}t} + \frac{A(^{238}\text{U})}{A(^{232}\text{Th})} (1 - e^{-\lambda_{230}t}) \quad (45)$$

### 10.3 The $^{230}\text{Th}$ -U method

Decay series:

$$A(^{230}\text{Th}) = A(^{230}\text{Th})^s + A(^{230}\text{Th})^x \quad (46)$$

$$\text{with: } A(^{230}\text{Th})^s = A(^{238}\text{U})(1 - e^{-\lambda_{230}t}) \quad (47)$$

$$\text{and: } A(^{230}\text{Th})^x = \frac{\lambda_{230}}{\lambda_{230} - \lambda_{234}} A(^{234}\text{U})_o^x (e^{-\lambda_{234}t} - e^{-\lambda_{230}t}) \quad (48)$$

Age equation:

$$\frac{A(^{230}\text{Th})}{A(^{238}\text{U})} = 1 - e^{-\lambda_{230}t} + \frac{\lambda_{230}}{\lambda_{230} - \lambda_{234}} (\gamma_o - 1) (e^{-\lambda_{234}t} - e^{-\lambda_{230}t}) \quad (49)$$

If  $\gamma_o = 1$ :

$$\frac{A(^{230}\text{Th})}{A(^{238}\text{U})} = 1 - e^{-\lambda_{230}t} \quad (50)$$

## 11 Error propagation

### 11.1 Basic definitions

Mean:

$$\begin{cases} \bar{x} \equiv \frac{1}{n} \sum_{i=1}^n x_i \\ \bar{y} \equiv \frac{1}{n} \sum_{i=1}^n y_i \end{cases} \quad (51)$$

Variance:

$$\begin{cases} s[x]^2 \equiv \frac{1}{n-1} \sum_{i=1}^n (x_i - \bar{x})^2 \\ s[y]^2 \equiv \frac{1}{n-1} \sum_{i=1}^n (y_i - \bar{y})^2 \end{cases} \quad (52)$$

Covariance:

$$s[x,y] \equiv \frac{1}{n-1} \sum_{i=1}^n (x_i - \bar{x})(y_i - \bar{y}) \quad (53)$$

General equation for the error propagation of a function  $t = f(x,y)$ :

$$s[t]^2 s[x]^2 \left( \frac{\partial f}{\partial x} \right)^2 + s[y]^2 \left( \frac{\partial f}{\partial y} \right)^2 + 2 s[x,y] \frac{\partial f}{\partial x} \frac{\partial f}{\partial y} \quad (54)$$

In matrix form:

$$s[t]^2 = \begin{bmatrix} \frac{\partial t}{\partial x} & \frac{\partial t}{\partial y} \end{bmatrix} \begin{bmatrix} s[x]^2 & s[x,y] \\ s[x,y] & s[y]^2 \end{bmatrix} \begin{bmatrix} \frac{\partial t}{\partial x} \\ \frac{\partial t}{\partial y} \end{bmatrix} \quad (55)$$

### 11.2 Examples

Let  $x$  and  $y$  indicate measured quantities associated with analytical uncertainty. And let  $a$  and  $b$  be some error free parameters.

1. addition ( $t = ax + by$ ):

$$s[t]^2 = a^2 s[x]^2 + b^2 s[y]^2 + 2ab s[x,y] \quad (56)$$

2. subtraction ( $t = ax - by$ ):

$$s[t]^2 = a^2 s[x]^2 + b^2 s[y]^2 - 2ab s[x,y] \quad (57)$$

3. multiplication ( $t = axy$ ):

$$\left( \frac{s[t]}{t} \right)^2 = \left( \frac{s[x]}{x} \right)^2 + \left( \frac{s[y]}{y} \right)^2 + 2 \frac{s[x,y]}{xy} \quad (58)$$

4. division ( $t = a \frac{x}{y}$ ):

$$\left( \frac{s[t]}{t} \right)^2 = \left( \frac{s[x]}{x} \right)^2 + \left( \frac{s[y]}{y} \right)^2 - 2 \frac{s[x,y]}{xy} \quad (59)$$

5. exponentiation ( $t = a e^{bx}$ ):

$$s[t]^2 = (bt)^2 s[x]^2 \quad (60)$$

6. logarithms ( $t = a \ln(bx)$ ):

$$s[t]^2 = a^2 \left( \frac{s[x]}{x} \right)^2 \quad (61)$$

7. power ( $t = ax^b$ ):

$$\left( \frac{s[t]}{t} \right)^2 = b^2 \left( \frac{s[x]}{x} \right)^2 \quad (62)$$

### 11.3 Standard error of the mean

If  $cov(x_i, x_j) = 0 \forall i, j$ :

$$s[\bar{x}]^2 = \frac{1}{n^2} \sum_{i=1}^n s[x_i]^2 = \frac{s[x]^2}{n} \Rightarrow s[\bar{x}] = \frac{s[x]}{\sqrt{n}} \quad (63)$$

### 11.4 Poissonian counting statistics

$$s[N]^2 = N \quad (64)$$