

Report

NPL REPORT AS 42

**GravCalc2 (version 2.3.0)
User Guide**

User Guide version 1

Andrew Brown

NOT RESTRICTED

June 2009

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EXECUTIVE SUMMARY

This report acts as a user guide for version 2.3.0 of GravCalc2, an NPL-developed Windows-based software program that calculates the amount fraction and uncertainty of all components in gravimetrically prepared gas mixtures using the method outlined in the International Standard ISO 6142. Detailed instructions for the installation, set-up and operation of the program are provided.

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National Physical Laboratory
Hampton Road, Teddington, Middlesex, TW11 0LW

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by Mr Alan Brewin, Business Leader, Analytical Science Team

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1. INTRODUCTION

1.1. Scope of GravCalc2 (version 2.3.0)

GravCalc2 is a software program designed to calculate the amount fraction and uncertainty of all components in a gravimetrically-prepared gas mixture, using the method outlined in the International Standard ISO 6142 [1].

The ISO 6142 method determines the amount fraction and uncertainty of each component given knowledge of:

- The mass of each component added to the mixture, and its uncertainty.
- The purity of each component, and the uncertainty of the purity analysis.
- The relative molar mass of each species, and its uncertainty.

1.2. Structure of GravCalc2

The program consists of two parts:

- *Planning stage.* The Planning stage of the program allows the user to plan the preparation of 'binary' (two-component) mixtures.
 - Planning stage 1 calculates the mass of each component required to prepare a mixture of a known amount fraction.
 - Planning stage 2 allows the uncertainty in the amount fraction of the minor component in the final mixture to be estimated.
- *Calculation stage.* This Calculation stage is the main part of the program and allows the user to calculate the composition and uncertainty of any binary or multi-component mixture in accordance with ISO 6142.

1.3. A note on uncertainties

It is critical that the uncertainties in mass, purity analysis and relative molar mass input into GravCalc2 are all stated to the same level of confidence. The uncertainties in amount fractions calculated by the program for the mixture being prepared will then be reported at this same level of confidence.

It is recommended that standard ($k = 1$) uncertainties are used throughout. The standard uncertainties in amount fractions calculated by the program can then be converted into expanded uncertainties through multiplication by a coverage factor of $k = 2$, thus providing a level of confidence of approximately 95 %.

2. INSTALLATION

Copy the contents of the Setup folder to a suitable location on the hard drive of the PC on which GravCalc2 is to be run. Open the folder and double click on setup.exe to start installation and follow the on-screen instructions.

Upon completion of installation, the GravCalc2 executable file (gravcalc.exe) and a file used to specify the defaults settings of the program (defaults.ini) will be copied to C:\Program Files\GravCalc. GravCalc2 can subsequently be run from any directory that contains these files.

3. FILES

Once installed, the following files are present

- Gravcalc.exe – see Section 3.1
- Defaults.ini – see Section 3.2

Examples of the following files are also provided with the software, but the user should create new files specific to their application:

- Molecular mass file (molmass.dat) – see Section 3.3
- Purity analysis files (<name>.txt) – see Section 3.4
- Ordering templates (<name>.txt) – see Section 3.5

The program generates the following files automatically when the composition of a mixture is calculated:

- Results file (<name>.res) – see Section 3.6
- File for subsequent use by GravCalc2 (<name>.txt) – see Section 3.7

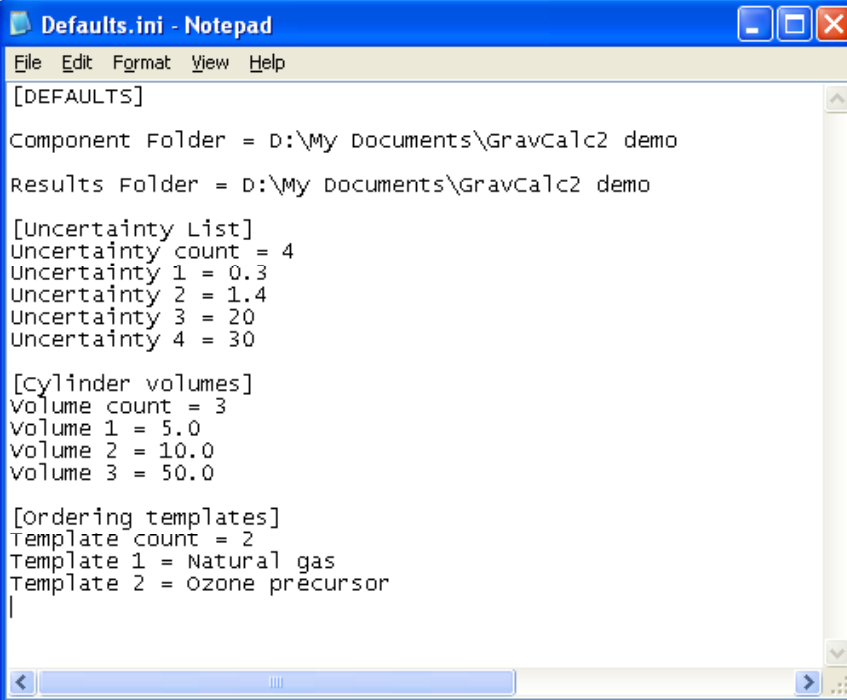
Each of these are discussed in turn below:

3.1. Gravcalc.exe

Gravcalc.exe is the program executable file. Double-click this file to run the program.

3.2. Defaults.ini

The defaults.ini file allows the user to specify where the files required to run the program are stored, and also to customise the options that appear in the drop-down menus when operating the program. An example file is given below:



```

File Edit Format View Help
[DEFAULTS]
(a) → Component Folder = D:\My Documents\GravCalc2 demo
(b) → Results Folder = D:\My Documents\GravCalc2 demo
[Uncertainty List]
(c) → Uncertainty count = 4
      Uncertainty 1 = 0.3
      Uncertainty 2 = 1.4
      Uncertainty 3 = 20
      Uncertainty 4 = 30
[Cylinder volumes]
(d) → Volume count = 3
      Volume 1 = 5.0
      Volume 2 = 10.0
      Volume 3 = 50.0
[Ordering templates]
(e) → Template count = 2
      Template 1 = Natural gas
      Template 2 = Ozone precursor
|

```

To setup and customise GravCalc2, modify the follow parts of the defaults.ini file:

- (a) Specifies the directory where the files needed to operate the program (gravcalc.exe, defaults.ini, molmass.dat, purity analysis files and ordering templates) are stored.
- (b) Specifies the directory where the results files are stored. It is recommended that this is the same as the directory specified in (a).
- (c) Specifies the number of gravimetric uncertainty options that will appear in the drop-down lists when running the program. The lines immediately beneath can be edited, added to or deleted to customise the values (*in milligrams*) that appear in these drop-down lists.
- (d) Specifies the number of cylinder volume options that will appear in the drop-down lists when running the program. The lines immediately beneath can be edited, added to or deleted to customise the values (*in litres*) that appear in these drop-down lists.
- (e) Specifies the number of ordering template options that will appear in the drop-down lists when running the program. The lines immediately beneath can be edited, added to or deleted to customise the names of the ordering templates that can be selected.

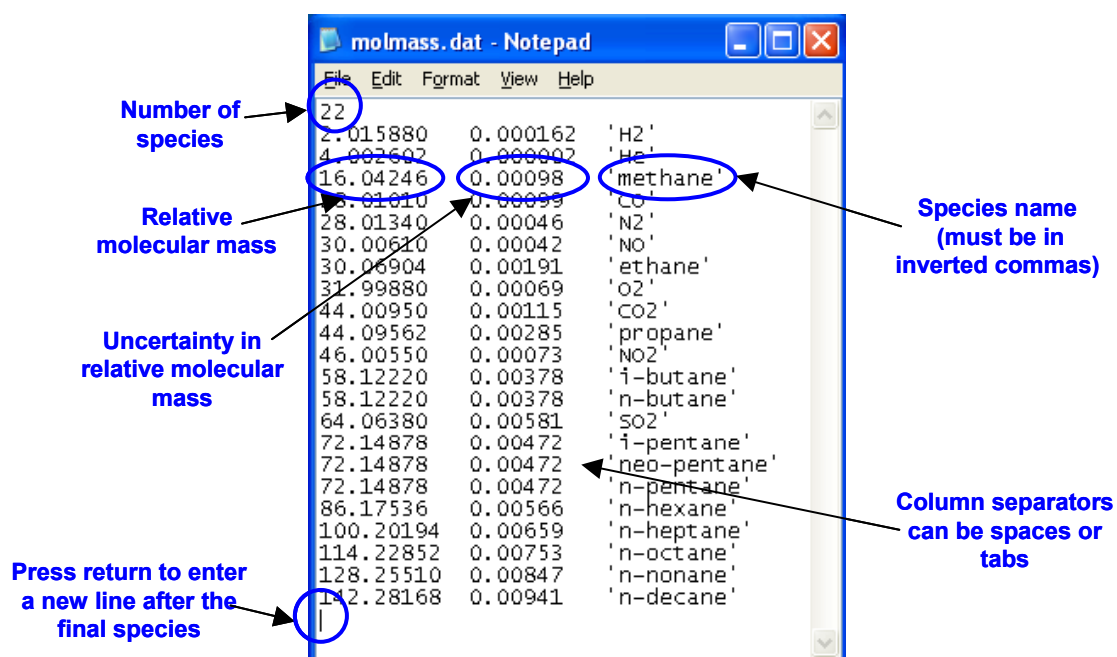
3.3. Molecular mass file (molmass.dat)

The molmass.dat file contains:

- An abbreviated name for each species (which must not include spaces).
- The molecular mass (or atomic mass) of each species, in atomic mass units.
- The uncertainty in the molecular mass (or atomic mass) of each species, in atomic mass units (see the note on uncertainty in section 3.8).

The molecular mass (or atomic mass), and uncertainty in molecular mass (or atomic mass) of each species should either be taken from the most recent version of ISO 14912 [2], or calculated from first principles using the most recent version of IUPAC's 'Atomic Weights of the Elements' [3].

An example molmass.dat file is shown below. The format of the file must be identical to that shown – note in particular the issues highlighted. The molmass.dat file can contain a maximum of 300 species.



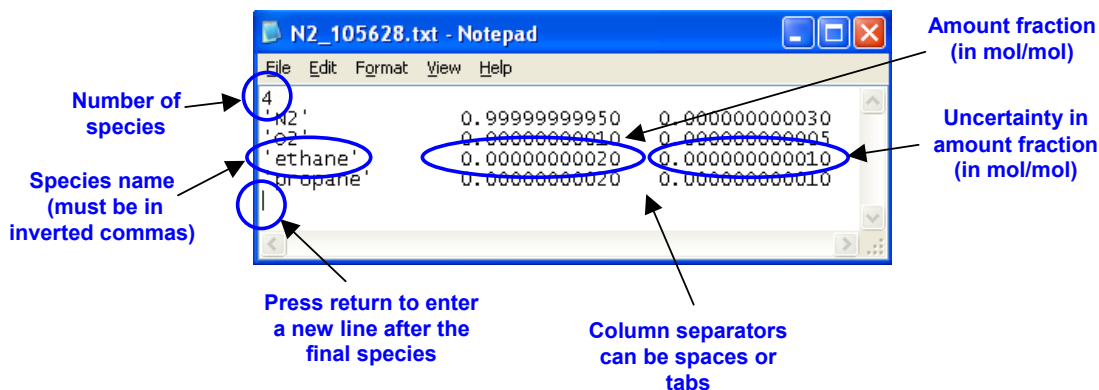
3.4. Purity analysis files (<name>.txt)

In order to be compliant with ISO 6142, every 'pure' component (gas or liquid) used to prepare a mixture should be purity analysed. The results of these analyses are stored in purity analysis files. Each file should be given a unique name (which must not include spaces) and it is recommended that these names have some traceability to the cylinder or bottle from which the 'pure' gas or liquid was taken.

Each purity analysis file contains:

- The abbreviated name for each species. This name must be identical to that in the molmass.dat file
- The mass fraction of each species, *in mol/mol*
- The uncertainty in the mass fraction of each species, *in mol/mol* (see the note on uncertainty in section 1.3).

An example purity file is shown below. The format of the file must be identical to that shown – note in particular the issues highlighted.

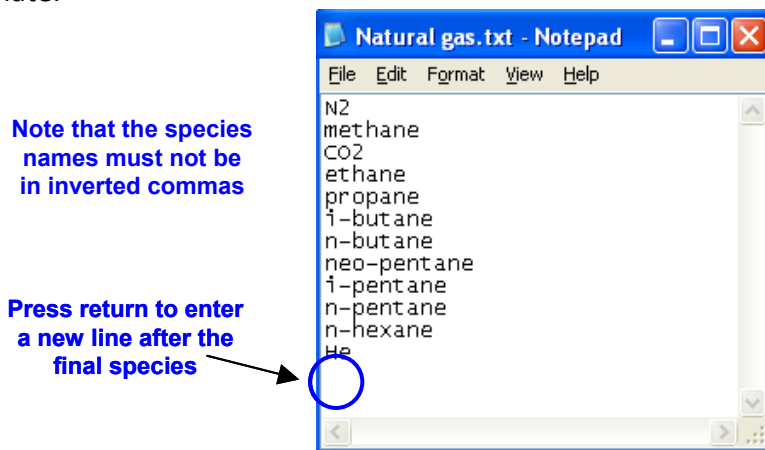


3.5. Ordering templates

Ordering templates are used to specify the order in which the species are listed in results files (see Section 3.6). The use of ordering templates is particularly beneficial when the result produced by GravCalc2 are required to be copied and pasted into a spreadsheet or other program in a specific order.

The files are simply a list of the abbreviated name for each species (these must be identical to that in the molmass.dat file).

An example ordering template is shown below. Note that any other species present in the final mixture will be listed in order of decreasing amount fraction after those in the ordering template.



3.6. Results files (<name>.res)

The program automatically generates a result files for each mixture calculated. The name of the file (which must not include spaces), is assigned automatically using the input to the 'cylinder number' field in the Calculation stage of the program (see Section 6). An example of a results file is given in Section 6.2.

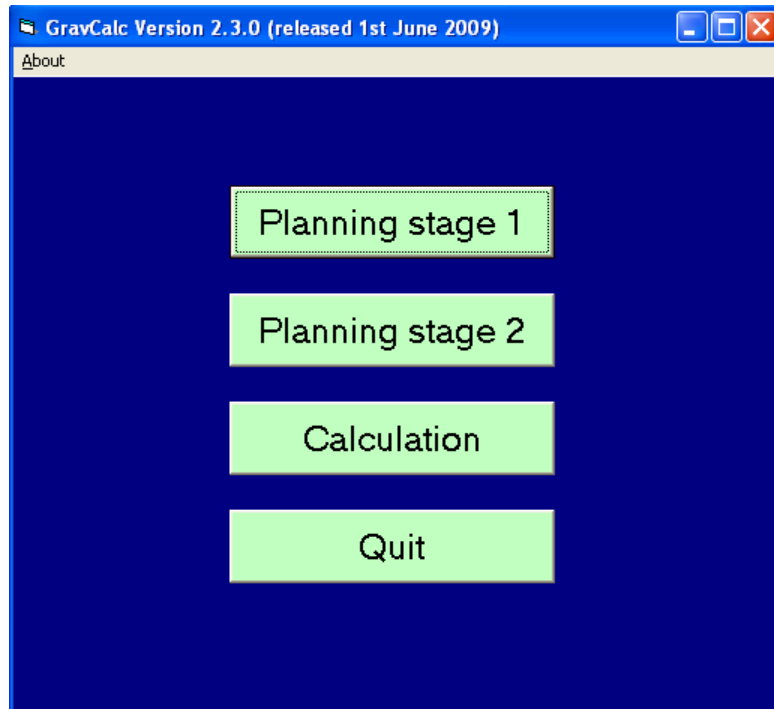
3.7. .txt files for subsequent use by GravCalc2

In addition to the results files, the program also creates a second file, with the same name as the results file, but with a .txt suffix. The program uses this file if the gas mixture is subsequently used as a 'parent' mixture when preparing another gas mixture. The format of each of these files is exactly the same as the format of the purity analysis files – an example is given in Section 6.2.

4. OPERATION OF GRAVCALC2

To run the program, double-click the gravcalc.exe file.

The following main menu window is displayed. The Planning stage of the program is described in Section 5, and the Calculation stage in Section 6.



5. PLANNING STAGE

The Planning stage of GravCalc2 can be used to plan the preparation of 'binary' (two-component) mixtures only.

Planning stage 1 allows the user to determine the mass of each component required to prepare the required gas mixture. Planning stage 2 allows the uncertainty in the amount fraction of the minor component to be estimated.

5.1. Planning stage 1

Planning stage 1 allows the user to determine how to prepare a binary mixture of a known amount fraction if one of the following three pieces of information is known:

- The mass of the target (minor) component to be added to the mixture.
- The mass of the major component to be added to the mixture.
- The final pressure of the mixture.

To run, Press the 'Planning stage 1' button. In the window that appears:

- Click on 'Target component cylinder'. Select the appropriate file by using the mouse or typing in the file name.
- Click on 'Major component cylinder'. Select the appropriate file by using the mouse or typing in the file name.
- Select the target (minor) component from the drop-down list. The background will change to green once a valid component has been selected.
- Enter the target amount fraction *in $\mu\text{mol/mol}$ (ppm)*.
- Enter the cylinder volume *in litres*.
- Input one of the three other values shown (target component mass, major component mass or pressure).
- Press 'process'.

An example calculation for a 10 % mol/mol (100,000 $\mu\text{mol/mol}$) carbon dioxide in nitrogen mixture in a 10 litre cylinder is given below. (The 'process' button has just been pressed):

GravCalc Version 2.3.0 (released 1st June 2009)

GRAV CALC - PLANNING STAGE 1

MANDATORY INFORMATION

Target component cylinder: CO2_707215.txt
 Major component cylinder: N2_105628.txt
 Target: CO2
 Target concentration (ppm): 100000
 Cylinder volume (l): 10

INPUT ONE OF:

Target component mass (g): 183.3729
 Major component mass (g): 1050.502
 Pressure (bar): 100.0

CLEAR
PROCESS

Transfer data to planning stage 2

Print Quit

Once the calculation has been carried out, press:

- 'Print' to send the information to the default printer.
- 'Transfer data to Planning stage 2' to start Planning stage 2 (which allows the uncertainty in the amount fraction of the minor component to be estimated).
- 'Quit' to return to the main menu.

5.2. Planning stage 2

Planning stage 2 can be run from the main menu, or by automatically transferring data from Planning stage 1 (see Section 5.1). In the window that appears:

- Click on 'Target component cylinder'. Select the appropriate file by using the mouse or typing in the file name.
- Click on 'Major component cylinder'. Select the appropriate file by using the mouse or typing in the file name.
- Enter the mass of the target and major components *in grams*.
- Select the target (minor) component from the drop-down list. The background will change to green once a valid component has been selected.
- Enter the cylinder volume *in litres*.

[The above five values will be entered automatically if transferring data from Planning stage 1]

- Enter the uncertainty in the mass of the target and major components *in milligrams* by selecting from the drop-down list, or typing in any other value.
- Press 'Process'.

An example is give for the data produced in Section 5.1, using an uncertainty of 30 mg in the mass added for both components. The 'process' button has just been pressed:

MANDATORY INFORMATION

	Mass (g)	u/c (mg)	Target component
Target component cylinder CO2_707215.txt	183.3729	30	CO2
Major component cylinder N2_105628.txt	1050.502	30	
Cylinder volume (l):	10		

CLEAR **PROCESS**

CALCULATED DATA

Target component	Conc (ppm)	u/c (ppm)	% u/c	pressure (bar)
CO2	99999.999	14.947	0.015	100.0

Print **Quit**

Once the calculation has been carried out, press:

- 'Print' to send the information to the default printer.
- 'Quit' to return to the main menu.

6. CALCULATION STAGE

6.1. Instructions

The Calculation stage of GravCalc2 is the main part of the program and allows the user to calculate the composition and uncertainty of *any binary or multi-component mixture* in accordance with ISO 6142.

To run, press the 'Calculation' button in the main menu. In the window that appears, complete the following fields:

- Cylinder ID (the identification number of the cylinder in which the mixture has been prepared). Note that this must not be the same as for a cylinder ID previously used, and must not contain spaces. The program uses the value entered in the field to name the out put files (*e.g.* entering '227750' here will result in the two output files being named '227750.res' and '227750.txt').
- Operator (the name of the person using the program).
- Made by (the name of the person who prepared the mixture).
- No of components (the number of components added to the mixture).
- Lab book.

Once information has been entered into *all* of these five fields, the bottom half of the window becomes visible. Repeat the following process for each component added to the mixture:

- Click on 'Select component x of y' and select the relevant component file by using the mouse or typing in the file name.
- Enter the mass of component x *in grams*.
- Enter the uncertainty in the mass of component y *in milligrams* by selecting from the drop-down list, or typing in any other value.
- Press 'Set in component x'.

If any data has been entered incorrectly, take the following corrective action:

- To delete a component, click on that component entry as shown in the rectangular box and press 'Delete component x'.
- To change the mass and/or uncertainty in mass of a component, click on that component entry as shown in the rectangular box, re-enter the mass of component and uncertainty in the mass of component, and press 'Set in component x'.

Once all the data for all components has been entered correctly:

- Select the ordering template required. The default option is 'Concentration order' which lists the species in the results file in order of decreasing amount fraction. (For details about ordering templates, see Section 3.5.).
- Press 'Process'.

If processing has been unsuccessful, a pop-up window will appear confirming this, and the program will automatically generate a results file (see Section 3.6) and a .txt file for

subsequent use by the program (see Sections 3.7). Examples of these files are given in Section 6.2.

If for any reason processing has been successful, a pop-up window will appear with an error message indicating the nature of the problem.

An example screenshot is given below (just before the 'Process' button is to be pressed) for a mixture prepared using the target values calculated in the Planning stage 1 (Section 5.1). The components added were:

- Carbon dioxide, cylinder 707215, mass (183.315 ± 0.030) g
- Nitrogen, cylinder 105628, mass (1050.891 ± 0.030) g

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GRAV CALC - CALCULATION

Cylinder ID: Operator: Made by:

No. of components: Lab book:

Mass added (g) Uncertainty (mg)

Component	Mass (g)	Uncertainty (mg)
1 CO2_707215.txt	183.315000	30.000
2 N2_105628.txt	1050.89100	30.000

Ordering template
 Concentration order
 Natural gas
 Ozone precursor

6.2. Output files

The two files produced by the program for the above example are shown below:

Results (.res) file:

GravCalc Version 2.3.0

Gravimetric composition of cylinder 272250

User-entered information

Date: 02/06/2009
 Time: 10:10:20
 Operator: ASB Mixture prepared by: ASB
 Lab book: 27

Calculated results

Component	umol/mol	uncertainty	% u/c
N2	900061.6896	14.98016112	0.002
CO2	99938.29499	14.98015673	0.015
CO	0.00999383	0.00299815	30.000
O2	0.00508692	0.00249846	49.115
ethane	0.00018001	0.00000900	5.000
propane	0.00018001	0.00000900	5.000

Component cylinders, masses and uncertainties

File	Mass (g)	u/c (g)
CO2_707215.txt	183.3150	0.03000
N2_105628.txt	1050.891	0.00030

Full details of the input data files used

INPUT DATA FILES

***** CO2_707215.txt *****

Component	mol/mol	uncertainty
CO	0.0000001000	0.0000000300
CO2	0.9999998000	0.0000000800
N2	0.0000000500	0.0000000250
O2	0.0000000500	0.0000000250

.txt file:

6

'N2'	0.90006168956885	0.00001498016112
'CO2'	0.09993829499037	0.00001498015673
'CO'	0.00000000999383	0.00000000299815
'O2'	0.00000000508692	0.00000000249846
'ethane'	0.00000000018001	0.00000000000900
'propane'	0.00000000018001	0.00000000000900

7. HELP & FURTHER INFORMATION

If any problems are experienced during the operation of GravCalc2, or if any further information is required, please contact gases@npl.co.uk or +44 (0) 20 8943 6372.

8. REFERENCES

- [1] ISO 6142:2006, *Gas analysis - Preparation of calibration gas mixtures - Gravimetric method.*
- [2] ISO 14912:2003, *Gas analysis - Conversion of gas mixture composition data.* *
- [3] M. E. Wieser, Atomic Weights of the Elements 2005, *Pure Appl. Chem.*, 2006, 78, 2051-2066. *

* indicates that these are the most recent versions of these documents at the time of publication.

ANNEX A - EQUATIONS USED BY GRAV CALC2

A.1. Planning stage 1

$$x_i = \frac{x_{i1}n_1 + x_{i2}n_2}{n_1 + n_2}$$

$$N = n_1 + n_2 \quad \text{where} \quad n_1 = \frac{m_1}{M_1}, \quad n_2 = \frac{m_2}{M_2} \quad \text{and} \quad N = \frac{PV}{RT} = \frac{PV}{24} \quad (\text{assuming } 22^\circ\text{C})$$

Where:

x_i = amount fraction of required (minor) component in the final mixture

x_{i1} = amount fraction of required (minor) component in mixture 1

x_{i2} = amount fraction of required (minor) component in mixture 2

n_1 = total number of moles from mixture 1

n_2 = total number of moles from mixture 2

N = total number of moles in the final mixture

m_1 = mass of mixture 1

m_2 = mass of mixture 2

M_1 = (average) relative molar mass of total mixture 1 [$M_1 = \sum_{i=1}^n x^i M^i$]

M_2 = (average) relative molar mass of total mixture 2 [$M_2 = \sum_{i=1}^n x^i M^i$]

M^i = relative molar mass of species i

x^i = amount fraction of species i

P = pressure of final mixture (bar)

V = Volume of cylinder containing final mixture (litres)

Planning stage 1 requires one of the three inputs m_1 , m_2 or P . In all three cases, x_i , x_{i1} , and x_{i2} are given.

Case One - given m_1 , calculate m_2 and P : $n_2 = n_1 \frac{x_{i1} - x_i}{x_i - x_{i2}}$ and $P = \frac{24N}{V}$

Case Two - given m_2 , calculate m_1 and P : $n_1 = n_2 \frac{x_{i2} - x_i}{x_i - x_{i1}}$ and $P = \frac{24N}{V}$

Case Three - given P , calculate m_1 and m_2 : $n_1 = N \frac{x_i - x_{i2}}{x_{i1} - x_{i2}}$ and $n_2 = N \frac{x_i - x_{i1}}{x_{i2} - x_{i1}}$

A.2. Planning stage 2

Amount fraction:
$$x_i = \frac{x_{i1}n_1 + x_{i2}n_2}{n_1 + n_2}$$

Pressure:
$$P = \frac{24N}{V}$$

Uncertainty in amount fraction: †

$$dx_i^2 = \left(\frac{\partial x_i}{\partial m_1} dm_1 \right)^2 + \left(\frac{\partial x_i}{\partial m_2} dm_2 \right)^2 + \left(\frac{\partial x_i}{\partial x_{i1}} dx_{i1} \right)^2 + \left(\frac{\partial x_i}{\partial x_{i2}} dx_{i2} \right)^2$$

$$\therefore dx_i^2 = \left(\frac{n_1 n_2 (x_{i1} - x_{i2})}{m_1 (n_1 + n_2)^2} dm_1 \right)^2 + \left(\frac{n_1 n_2 (x_{i2} - x_{i1})}{m_2 (n_1 + n_2)^2} dm_2 \right)^2 + \left(\frac{n_1}{n_1 + n_2} dx_{i1} \right)^2 + \left(\frac{n_2}{n_1 + n_2} dx_{i2} \right)^2$$

† Note that this equation is derived assuming that $u(M) = 0$. Although values of $u(M)/M$ are generally very small, this is a simplification and this equation is only used in the Planning stage, where only approximate data are required

A.3. Calculation stage

Amount fraction of each species:

$$y_k = \frac{\sum_{j=1}^n \frac{m_j y_{k,j}}{\sum_{i \in I(j)} y_{i,j} M_i}}{\sum_{j=1}^n \frac{m_j}{\sum_{i \in I(j)} y_{i,j} M_i}}$$

Where:

y_k = amount fraction of component k

m_j = mass taken from parent cylinder j

$y_{k,j}$ = amount fraction of component k in parent cylinder j

$y_{i,j}$ = amount fraction of component i from parent cylinder j

M_i = relative molar mass of component i

$I_{i,j}$ = indices of those components in parent cylinder j

n = number of parent cylinders

Uncertainty in amount fraction of each species:

$$dy_k = \left[\sum_{j=1}^n \left(\frac{\partial y_k}{\partial m_j} dm_j \right)^2 + \sum_{i=1}^G \left(\frac{\partial y_k}{\partial M_i} dM_i \right)^2 + \sum_{j=1}^n \sum_{i=1}^G \left(\frac{\partial y_k}{\partial y_{i,j}} dy_{i,j} \right)^2 \right]^{1/2}$$

Where:

dM_i = standard uncertainty in the relative molar mass of component i

dm_j = standard uncertainty in the mass taken from parent cylinder j

$dy_{i,j}$ = standard uncertainty in the amount fraction of component i in parent cylinder j

G = number of components