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A MODIFIED FORTRAN IV PROGRAM FOR GAS PHASE
RADIOLYSIS DATA REDUCTION

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A MODIFIED FORTRAN IV PROGRAM FOR GAS PHASE RADIOLYSIS DATA REDUCTION

George J. Werkema

Abstract. This program is a modification of one written earlier (USAEC Report RFP-624, Rocky Flats Division, The Dow Chemical Co., November 1965) for a small computer. The availability of a computer having a medium-to-large memory permits various improvements to be made in operating convenience. The present version, RADF-2, is written in E-level FORTRAN IV for the IBM 360/40G computer. The RADF-2 program converts analytical data obtained at several times during a gas phase radiolysis experiment into the molar and molecular quantities which may be plotted or further reduced to "G" values. The computed results are output in tabular form for each gas, along with the computed radiation dose, as a function of time.

INTRODUCTION

Although the algorithm for the reduction of gas analysis data is trivial, it is a tedious and time-consuming exercise, and is quite subject to errors. For accurate work, accounting for the small amounts of gas that are removed with each sampling increases the complexity of the arithmetic. The RADF* computer code, and the present modification, RADF-2, were written to reduce analytical data arising from gas phase radiolysis experiments.

This computer code implies few experimental qualifications. It is assumed that the radiolytic reaction takes place in a constant, sealed volume, and that small samples of the gaseous reaction mixture are periodically withdrawn for analysis. The results of the chemical analysis are dimensioned in volume percentages of each gas, which are input to the RADF-2 program. For chemical kinetics studies, it is necessary to know the total quantity of each gas present at each sampling time, which is equal to the measured quantity at each time plus the amount of each gas removed in all previous samplings. RADF-2 provides this sample accounting feature, and all calculated gas quantities are the sum of the current quantity plus the past sample quantities for each gas.

It is also useful to know the amount of radiation to which the reaction mixture has been exposed at each

sampling period. RADF-2 computes radiation dose as a function of elapsed time for each sampling. The user may choose between two dose calculation options. One option is based on an exponential source decay, and the other assumes a constant dose rate.

MATHEMATICAL METHODS

The total number of moles of all gases in the reaction vessel at some time (t_j) is computed using the equation of state of an ideal gas:

$$n_j = \frac{P_j V}{RT_j}$$

The number of moles of each gas ($n_{j,i}$) is computed from the expression

$$n_{j,i} = n_j \cdot \left(\frac{V_i}{V} \right)_j$$

where $\left(\frac{V_i}{V} \right)_j$ is the volume fraction of gas (i) in the reaction at some time (t_j). Next, the number of moles of each gas ($S_{j,i}$) in the sample volume (V_s) is given by

$$S_{j,i} = n_{j,i} \cdot \frac{V_s}{V}$$

Finally, the total number of moles of each gas ($N_{j,i}$) is:

$$N_{j,i} = n_{j,i} + \sum_1^j S_{j,i}$$

The number of molecules of each gas ($M_{j,i}$) is obtained by multiplying $N_{j,i}$ by Avogadro's number. The change in molecular population from zero time is given by

$$\Delta M_{j,i} = M_{j,i} - M_{1,i}$$

where $M_{1,i}$ is the initial population of gas (i).

The computation of accumulated radiation dose is similarly direct. For an exponentially decaying source, the dose accumulated at some time (t_j) is given by

$$(\text{DOSE})_j = \frac{A_0 \bar{E}}{\lambda} \cdot C [1 - \exp(-\lambda t_j)]$$

*RADF - Abbreviation for RADiOLYSIS FORTRAN.

where

A_0 = activity of source at the start of the experiment (curies),

$\bar{E}$ = average energy of source emission (MeV),

λ = decay constant for source = $\log_e 2/t_{1/2}$ (hr^{-1}),

t_j = elapsed time from the beginning of the experiment to the j th sampling (hours), and

C = 1.332×10^{20} which is an internal constant used to dimension DOSE in electron volts.

Alternatively, the value of $(\text{DOSE})_j$ when a constant activity source is used is simply the product of the source activity and time (t_j). The dose rate for a constant activity source is input to the program in the λ data field. Blank data fields for A_0 and $\bar{E}$ signal the program to use the constant source routine for the calculation of $(\text{DOSE})_j$.

The program calls one special library subroutine, EXP(a). This is normally available in most FORTRAN compiler libraries.

FORTRAN NOTATION FOR MATHEMATICAL SYMBOLS

Symbol	FORTRAN Label
t_j	TIME (J)
n_j	ALL
P_j	P
T_j	T
V	V
$n_{j,i}$ and $N_{j,i}$	GASMOL (J,I)
$\left(\frac{V_i}{V}\right)_j \cdot 100$	GASVP (I)
$\sum_1^j S_{j,i}$	SUMSAM (I)
V_s	SV
$(\text{DOSE})_j$	DOSE (J)
A_0	AZRO
$\bar{E}$	EBAR
λ	FLAM
number of gases, $1 \leq i \leq k$	I,K(I is running)

number of samples, $1 \leq j \leq L$	J,L(J is running)
$M_{j,i}$	AVOGAS (J,I)
$\Delta M_{j,i}$	DELMCL (J,I)
number of experiments	NJOB

INPUT

Card	Card Column	Data Required	Format
1	5-8	Number of experiments to be run	I4
2	5-68	TITLE, Alphanumeric information, e.g. experiment identification	I6A4
3	11-14	L-number of samples	I4
	15-18	K-number of gases	I4
	19-30	V-reaction vessel volume (cc.)	F12.6
	31-42	A_0 (curies)	F12.6
	43-54	$\bar{E}$ (MeV)	F12.6
	55-64	λ (hr^{-1}) Alternatively, the λ data field may be used to input the dose rate for a constant activity source if the A_0 and $\bar{E}$ data fields are blank.	E10.3
4	13-22	P_j - reaction pressure at time of sampling (mm.Hg)	F10.4
	23-32	T_j - temperature at time of sampling (deg. C)	F10.4
	33-42	V_s - sample volume (cc.)	F10.4
	43-52	t_j - elapsed time at which sample is taken (hrs.)	F10.4
5,6,7, . . . etc. for each of K gases in sample	13-20	Gas Formula	2A4
	21-28	Gas Volume percent	F8.4

Prepare one set of cards 4,5,6,7 . . . for each of the L samples. The total number of cards to be prepared is thus

$$3 + (1 + K) \cdot L.$$

The composition of a deck to process data from several experiments is illustrated in Figure 1. The sequence of gas formulae and data cards must be constant for all sample sets in one experiment.

OUTPUT

RADF-2 generates three tables of output. The identifying characters, "RAD", are printed at the top of the first

page. Each table is headed by a verbatim listing of the information in the TITLE input field. The first table lists micromolar quantities of each analyzed gas in the sample; the second table lists the number of molecules of the sample gases; and the third table lists the change in

molecular population from zero time. Column headings across the top of each table indicate TIME (= t_j), DOSE = (DOSE)_j, and the formulae for the analyzed gases. A sample of the output tables for ten gases analyzed six different times is shown on pages 7-9.

[illegible]

RAD
RADIOLYSIS DATA REDUCTION PROGRAM TEST

MICROMOLES OF GASES IN REACTION MIXTURE

TIME	DOSE	GAS 1	GAS 2	GAS 3	GAS 4	GAS 5	GAS 6	GAS 7	GAS 8
0.0	0.0	2.84E 01	8.53E 03	2.84E 01	0.0	0.0	7.09E 01	1.42E 01	1.32E 05
2.0000	3.16E 21	2.86E 01	8.59E 03	4.29E 01	1.43E 02	0.0	0.0	0.0	1.33E 05
4.0000	5.23E 21	4.27E 01	8.58E 03	2.86E 01	1.71E 02	0.0	0.0	0.0	1.33E 05
6.0000	6.60E 21	2.85E 01	8.61E 03	2.85E 01	1.99E 02	0.0	0.0	0.0	1.33E 05
8.0000	7.49E 21	4.25E 01	8.58E 03	2.85E 01	1.71E 02	0.0	0.0	0.0	1.33E 05
10.5000	8.19E 21	2.85E 01	8.62E 03	4.24E 01	1.56E 02	0.0	9.72E 01	2.78E 01	1.32E 05

RAD
RADIOLYSIS DATA REDUCTION PROGRAM TEST

MICROMOLES OF GASES IN REACTION MIXTURE

TIME	DOSE	GAS 9	GAS 10
0.0	0.0	8.09E 02	1.42E 01
2.0000	3.16E 21	6.86E 02	5.72E 01
4.0000	5.23E 21	6.42E 02	5.70E 01
6.0000	6.60E 21	5.98E 02	7.10E 01
8.0000	7.49E 21	5.70E 02	8.49E 01
10.5000	8.19E 21	5.41E 02	8.48E 01

Sample Output

RAD

RADIOLYSIS DATA REDUCTION PROGRAM TEST

MOLECULES OF GASES IN REACTION MIXTURE

TIME	DOSE	GAS 1	GAS 2	GAS 3	GAS 4	GAS 5	GAS 6	GAS 7	GAS 8
0.0	0.0	1.71E 19	5.14E 21	1.71E 19	0.0	0.0	4.27E 19	8.55E 18	7.97E 22
2.0000	3.16E 21	1.72E 19	5.17E 21	2.58E 19	8.61E 19	0.0	0.0	0.0	8.03E 22
4.0000	5.23E 21	2.57E 19	5.17E 21	1.72E 19	1.03E 20	0.0	0.0	0.0	8.01E 22
6.0000	6.60E 21	1.72E 19	5.18E 21	1.72E 19	1.20E 20	0.0	0.0	0.0	7.99E 22
8.0000	7.49E 21	2.56E 19	5.17E 21	1.72E 19	1.03E 20	0.0	0.0	0.0	7.99E 22
10.5000	8.19E 21	1.72E 19	5.19E 21	2.55E 19	9.42E 19	0.0	5.86E 19	1.67E 19	7.97E 22

RAD

RADIOLYSIS DATA REDUCTION PROGRAM TEST

MOLECULES OF GASES IN REACTION MIXTURE

TIME	DOSE	GAS 9	GAS 10
0.0	0.0	4.87E 20	8.55E 18
2.0000	3.16E 21	4.13E 20	3.44E 19
4.0000	5.23E 21	3.86E 20	3.43E 19
6.0000	6.60E 21	3.60E 20	4.28E 19
8.0000	7.49E 21	3.43E 20	5.11E 19
10.5000	8.19E 21	3.26E 20	5.11E 19

RAD

RADIOLYSIS DATA REDUCTION PROGRAM TEST

CHANGE IN MOLECULE POPULATION FROM ZERO TIME

TIME	DOSE		GAS 1	GAS 2	GAS 3	GAS 4	GAS 5	GAS 6	GAS 7	GAS 8
0.0	0.0		0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
2.0000	3.16E	21	1.23E 17	3.69E 19	8.73E 18	8.61E 19	0.0	-4.27E 19	-8.55E 18	5.81E 20
4.0000	5.23E	21	8.61E 18	3.14E 19	1.23E 17	1.03E 20	0.0	-4.27E 19	-8.55E 18	3.73E 20
6.0000	6.60E	21	9.55E 16	4.87E 19	9.59E 16	1.20E 20	0.0	-4.27E 19	-8.55E 18	2.12E 20
8.0000	7.49E	21	8.49E 18	3.38E 19	7.46E 16	1.03E 20	0.0	-4.27E 19	-8.55E 18	1.55E 20
10.5000	8.19E	21	1.02E 17	5.33E 19	8.42E 18	9.42E 19	0.0	1.58E 19	8.18E 18	-1.55E 19

RAD

RADIOLYSIS DATA REDUCTION PROGRAM TEST

CHANGE IN MOLECULE POPULATION FROM ZERO TIME

TIME	DOSE		GAS 9	GAS 10
0.0	0.0		0.0	0.0
2.0000	3.16E	21	-7.40E 19	2.59E 19
4.0000	5.23E	21	-1.01E 20	2.58E 19
6.0000	6.60E	21	-1.27E 20	3.42E 19
8.0000	7.49E	21	-1.44E 20	4.26E 19
10.5000	8.19E	21	-1.61E 20	4.25E 19

Program Listing

```

C  RADF  060166
      DIMENSION TITLE(16),DOSE(100),TIME(100),SUMSAM(16),GASVP(16)
      DIMENSION  LABL1(16),LABL2(16),GASMOL(100,16),AVOGAS(100,16),
1DELMCL(100,16)
2010  FORMAT(4X,16A4)
2101  FORMAT(4H1RAD)
      INPT = 1
      LIST = 3
      READ(INPT,2110) NJOB
2110  FORMAT(4X,I4)
      DO 110 JOB = 1,NJOB
      WRITE(LIST,2101)
21   READ(INPT,2010)TITLE
      READ(INPT,2011)L,K,V,AZRO,EBAR,FLAM
2011  FORMAT(10X,2I4,3F12.6,E10.3)
      TEN17 = 10.0**17
      AVNR = 6.023*TEN17
      AMPL = 1332.0*TEN17*AZRO*EBAR/FLAM
      DO 31 I = 1,K
31   SUMSAM(I) = 0.0
      DO 45 J=1,L
      READ(INPT,2013)P,T,SV,TIME(J)
2013  FORMAT(12X,4F10.4)
      ALL = (P*V)/(0.08205*76.0*(T+273.16))
      IF(EBAR)110,35,36
35   DOSE(J) = FLAM*TIME(J)
      GO TO 37
36   DOSE(J) = AMPL*(1.0-EXP(-FLAM*TIME(J)))
37   SBYV = SV/V
      DO 45 I = 1,K
      READ(INPT,2014)LABL1(I),LABL2(I),GASVP(I)
2014  FORMAT(12X,2A4,F8.4)
      GASMOL(J,I) = ALL*GASVP(I)
      IF(J-1) 43,43,42
42   SUMSAM(I) = SUMSAM(I) + SBYV*GASMOL(J,I)
      GASMOL(J,I) = GASMOL(J,I) + SUMSAM(I)
43   AVOGAS(J,I) = AVNR*GASMOL(J,I)
45   DELMCL(J,I) = AVOGAS(J,I) - AVOGAS(1,I)
      I1 = 1
      IF(K-8) 50,50,55
50   MK = K
      GO TO 60
55   MK = 8
60   WRITE(LIST,2010)TITLE
      WRITE(LIST,2015)
2015  FORMAT(40HOMICROMOLES OF GASES IN REACTION MIXTURE)
      WRITE(LIST,2016)(LABL1(I),LABL2(I),I = I1,MK)
2016  FORMAT(21H0      TIME      DOSE      ,8(2X,2A4))

```

```

DO 65 J = 1,L
65  WRITE(LIST,2116)TIME(J),DOSE(J),(GASMOL(J,I),I=I1,MK)
2116  FORMAT(1X,F10.4,1P9E10.2)
      IF(K-MK)222,70,66
66  MK = K
      I1 = 9
      WRITE(LIST,2101)
      GO TO 60
70  MK = K-8
      I1 = 1
      IF(MK)72,72,75
72  MK = K
      GO TO 80
75  MK = 8
80  WRITE(LIST,2101)
      WRITE(LIST,2010)TITLE
      WRITE(LIST,2017)
2017  FORMAT(39HOMOLECULES OF GASES IN REACTION MIXTURE)
      WRITE(LIST,2016)(LABL1(I),LABL2(I),I=I1,MK)
      DO 85 J = 1,L
85  WRITE(LIST,2116)TIME(J),DOSE(J),(AVOGAS(J,I),I = I1,MK)
      IF(K-MK)222,90,86
86  MK = K
      I1 = 9
      GO TO 80
90  I1 = 1
      IF(K-8)92,92,95
92  MK = K
      GO TO 100
95  MK = 8
100  WRITE(LIST,2101)
      WRITE(LIST,2010)TITLE
      WRITE(LIST,2122)
2122  FORMAT(45HCHANGE IN MOLECULE POPULATION FROM ZERO TIME)
      WRITE(LIST,2016)(LABL1(I),LABL2(I),I=I1,MK)
      DO 105 J = 1,L
105  WRITE(LIST,2116)TIME(J),DOSE(J),(DELMCL(J,I),I = I1,MK)
      IF (K-MK)222,110,106
106  MK = K
      I1 = 9
      GO TO 100
110  CONTINUE
222  CALL EXIT
      STOP
      END

```