

The Rachford-Rice Contest

If you're a student, here's your chance to win \$1000! At least the first three who outperform the Rachford-Rice algorithm of phantom-engineer Aaron Zick. Professionals who beat his routine win a box of Norwegian chocolates (plus having lots of fun competing).

Zick's algorithm is fast and "fail-safe" (within machine roundoff accuracy). At least that's what he claims. Well why doesn't he publish such a great algorithm? The simple truth is that he's a bit lazy. "Too bad," some say. "A bluff," others claim. So I decided to sponsor this little contest. As long as Aaron refuses to get off his butt and publish the algorithm, the best I can do is give "doubters" the chance to outperform his routine.

A few contest rules. Beating Zick's time is only part of the problem. You also have to make sure the answers are right -- and not just for the easily-obtained vapor (or liquid) fractions! All of the material balances that are represented by the Rachford-Rice equation must also be satisfied! And satisfied they must be to nearly machine accuracy (specifically, to within a factor of 10^{-15} of the correct, double-precision results). Keep in mind that you won't get the right answers by quitting prematurely on the tough problems (to lower your execution time). And if your routine crashes during any of the tests (overflow, divide by zero, etc.), then sorry, you lose.

If you don't want to send the source to your routine (cause we're not giving Zick's away), then you'll have to send in an object file using one of the following FORTRAN compilers for the PC (Lahey, Lahey-32 extended, Salford, or Microsoft Fortran); else Language Systems FORTRAN or Absoft F77 for the Power Mac.

You have until the end of 1995 to win the contest. You have the rest of your life to keep on trying (if you don't win this year). Note that Aaron's code contains about 110 lines. Results from his routine are available upon request (RRTEST.OUT and RRTEST.ERR files).

The Rachford-Rice Problem

Now for the specifics. If you don't know about the Rachford-Rice two-phase flash problem, here's a short summary. We have one mole of a multi-component mixture with molar composition z_i . A set of K -values, representing the ratio of equilibrium gas molar composition y_i to equilibrium oil composition x_i ($K_i = y_i/x_i$) are known. The question then, is what are the equilibrium molar compositions y_i and x_i , and how many moles of equilibrium vapor V and equilibrium liquid L make up the two-phase mixture.

The mathematics of the problem look like this:

$$z_i = V y_i + L x_i \quad , \quad i=1,\dots,N \quad (1)$$

$$1 = V + L \quad (2)$$

$$K_i = \frac{y_i}{x_i} \quad , \quad i=1,\dots,N \quad (3)$$

$$\sum_{i=1}^N z_i = \sum_{i=1}^N y_i = \sum_{i=1}^N x_i = 1 \quad (4)$$

In 1952, Rachford and Rice¹ (some years after Muskat and McDowell², 1949) showed that a very efficient way to solve this problem is to introduce the following relation,

$$\sum_{i=1}^N (y_i - x_i) = 0 \quad (5)$$

Combining the equations above leads to

$$f(V) = \sum_{i=1}^N \frac{z_i(K_i-1)}{1 + V(K_i-1)} = 0 \quad (6)$$

or as originally proposed by Muskat and McDowell,

$$f(V) = \sum_{i=1}^N \frac{z_i}{c_i + V} = 0 \quad (7)$$

where $c_i = 1/(K_i-1)$.

Physically, V and L should be bound by 0 to 1. Furthermore, $x_i > 0$ and $y_i > 0$. It has been shown that relaxing the physical bounds on V and L can be very useful (the "negative flash"), and thus we only retain the two physical limitations $x_i > 0$ and $y_i > 0$ in solving this mathematical problem. [If the results gives $V < 0$ or $V > 1$, then we can interpret this physically to mean that the overall mixture z_i doesn't want to split into two phases (i.e. it remains a single phase).]

Phase compositions y_i and x_i are calculated after solving $f(V)=0$,

$$x_i = \frac{z_i}{V(K_i-1) + 1} \quad \text{and} \quad y_i = K_i x_i \quad (8)$$

The FORTRAN Routine RRSOLV

You should write a self-contained FORTRAN routine with the following interface:

```
SUBROUTINE RRSOLV (NC,Z,EK,X,Y,FL,FV,NITER)
  INTEGER NC,NITER
  DOUBLE PRECISION Z(*),EK(*),X(*),Y(*),FL,FV
```

On input, this routine should pass the following information to RRSOLV:

NC = [N] Number of components. This will be between 2 and 50.
 Z(i) = [z_i] Mole fraction of component i. Z(i) will always be greater than or equal to 1.0E-30, and the sum of all Z(i) will always equal 1 (to within machine precision). The routine will not have to check these assumptions.
 EK(i) = [K_i] K-value of component i. EK(i) will always be between 1.0E-50 and 1.0E+50. At least one EK(i) will be greater than or equal to 1+ε_m (where ε_m is the machine epsilon), and at least one EK(i) will be less than or equal to 1-ε_m. The routine will not have to check these assumptions.
 FL = [L] Estimated liquid phase mole fraction.
 FV = [V] Estimated vapor phase mole fraction.

On output, this routine should return:

X(i) = [x_i] Mole fractions of components i in the liquid phase.
 Y(i) = [y_i] Mole fractions of components i in the vapor phase.
 FL = [L] Converged liquid phase mole fraction.

FV = [V] Converged vapor phase mole fraction.
 NITER = Number of iterations to converge solution (NITER>0);
 Non-converged solution, NITER = -maximum iterations.

RRSOLV should not change the values of NC, Z(I), or EK(I).

The test problem always uses phase fractions from the previous calculation as initial estimates for the next call to RRSOLV. This is only an advantage for some of the calculations. You should also be aware that the initial phase fraction estimates passed to RRSOLV may not always be within the range of valid phase fractions, thereby forcing the RRSOLV routine to come up with its own initial estimates.

Checking the Results

The computed results must satisfy the following equations to within the specified tolerances (where ϵ_t is the primary tolerance and ϵ_m is the machine epsilon):

1. $y_i > 0$
2. $x_i > 0$
3. $R_y = |1 - \sum_{i=1}^N y_i| \leq \epsilon_y = \epsilon_t + N \epsilon_m$
4. $R_x = |1 - \sum_{i=1}^N x_i| \leq \epsilon_x = \epsilon_t + N \epsilon_m$
5. $R_F = \frac{|L + V - 1|}{|L| + |V| + 1} \leq \epsilon_F = \epsilon_t$
6. $R_z = \max_i \left\{ \frac{|L x_i + V y_i - z_i|}{|L x_i| + |V y_i| + z_i} \right\} \leq \epsilon_z = \epsilon_t$
7. $R_K = \max_i \left\{ \frac{|(y_i - K_i x_i)|}{|y_i| + |K_i x_i|} \right\} \leq \epsilon_K = \epsilon_t$

These equations must be satisfied even if FL or FV turns out negative (i.e., a "negative flash"). FL and FV can range between $-1/\epsilon_m$ and $+1/\epsilon_m$, and all results must be valid over that entire range.

A quantity call "severity" is used to quantify each residual, relative to its absolute tolerance: severity = $\log_{10}(R/\epsilon)$. A positive severity indicates an error, i.e. a calculation that hasn't been made with sufficient accuracy to satisfy its tolerance. Calculations that are within their tolerances will have negative (or zero) severities. If you want to compete with Zick's routine on this Test Problem, your severities should never be positive.

RRSOLV should be designed to work for $\epsilon_t=10^{-15}$ on a processor using IEEE Standard 754 double-precision floating-point arithmetic (where $\epsilon_m=2.2 \cdot 10^{-16}$).

Test Problem

The test problem consists of 13504 test calculations. The main program sets up the tests and calls RRTEST to administrate them. RRTEST calls RRSOLV.

The test mixtures consist of normal paraffin hydrocarbons with carbon numbers ranging consecutively from 1 to N, with N=5,50(5). Physical properties are estimated from the Twu³

and Lee-Kesler⁴ correlations. A simple K-value equation (that exhibits the most important characteristics of K-values for a real system) is the modified Wilson equation,⁵

$$K_i = \left(\frac{P_{ci}}{P_k}\right)^{A-1} \cdot \frac{\exp[5.37 A (1+\omega_i)(1-T_{ri}^{-1})]}{P_{ri}} \quad (9)$$

where A is a function of pressure, with A=1 at "low" pressures and A=0 at $p=p_k$; an approximate pressure dependence for A is $A=1-(p/p_k)^n$, with n ranging from 0.5 to 0.8. In all test problems, $n=0.7$, $p_k=10000.1$ psi, and $T=700^\circ\text{R}$. Pressures are calculated by the relation $p=j\cdot 10^k$ psia ($p < p_k$), where $j=1,9(1)$ and $k=-2,4(1)$. If $K_{\min} > 1+\epsilon_m$ or $K_{\max} < 1-\epsilon_m$ at a given pressure, the K-values are rejected. In some problems, the first or last K-value is set equal to 10^{-50} or 10^{+50} .

Feed compositions cover a wide range including numerous cases where some of the components have $z_i=10^{-20}$.

Many of the tests use a slightly different strategy for coming up with z_i and K_i . These tests make use of K-values [from Eq. (9)] for pressures 9000 and 10000 psia. First, "mixing" compositions y_i^* and x_i^* are calculated: $y_i^*=Y_i/\Sigma Y_i$ and $x_i^*=X_i/\Sigma X_i$, where $Y_i=z_i K_i$ and $X_i=z_i/K_i$. The mixing compositions are recombined using "difficult" phase fractions V and L to create new mixture compositions z_i^* , which are used as input to RRSOLV together with the K-values given by $K_i^*=y_i^*/x_i^*$.

Summary and Error Files

Up to three files may be created by the test program: RRTEST.OUT, RRTEST.ERR, and RRTEST.DBG. If a timing-only run is made (selected interactively at run time), then only final results are printed to the file RRTEST.OUT (to minimize I/O effects on timing).

Example Brief RRTEST.OUT file:

THE RACHFORD-RICE CONTEST RESULTS		

Total Number of Test Cases	=	13504
Reported Number of Convergence Problems	=	0
Cases with Material Balance Errors	=	0
Total Number of Material Balance Errors	=	0
Number of Negative Mole Fractions	=	0
Maximum "Severity" of Errors	=	-0.4
Average of All Positive "Severities"	=	0.0
Maximum Number of Iterations Reported	=	31
Average Number of Iterations Reported	=	3.382
Number of Timed Repetitions	=	2
Solution Time (seconds)	=	30.094
Overhead Time (seconds)	=	34.875
Total Run Time (seconds)	=	64.969

If a run is made without timing, both RRTEST.OUT and RRTEST.ERR files are created, with summary results of each test calculation.

Example Complete RRTEST.OUT file:

```

Summary Report:
-----
Test #      #      V      L      #      Maximum
#      ITERS.  V      L      ERRORS  Positive
#      ITERS.  V      L      ERRORS  Severity
-----
1         5      3.9606E+00 -2.9606E+00 0
2         5      1.6876E+00 -6.8762E-01 0
3         6      1.2202E+00 -2.2024E-01 0
4         5      9.8481E-01  1.5186E-02 0
5         5      8.2715E-01  1.7285E-01 0
6         4      7.0686E-01  2.9314E-01 0
7         4      6.0827E-01  3.9173E-01 0
8         5      5.2370E-01  4.7630E-01 0
9         6      4.4875E-01  5.5125E-01 0
10        8      1.5588E-19  1.0000E+00 0
...
13500     2      1.0000E+00  1.5228E-20 0
13501     2      1.0000E+00  1.7910E-20 0
13502     2      1.0000E+00  2.1955E-20 0
13503     2      1.0000E+00  2.8721E-20 0
13504     2      1.0000E+00  4.2286E-20 0

THE RACHFORD-RICE CONTEST RESULTS
-----
Total Number of Test Cases           = 13504
Reported Number of Convergence Problems = 0
Cases with Material Balance Errors    = 0
Total Number of Material Balance Errors = 0
Number of Negative Mole Fractions     = 0
Maximum "Severity" of Errors          = -0.4
Average of All Positive "Severities"  = 0.0
Maximum Number of Iterations Reported = 31
Average Number of Iterations Reported = 3.382
Total Run Time (seconds)              = 54.055
    
```

Example Complete RRTEST.ERR file:

```

-----
Severity = log10(residual/tolerance)
(should never be positive)
-----
Occurrences
=====
Test #  y<0  x<0  y      x      z      K      V+L
-----
1       0    0   -10.0  -1.3   -1.1   -10.0  -10.0
2       0    0    -1.3  -10.0  -1.0   -10.0  -10.0
3       0    0   -10.0 -10.0  -1.1   -10.0  -10.0
4       0    0   -10.0  -1.0   -1.0   -10.0  -10.0
5       0    0   -10.0 -10.0  -1.1   -10.0  -1.3
6       0    0    -1.3 -10.0  -1.1   -10.0  -10.0
7       0    0   -10.0 -10.0  -1.1   -10.0  -10.0
8       0    0   -10.0 -10.0  -1.4   -10.0  -10.0
9       0    0   -10.0 -10.0  -1.1   -10.0  -1.6
10      0    0    -1.3 -10.0  -1.3   -10.0  -4.3
...
13500   0    0   -10.0  -1.7   -1.0   -10.0  -10.0
13501   0    0   -10.0  -1.7   -1.0   -10.0  -10.0
13502   0    0    -2.0  -2.0   -0.8   -10.0  -10.0
13503   0    0    -2.0 -10.0  -1.1   -10.0  -10.0
13504   0    0    -2.0  -2.0   -1.1   -10.0  -10.0

Max:    0    0   -0.5  -0.5  -0.4   -10.0  -0.9
    
```

If you want to study the input and the calculated results for one or more specific tests (to do some debugging of your routine), specify the test numbers on an optional input file RRTEST.CHK. If this file exists and contains one or more valid test numbers, then detailed information will be printed to the file RRTEST.DBG (for the test numbers specified). A maximum of 100 test numbers can be specified in RRTEST.CHK.

Example RRTEST.DBG file (for test #30):

```
* Format:
* ITEST NC ITER
* FV(initial) FL(initial) FV(final) FL(final)
* K(i)
* Z(i)
* Y(i)
* X(i)
      30      5      7
-7.910114510118954E-01  1.791011451011896E+00 -1.195464430491447E+00  2.195464430491447E+00
 1.836494984287326E+00  1.129526528280343E+00  7.893881042067106E-01  5.827503100615659E-01
 4.439432256481072E-01
 9.999999999999999E-21  2.500000000000000E-01  2.500000000000000E-01  2.500000000000000E-01
 2.500000000000000E-01
 3.443581928239257E-01  3.341179042352673E-01  1.576532449519760E-01  9.720234938573431E-02
 6.666830860309676E-02
 1.875083764291129E-01  2.958035033882275E-01  1.997157597281104E-01  1.667993095970471E-01
 1.501730508575022E-01
```

Sponsor

Curtis H. Whitson, Dept. Petroleum Engineering and Applied Geophysics, U. Trondheim, NTH, 7034 Trondheim, Norway. Contest awards paid by Pera a/s. Email curtis@ipt.unit.no. Telephone/fax 47 73 59 49 77.

References

1. Rachford, H.H. and Rice, J.D.: "Procedure for Use of Electrical Digital Computers in Calculating Flash Vaporization Hydrocarbon Equilibrium," *JPT* (Oct. 1952) No. 4, 19-20; *Trans.*, AIME, **195**.
2. Muskat, M. and McDowell, J.M.: "An Electrical Computer for Solving Phase Equilibrium Problems," *Trans.*, AIME (1949) **186**, 291-298.
3. Twu, C.H.: "Prediction of Thermodynamic Properties of Normal Paraffins Using Only Normal Boiling Point," *Fluid Phase Equilibria* (1983) 11, 65-81.
4. Kesler, M.G. and Lee, B.I.: "Improve Predictions of Enthalpy of Fractions," *Hydro. Proc.* (March 1976) 55, 153-158.
5. Whitson, C.H. and Torp, S.B.: "Evaluating Constant Volume Depletion Data," paper SPE 10067 presented at the 1981 SPE Annual Technical Conference and Exhibition, Texas, Oct. 5-7; *JPT* (March 1983) 610-620; *Trans.*, AIME, **275**.