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Title: A Hybrid Monte Carlo Method for Equilibrium Equation of State of Detonation Products

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A HYBRID MONTE CARLO METHOD FOR EQUILIBRIUM EQUATION OF STATE OF OF DETONATION PRODUCTS

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MONTE CARLO SIMULATION METHODS

Benchmark for perturbation theory methods

- NPT, NVT - single species or fixed composition mixture
- Gibbs ensemble - phase separation
- N_aPT - chemical equilibrium: fluid only

Hybrid Monte Carlo Method - extension of $N_a PT$

- solid carbon + chemical equilibrium + phase separation
- 'Real' explosives - calculate final EOS directly
- any potential is easy
- equilibrium surface chemistry of carbon clusters
- benchmark on whole, not just part
- higher level quantum energy -
  - sample from lower level distribution

Partition function separated into three parts:

0=solid, 1=fluid1, and 2=fluid2. V=$V_0 + V_1 + V_2$.

Classical partition function - identical atoms

$$Q(N, V, T) = \left[\frac{V^N}{N!\Lambda^{3N}}\right] \int e^{-\beta U} d\mathbf{s}_1 \cdots d\mathbf{s}_N \quad (1)$$

scaled coordinates, $\mathbf{s}_i$.

Isothermal-isobaric ensemble

$$\Delta(N, P, T) = \int_0^\infty e^{-\beta PV} Q(N, V, T) dV \quad (2)$$

A_i the total number of atoms of type i - fixed

${}^k M_j$ the number of molecules of type j in box k.

$$\Delta(A_1, ..., A_I, P, T) = \quad (3)$$

$$\int \int \int e^{-\beta P(V_0+V_1+V_2)} \sum{}' Q_0 Q_1 Q_2 dV_0 dV_1 dV_2$$

which can be rewritten as

$$\int \int \sum{}' e^{-\beta G_c(N_c,P,T)} e^{-\beta P(V_1+V_2)} Q_1 Q_2 dV_1 dV_2$$

where $e^{-\beta G_c(N_c,P,T)} = e^{W_0} = \Delta_c(N_c, P, T)$

approximate analytic scheme for solid carbon

e.g. cold curve plus Debye model

Q_k denotes $Q_k({}^k M_1, ..., {}^k M_J, V_k, T)$

The prime on the summation -

only those sets of molecules with A_i's conserved (over 3 boxes)

Include distinguishability, mass, internal degrees of freedom q_j

$$Q_k({}^k M_1, ..., {}^k M_J, V_k, T) = \tag{4}$$

$$\frac{{V_k}^{M_k} {q_k}^{{}^k M_1} \cdots {q_k}^{{}^k M_J}}{{}^k M_1! \cdots {}^k M_J! \Lambda_1^{3 {}^k M_1} \cdots \Lambda_J^{3 {}^k M_J}}$$

$$\times \int e^{-\beta U_k} d^{\mathbf{k}}\mathbf{s}_1 \cdots d^{\mathbf{k}}\mathbf{s}_{M_k}$$

M_k - total number of molecules in box k

U_k total potential energy of the molecules in box k

$$\Delta(P,T) = \int_0^\infty \int_0^\infty \int \int \sum{}' \Big[e^W dV_1 dV_2$$

$$d^{\mathbf{1}}\mathbf{s}_1 \cdots d^{\mathbf{1}}\mathbf{s}_{M_1} d^{\mathbf{2}}\mathbf{s}_1 \cdots d^{\mathbf{2}}\mathbf{s}_{M_2} \Big] \tag{5}$$

$$W = -\beta G_c(N_c, P, T) - \beta[U_1 + PV_1] - \beta[U_2 + PV_2]$$

$$+M_1 lnV_1 + M_2 lnV_2 \quad (6)$$

$$+\sum_{j=1}^{J}\sum_{k=1}^{2}\left[{}^kM_j(lnq_j - 3\Lambda_j) - ln({}^kM_j!)\right]$$

Monte Carlo simulation -

Markov chain with a limiting distribution proportional to e^W

Accept trial move from r to s with probability:

$$P_{r\to s} = Min[1, exp(W_s - W_r)p_{s\to r}/p_{r\to s}] \quad (7)$$

$p_{r\to s}$ is the unweighted probability of a move from r to s.

Four types of moves:

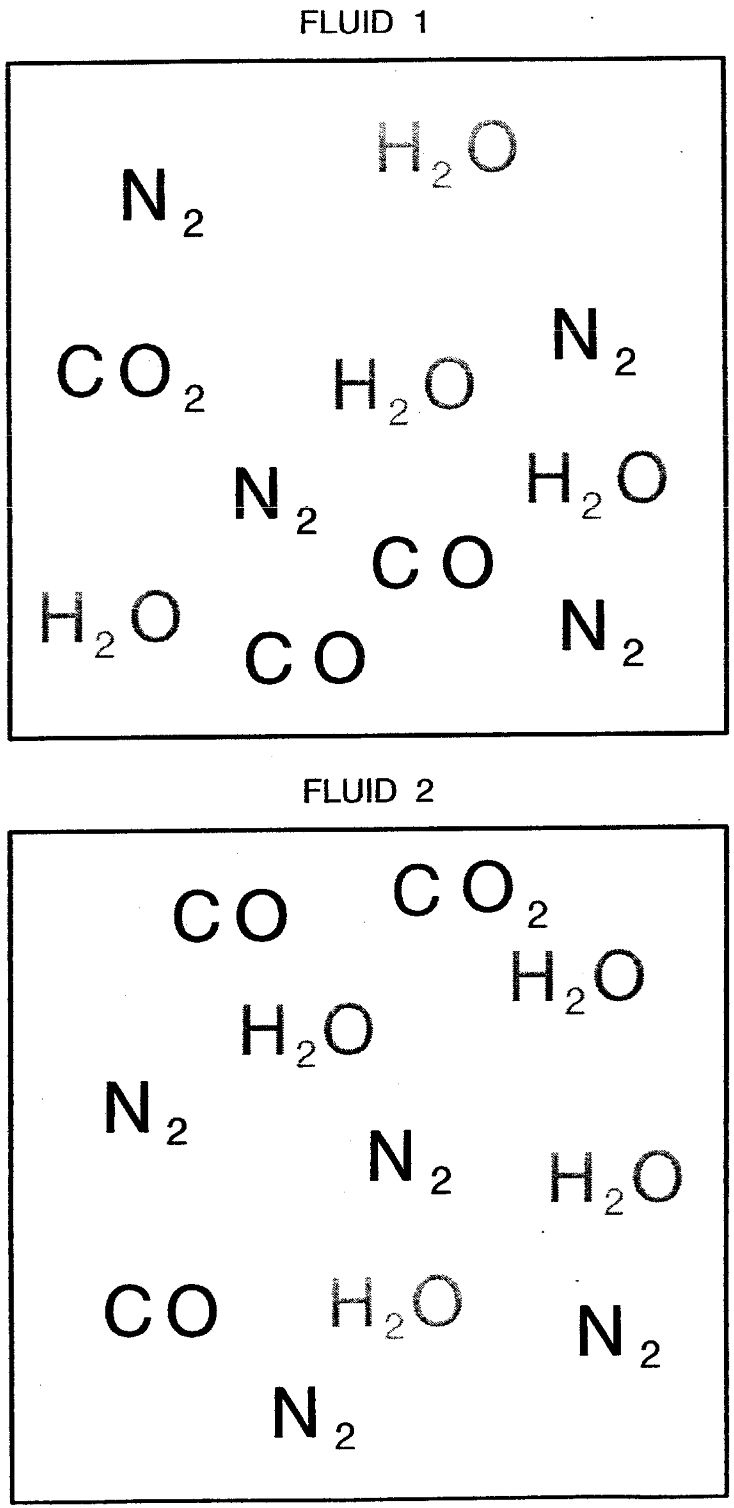
Position moves - $-\beta U$ terms and $p_{r\to s} = p_{s\to r}$.

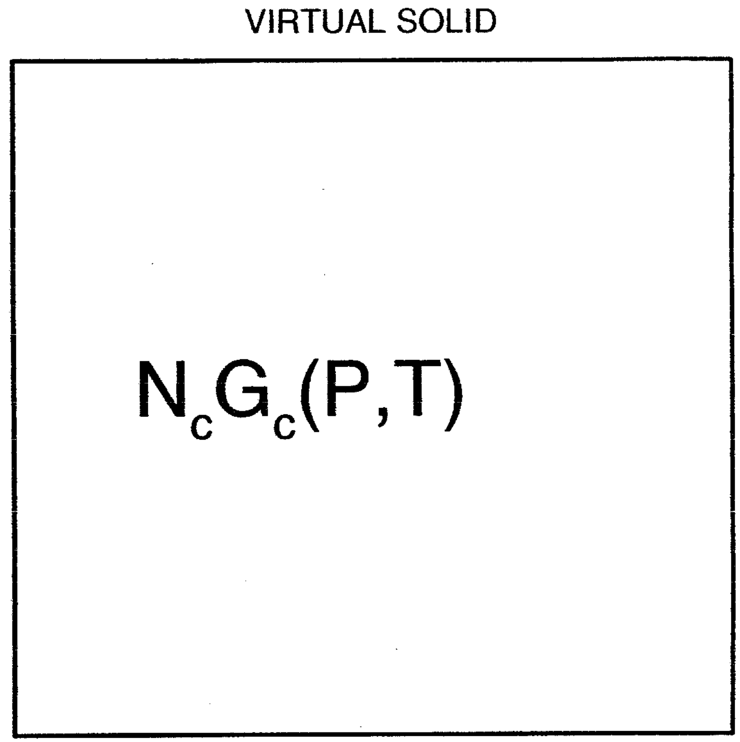
Volume moves - uniform scaling

$p_{r\to s} \neq p_{s\to r}$ - count the number of ways to choose particles

Between fluids - interchange particles or move a particle from one box to another

Chemistry moves - generalizations of the $N_{atoms}PT$ ensemble to include solids.





N_aPT ensemble

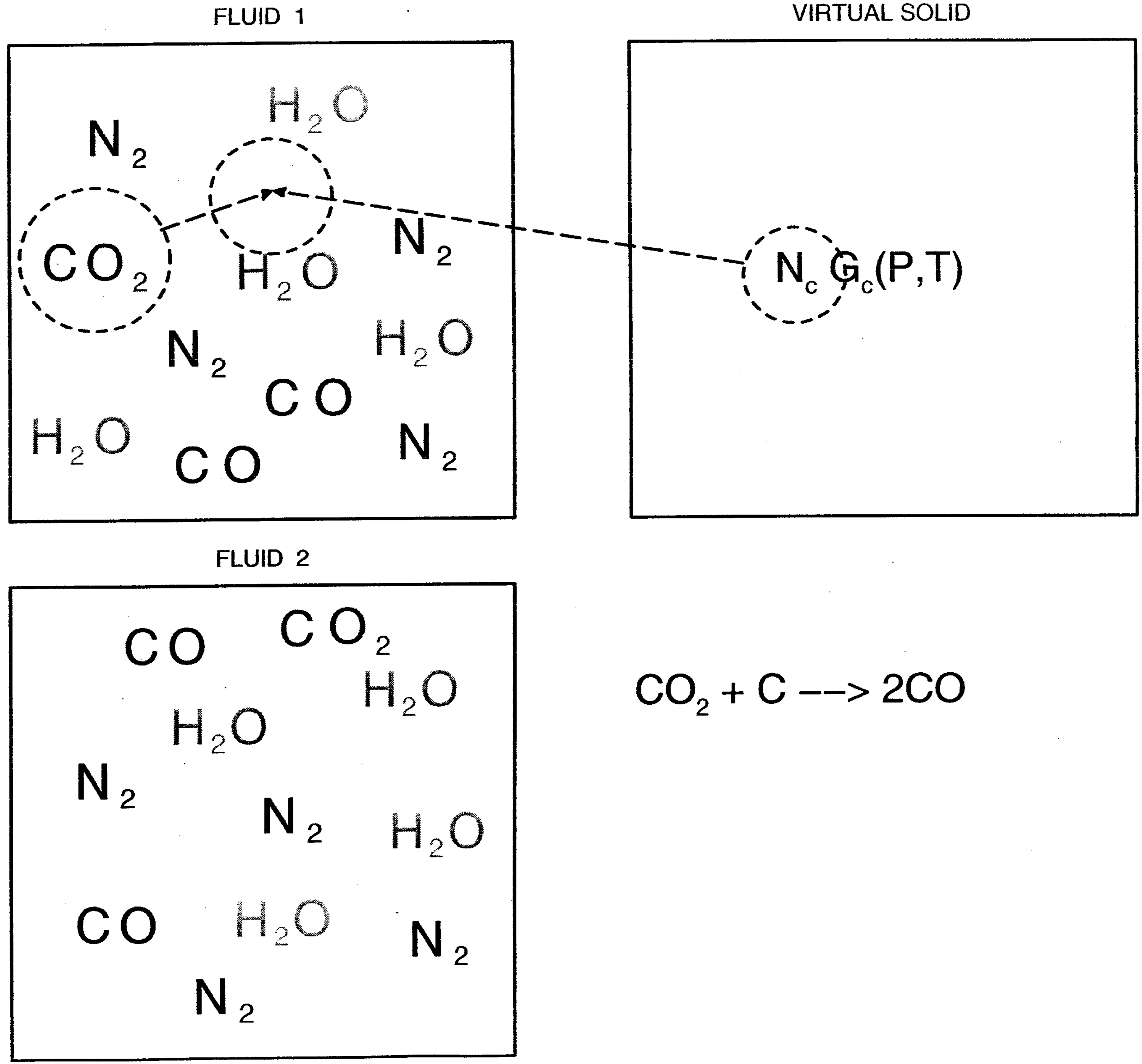
move types:

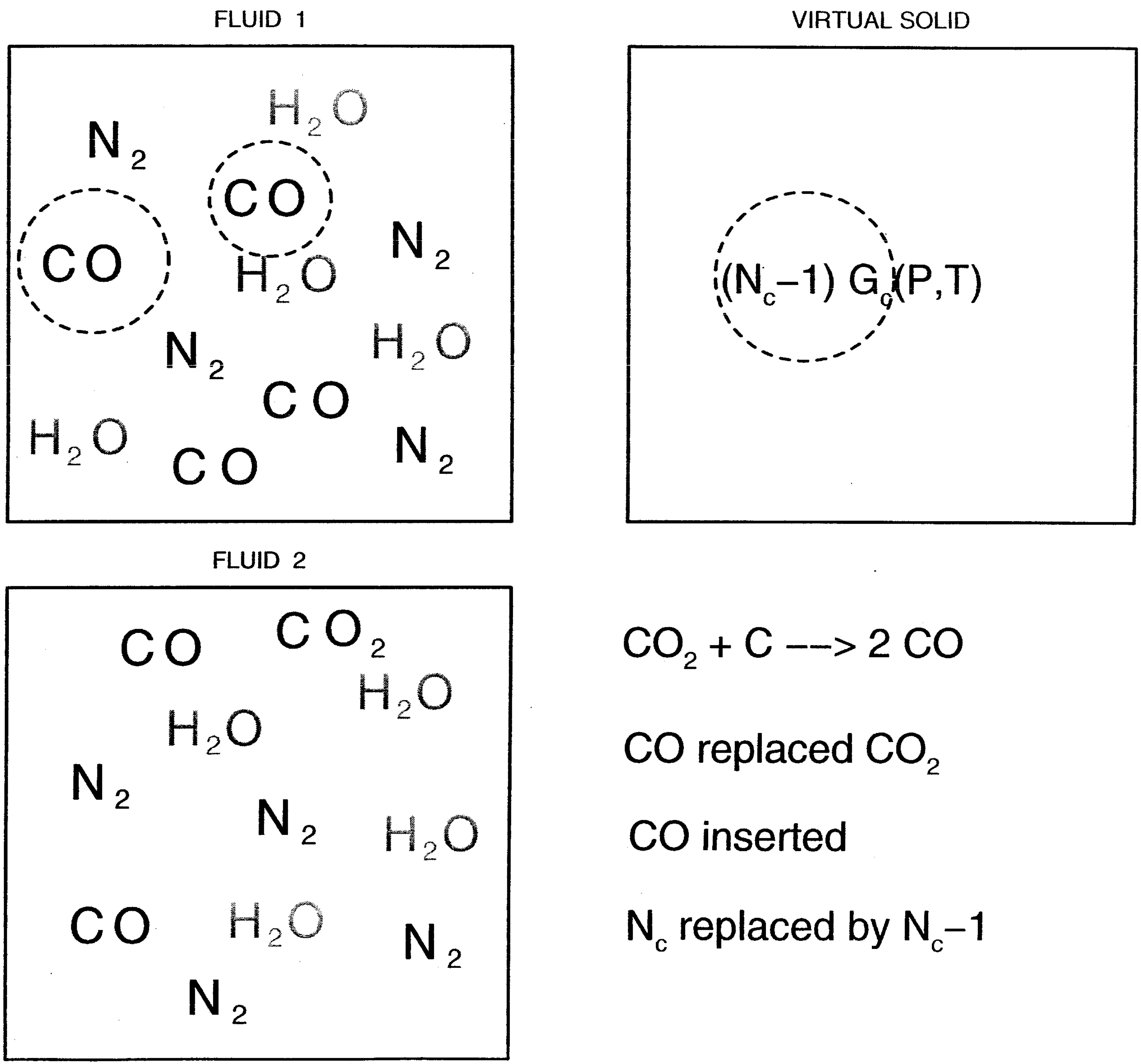
position

volume

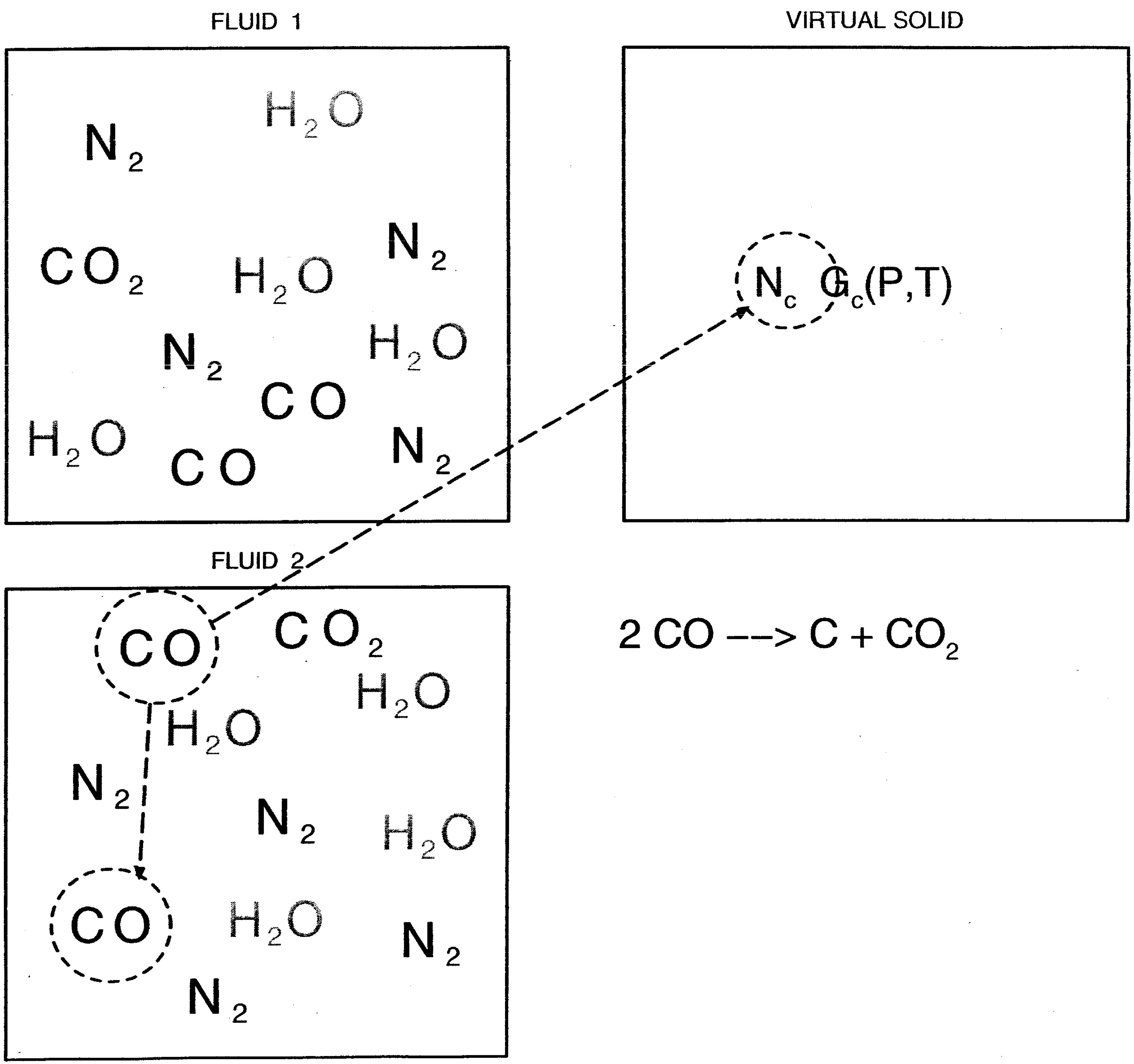
between F_1 & F_2

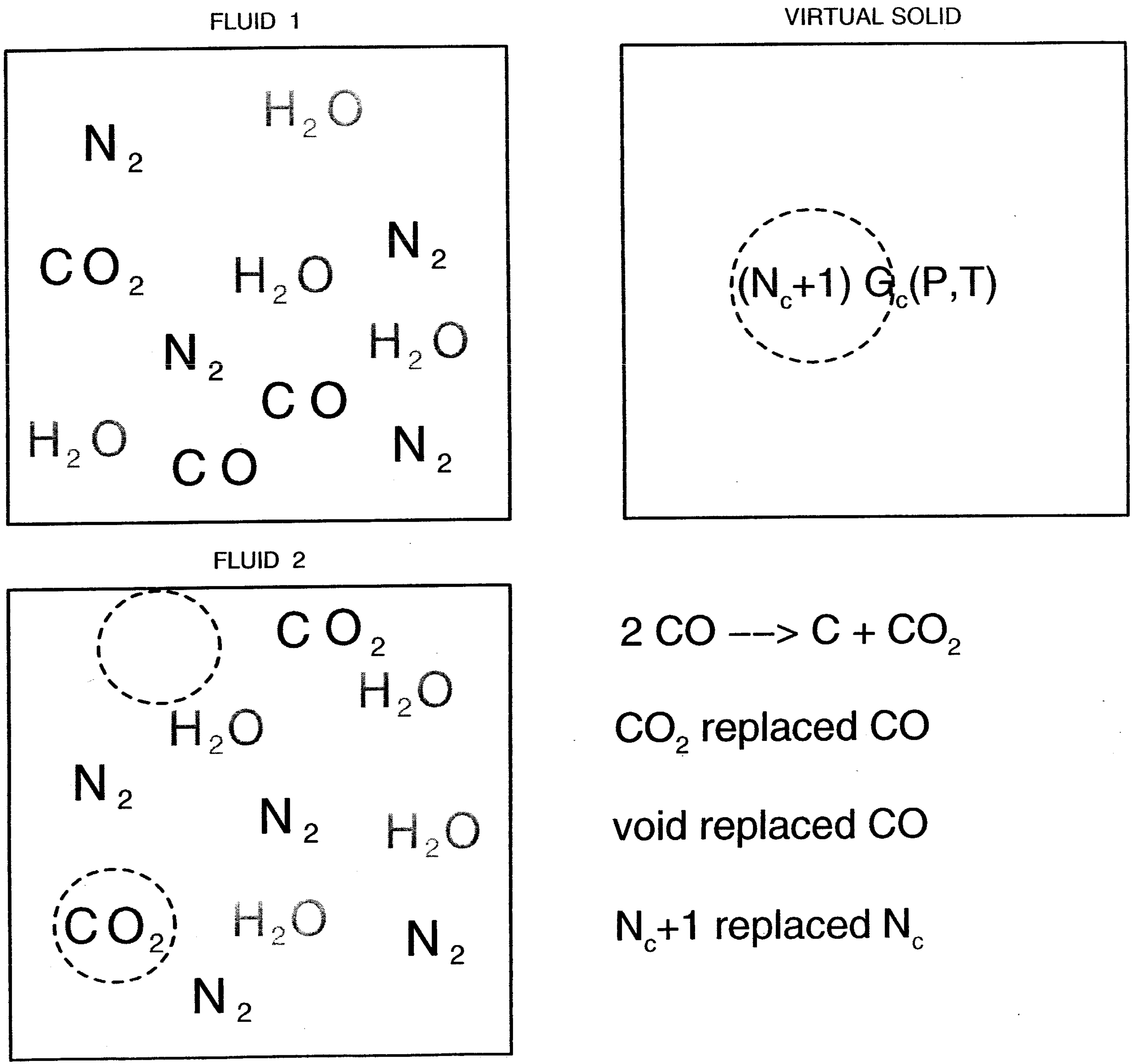
chemistry


FLUID 1
VIRTUAL SOLID
N2
H2O
CO2
H2O
N2
Nc Gc(P,T)
N2
H2O
CO
H2O
CO
N2
FLUID 2
CO
CO2
H2O
H2O
N2
N2
H2O
CO
H2O
N2
N2
CO2 + C --> 2CO



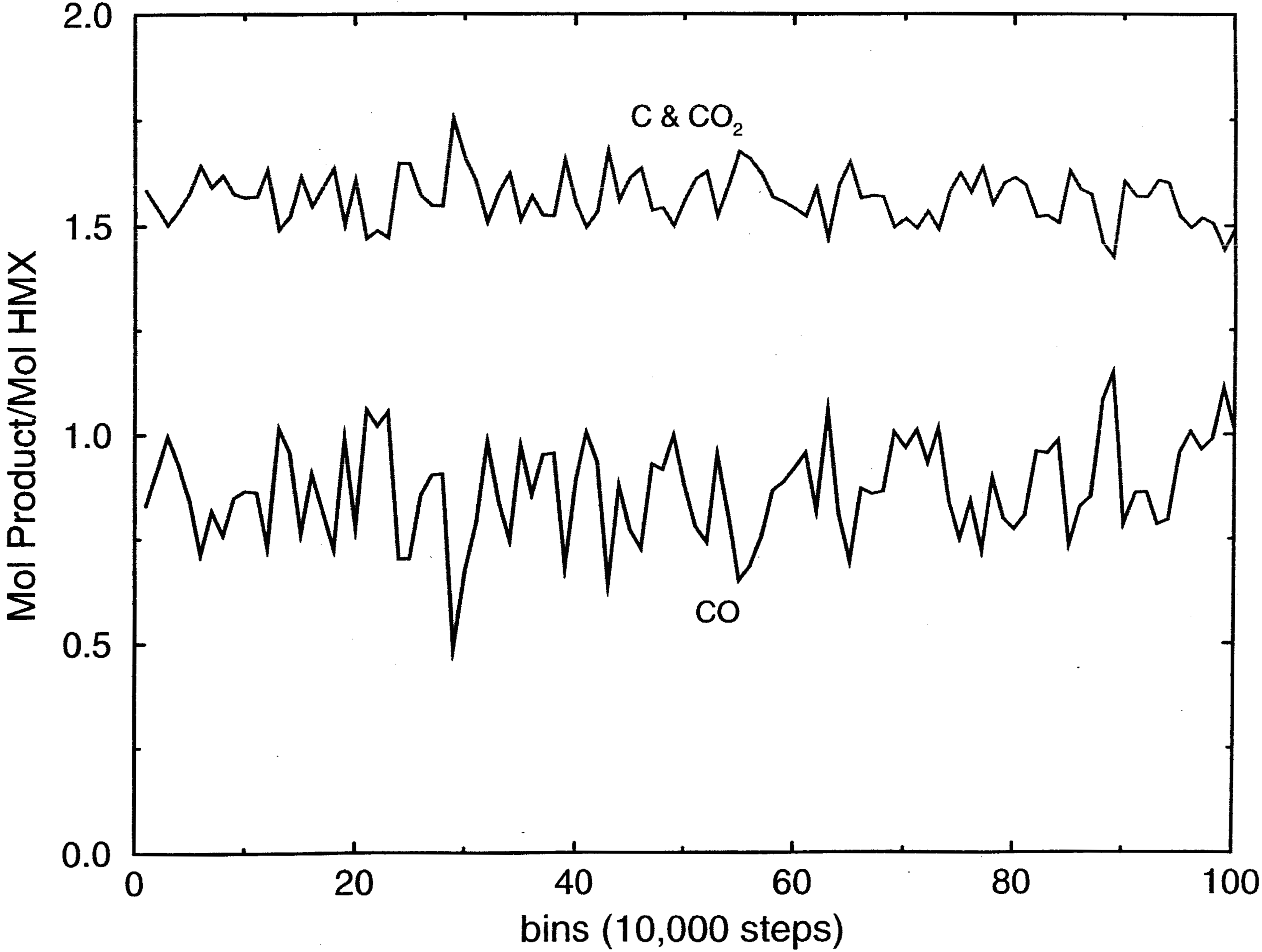
FLUID 1
VIRTUAL SOLID
N_2
H_2O
CO
CO
N_2
H_2O
N_2
H_2O
CO
H_2O
CO
N_2
$(N_c-1)\ G_c(P,T)$
FLUID 2
CO
CO_2
H_2O
H_2O
N_2
N_2
H_2O
CO
H_2O
N_2
N_2
$CO_2 + C \text{---} > 2\ CO$
CO replaced CO_2
CO inserted
N_c replaced by N_c-1

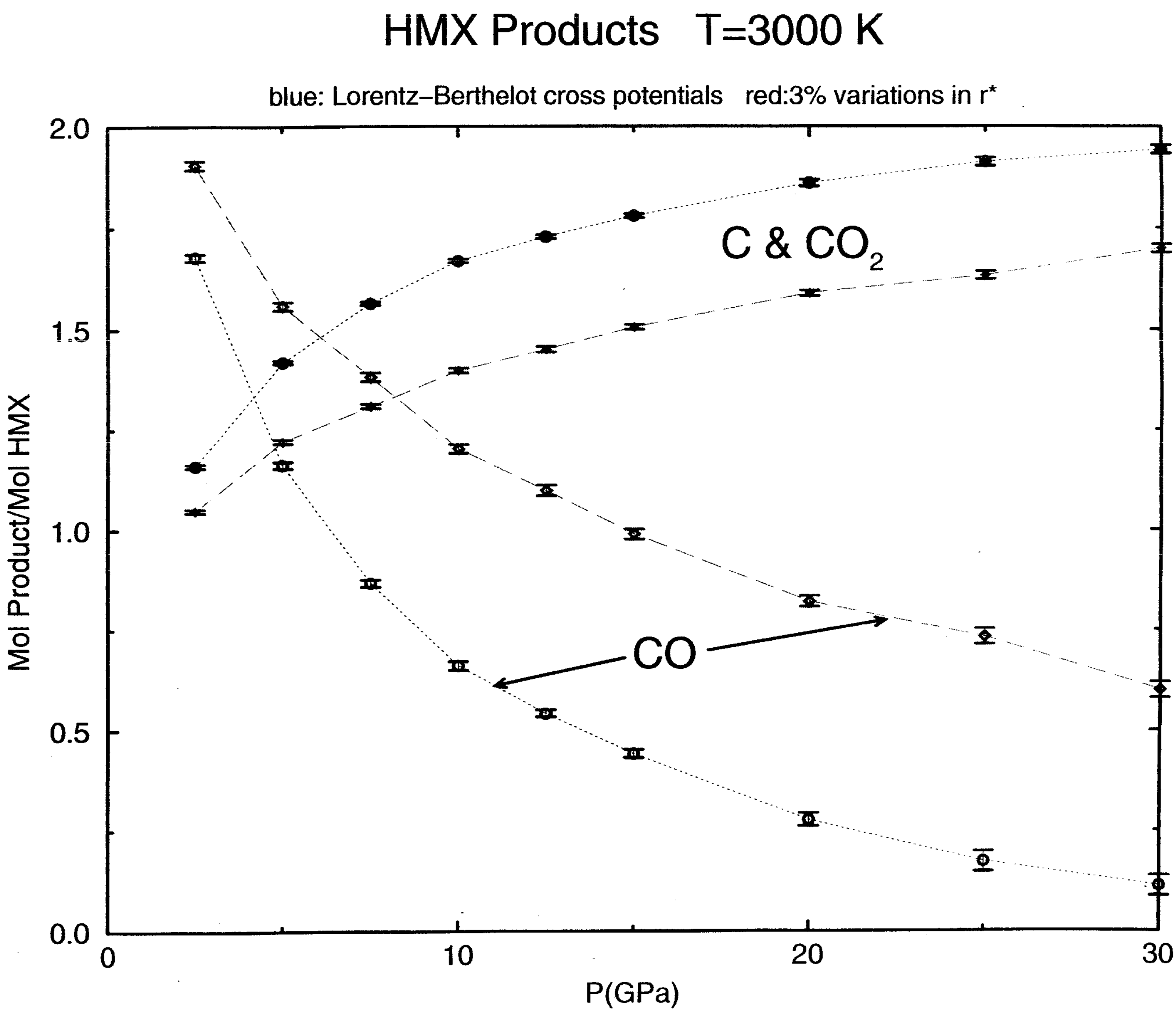

FLUID 1
VIRTUAL SOLID
N2
H2O
CO2
CO
N_c $G_c(P,T)$
FLUID 2
2 CO --> C + CO2


FLUID 1
N_2
H_2O
CO_2
CO
VIRTUAL SOLID
$(N_c+1)\ G_c(P,T)$
FLUID 2
$2\ CO \dashrightarrow C + CO_2$
CO_2 replaced CO
void replaced CO
N_c+1 replaced N_c

Hybrid MC – HMX Products 7.5 GPa 3000K

$C_4H_8N_8O_8 \rightarrow 4N_2 + 4H_2O + (4-2x)CO + xCO_2 + xC$




HMX Products T=3000 K
blue: Lorentz–Berthelot cross potentials red:3% variations in r*
2.0
1.5
1.0
0.5
0.0
Mol Product/Mol HMX
0
10
20
30
P(GPa)
C & CO_2
CO