*Electronic Supplementary Information*

# Catalytic Resonance Theory: SuperVolcanoes, Catalytic Molecular Pumps, and Oscillatory Steady State

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# of Figures: 2
# of Tables: 8
# of Equations: 6

Table of Contents:

**Section S5. Binding Energy Derivation**

**Section S1. Matlab 2017b and 2019a Code**

CSTR Model

```
% CSTR model
% Description:
% Continuously Stirred Tank Reactor (CSTR) with reaction A -> B.
% The binding energies of A and B are the controls.

function xdot = cstr1(t,x)
global Rg R TK Caf Cbf qdot w u delHovr alpha beta gamma delta BEb0 delBEb

% Input (1):
% Number of catalytic active sites (gmol)
Ns = u;

% States (2):
% Concentration of A in CSTR (M)
Ca = x(1,1);
% Concentration of B in CSTR (M)
Cb = x(2,1);
% Amount of adsorbed A in CSTR (gmol)
Ca_star = x(3,1);
% Amount of adsorbed B in CSTR (gmol)
Cb_star = x(4,1);
% Number of vacant sites in CSTR (gmol)
C_star = Ns - Ca_star - Cb_star;

% Convert units
% Pressure of A in CSTR (bar)
Pa = Ca*Rg*TK;
% Pressure of B in CSTR (bar)
Pb = Cb*Rg*TK;
% Surface coverage of A in CSTR (unitless)
Theta_A_star = Ca_star/Ns;
% Surface coverage of B in CSTR (unitless)
Theta_B_star = Cb_star/Ns;
% Surface coverage of * in CSTR (unitless)
Theta_star = C_star/Ns;

% Reactor parameters:
% Volume of CSTR
% Catalyst density (g/mL)
rho = 3.58;
% Bed void fraction (unitless)
epsilon = 0.375;
% Volume calculation (L)
V = (w/1000)*(1/rho)*(1/1000)*(1/(1-epsilon));
```

```
% Reaction parameters:
% Binding energies
% Volcano x-axis zero point (eV)
BEa0 = (BEb0 - ((1-gamma)*delta) - (delHovr/96.485e3))/gamma;

% Binding energy of B (J/gmol)
BEb = (BEb0 + delBEb)*96.485e3;
% Restrict binding energy of B to positive values
if BEb < 0
   BEb = 0;
End

% Binding energy of A (J/gmol)
BEa = (BEa0 + ((1/gamma)*delBEb))*96.485e3;
% Restrict binding energy of A to positive values
if BEa < 0
   BEa = 0;
End

% Heats of reaction (J/gmol)
delH1 = -BEa; % A -> A*
delH2 = delHovr + BEa - BEb; % A* -> B*
delH3 = BEb; % B* -> B

% Ea - Activation energies in the Arrhenius equation (J/gmol)
Ea1f = 0e3; % A -> A*
Ea2f = alpha*delH2 + beta; % A* -> B*
% Restrict activation energy to positive values
if Ea2f < 0
   Ea2f = 0;
end
Ea3f = delH3; % B* -> B

% Pre-exponential factors
A1f = 1e6; % 1/bar-sec
A2f = 1e13; % 1/sec
A3f = 1e13; % 1/sec

% Equilibrium constants
K1 = 1e-7*exp(-delH1/(R*TK)); % 1/bar
K2 = 1*exp(-delH2/(R*TK)); % unitless
K3 = 1e7*exp(-delH3/(R*TK)); % bar

% Rate constants
k1f = A1f*exp(-Ea1f/(R*TK)); % 1/bar-sec
k1r = k1f/K1; % 1/sec
k2f = A2f*exp(-Ea2f/(R*TK)); % 1/sec
k2r = k2f/K2; % 1/sec
k3f = A3f*exp(-Ea3f/(R*TK)); % 1/sec
k3r = k3f/K3; % 1/bar-sec
```

```
% Compute xdot:
xdot(1,1) = (qdot/V*(Caf - Ca) - k1f*Pa*Theta_star*(Ns/V) + k1r*Theta_A_star*(Ns/V)); % M/sec
xdot(2,1) = (qdot/V*(Cbf - Cb) + k3f*Theta_B_star*(Ns/V) - k3r*Pb*Theta_star*(Ns/V)); % M/sec
xdot(3,1) = k1f*Pa*Theta_star*Ns - k1r*Theta_A_star*Ns - k2f*Theta_A_star*Ns +
k2r*Theta_B_star*Ns; % gmol/sec
xdot(4,1) = - k3f*Theta_B_star*Ns + k3r*Pb*Theta_star*Ns + k2f*Theta_A_star*Ns -
k2r*Theta_B_star*Ns; % gmol/sec
```

Batch Reactor Model

```
% Batch reactor model
% Description:
% Batch reactor with reaction A -> B.
% The binding energies of A and B are the controls.

function xdot = batch1(t,x)
global Rg R TK w u delHovr alpha beta gamma delta BEb0 delBEb

% Input (1):
% Number of catalytic active sites (gmol)
Ns = u;

% States (2):
% Concentration of A in batch reactor (M)
Ca = x(1,1);
% Concentration of B in batch reactor (M)
Cb = x(2,1);
% Amount of adsorbed A in batch reactor (gmol)
Ca_star = x(3,1);
% Amount of adsorbed B in batch reactor (gmol)
Cb_star = x(4,1);
% Number of vacant sites in batch reactor (gmol)
C_star = Ns - Ca_star - Cb_star;

% Convert units
% Pressure of A in batch reactor (bar)
Pa = Ca*Rg*TK;
% Pressure of B in batch reactor (bar)
Pb = Cb*Rg*TK;
% Surface coverage of A in batch reactor (unitless)
Theta_A_star = Ca_star/Ns;
% Surface coverage of B in batch reactor (unitless)
Theta_B_star = Cb_star/Ns;
% Surface coverage of * in batch reactor (unitless)
Theta_star = C_star/Ns;

% Reactor parameters:
% Volume of batch reactor
% Catalyst density (g/mL)
rho = 3.58;
```

```
% Bed void fraction (unitless)
epsilon = 0.375;
% Volume calculation (L)
V = (w/1000)*(1/rho)*(1/1000)*(1/(1-epsilon));

% Reaction parameters:
% Binding energies
% Volcano x-axis zero point (eV)
BEa0 = (BEb0 - ((1-gamma)*delta) - (delHovr/96.485e3))/gamma;

% Binding energy of B (J/gmol)
BEb = (BEb0 + delBEb)*96.485e3;
% Restrict binding energy of B to positive values
if BEb < 0
   BEb = 0;
End

% Binding energy of A (J/gmol)
BEa = (BEa0 + ((1/gamma)*delBEb))*96.485e3;
% Restrict binding energy of A to positive values
if BEa < 0
   BEa = 0;
End

% Heats of reaction (J/gmol)
delH1 = -BEa; % A -> A*
delH2 = delHovr + BEa - BEb; % A* -> B*
delH3 = BEb; % B* -> B

% Ea - Activation energies in the Arrhenius equation (J/gmol)
Ea1f = 0e3; % A -> A*
Ea2f = alpha*delH2 + beta; % A* -> B*
% Restrict activation energy to positive values
if Ea2f < 0
   Ea2f = 0;
end
Ea3f = delH3; % B* -> B

% Pre-exponential factors
A1f = 1e6; % 1/bar-sec
A2f = 1e13; % 1/sec
A3f = 1e13; % 1/sec

% Equilibrium constants
K1 = 1e-7*exp(-delH1/(R*TK)); % 1/bar
K2 = 1*exp(-delH2/(R*TK)); % unitless
K3 = 1e7*exp(-delH3/(R*TK)); % bar

% Rate constants
k1f = A1f*exp(-Ea1f/(R*TK)); % 1/bar-sec
k1r = k1f/K1; % 1/sec
```

```
k2f = A2f*exp(-Ea2f/(R*TK)); % 1/sec
k2r = k2f/K2; % 1/sec
k3f = A3f*exp(-Ea3f/(R*TK)); % 1/sec
k3r = k3f/K3; % 1/bar-sec

% Compute xdot:
xdot(1,1) = -k1f*Pa*Theta_star*(Ns/V) + k1r*Theta_A_star*(Ns/V); % M/sec
xdot(2,1) = k3f*Theta_B_star*(Ns/V) - k3r*Pb*Theta_star*(Ns/V); % M/sec
xdot(3,1) = k1f*Pa*Theta_star*Ns - k1r*Theta_A_star*Ns - k2f*Theta_A_star*Ns +
k2r*Theta_B_star*Ns; % gmol/sec
xdot(4,1) = - k3f*Theta_B_star*Ns + k3r*Pb*Theta_star*Ns + k2f*Theta_A_star*Ns -
k2r*Theta_B_star*Ns; % gmol/sec
```

Dynamic Catalysis CSTR Shell Code with Square Waveform

```
% Remove prior data and runs
clear
clc

% Step test for Model 1 - CSTR

global Rg R TK Caf Cbf qdot w u delHovr alpha beta gamma delta BEb0 delBEb

% Constants:
% Gas constant
Rg = 8.314459848e-2; % L-bar/K-gmol
R = 8.314459848; % J/K-gmol

% Reactor parameters:

% Temperature
Tc = 150; % deg C
TK = Tc + 273.15; % K

% Feed pressure (bar)
Paf = 100;
Pbf = 0;
% Feed concentration (M)
Caf = Paf/(Rg*TK);
Cbf = Pbf/(Rg*TK);

% Volumetric flowrate
qsdot = 50; % mL/min
qdot = qsdot/60000; % L/sec

% Steady state initial conditions for the states
Ca_ss = Caf; % M
Cb_ss = Cbf; % M
Ca_star_ss = 0; % gmol
Cb_star_ss = 0; % gmol
x_ss = [Ca_ss;Cb_ss;Ca_star_ss;Cb_star_ss];
```

```
% Steady state initial condition for the control
u_ss = 0; % gmol active sites
% Open loop step change
% Catalyst weight (mg)
w = 138;
% Active site density (gmol/g catalyst)
srho = 20e-6;
% Active site calculation (gmol)
u = (w/1000)*srho;

% Reaction parameters:
% Overall heat of reaction for A -> B (J/gmol)
delHovr = 0e3;
% Brønsted-Evans-Polanyi relationship parameters
alpha = 0.6; % unitless
beta = 102e3; % J/gmol
% Binding energy relationship parameters
gamma = 0.5; % unitless
delta = 1.4; % eV

% Volcano plot parameter:
% x-axis zero point (eV)
BEb0 = delta + delHovr/96.485e3;

% Volcano plot peak calculation
% Iterate binding energies of A and B (eV)
is = -delta;
ii = 0.01;
ie = delta;
% Preallocate BEb, TOF, and surface coverage matrices
je = ((ie - is)/ii + 1); % final index
delBEbv = zeros(round(je),1); % eV
TOFbvf = zeros(round(je),1); % 1/sec
Theta_A_starvf = zeros(round(je),1); % unitless
Theta_B_starvf = zeros(round(je),1); % unitless

% Begin iteration (eV)
for i = is:ii:ie
% Set binding energy of B (eV)
delBEb = i; % eV
% Iterate at each binding energy
for n = 1:inf % index

% Final Time (sec)
tfv = 5e100;
% Generate CSTR data
opts = odeset('RelTol',1e-8,'AbsTol',1e-9);
[tv,xv] = ode15s('cstr1',[0 tfv],x_ss,opts); % Time and state outputs

% Parse out the state values (M)
```

```
Cav = xv(:,1);
Cbv = xv(:,2);
% Measure reactor performance
Ybv = (Cbv./(Cav + Cbv))*100; % mol %

% Converge on C yield of B (mol %)
C = 1;
if abs(Ybv(end) - C) > 0.01 % Convergence criterion
   qdot = qdot*Ybv(end)/C; % L/sec
   nv = n; % Indicates that volcano criterion was not met
   nv; % Display iteration count
   clear tv xv Cav Cbv Ybv

else
   % Compute matrix index
   j = ((i - is)/ii) + 1; % unitless

   % Parse out state values (gmol)
   Ca_starv = xv(:,3);
   Cb_starv = xv(:,4);

   % Measure reactor performance
   TOFbv = Cbv*qdot/u; % 1/sec

   % Convert units
   Theta_A_starv = Ca_starv/u; % unitless
   Theta_B_starv = Cb_starv/u; % unitless

   % Store volcano plot results
   delBEbv(round(j)) = i; % eV
   TOFbvf(round(j)) = TOFbv(end); % 1/sec
   Theta_A_starvf(round(j)) = Theta_A_starv(end); % unitless
   Theta_B_starvf(round(j)) = Theta_B_starv(end); % unitless

   clear tv xv Cav Cbv Ybv Ca_starv Cb_starv TOFbv Theta_A_starv Theta_B_starv
   break
end
end
end

% Extract volcano plot peak information
peakTOF = max(TOFbvf); % 1/sec

% Preallocate relative binding energy matrix (eV)
peakdelBEb = zeros(round(je),1);
% Iterate relative binding energy of B (eV)
for k = 1:je % index
   if abs(TOFbvf(k) - peakTOF) < peakTOF/100 % Convergence criterion
      peakdelBEb(k) = delBEbv(k); % Store relative binding energy
   end
end
```

```
% Calculate volcano plot peak position (eV)
peakdelBEb = mean(nonzeros(peakdelBEb));
% Display volcano plot peak results
peakdelBEb; % eV
peakTOF; % 1/sec

% Transition to dynamic catalysis

% Dynamic catalysis parameters
% Oscillation frequency
tau2 = 5e-4; % sec
taur = 1.0; % unitless
tau1 = taur*tau2; % sec
fosc = 1/(tau1 + tau2); % Hz
% Number of oscillations (unitless)
Nosc = round(fosc) + 1;
% Set minimum number of oscillations
if Nosc < 11
   Nosc = 11;
end
% Oscillation endpoints (eV)
delBEb0 = peakdelBEb;
delU = 0.6;
UR = delBEb0 + delU/2.0;
UL = UR - delU;

% Static catalysis calculation
% Starting time
ts = 0;
% Final time
te = 5e3;

% Generate CSTR data
% Reset volumetric flowrate (L/sec)
qdot = qsdot/60000;
% Static catalysis at volcano plot peak
delBEb = delBEb0; % eV

% Start static catalysis timer (sec)
tic

% Iterate until convergence
for n = 1:inf % index

% Generate time span matrix (sec)
% Time interval
ti = te/40;
% Time span matrix
tspan = ts:ti:te;
[t,x] = ode15s('cstr1',tspan,x_ss,opts); % Time and state outputs
```

```
% Parse out the state values
Ca(:,1) = x(:,1); % M
Cb(:,1) = x(:,2); % M

% Measure reactor performance
Yb = (Cb./(Ca + Cb))*100; % mol %

% Converge on C yield of B (mol %)
if abs(Yb(end) - C) > 0.01 % Convergence criterion
   qdot = qdot*Yb(end)/C; % L/sec
   ns = n; % Indicates that static catalysis criterion was not met
   ns; % Display iteration count
   clear t x Ca Cb Yb
else
   % Stop static catalysis timer (sec)
   toc

   % Store static catalysis results
   tsv(:,1) = t; % sec
   Ca_star(:,1) = x(:,3); % gmol
   Cb_star(:,1) = x(:,4); % gmol
   TOFb = Cb*qdot/u; % 1/sec

   % Remove static catalysis data and run
   clear t x

   % Reset volumetric flowrate (L/sec)
   qdot = qsdot/60000;

   break
end
end

% Begin dynamic catalysis

% Initial conditions for dynamic catalysis
x_ss(:,2) = [Ca(end,1);Cb(end,1);Ca_star(end,1);Cb_star(end,1)];

% Start dynamic catalysis timer (sec)
tic

% Iterate until convergence
for n = 1:inf % index
% Begin dynamic catalysis
for l = 2:Nosc % index

% Even numbered oscillations
if mod(l,2) == 0
% Operate at strong binding (eV)
delBEb = UR;
```

```
% Construct new time span matrix (sec)
% Final time
te = tau1;
% Time interval
ti = te/40;
% Time span matrix
tspan = ts:ti:te;
% Generate CSTR data
[t,x] = ode15s('cstr1',tspan,x_ss(:,l),opts); % Time and state outputs

% Parse out the state values
tsv(:,l) = t + tsv(end,l-1); % sec
Ca(:,l) = x(:,1); % M
Cb(:,l) = x(:,2); % M
Ca_star(:,l) = x(:,3); % gmol
Cb_star(:,l) = x(:,4); % gmol

% Initial conditions for the next oscillation
x_ss(:,l+1) = [Ca(end,l);Cb(end,l);Ca_star(end,l);Cb_star(end,l)];
clear t x

% Odd numbered oscillations
else
% Operate at weak binding (eV)
delBEb = UL;
% Construct new time span matrix (sec)
% Final time
te = tau2;
% Time interval
ti = te/40;
% Time span matrix
tspan = ts:ti:te;
% Generate CSTR data
[t,x] = ode15s('cstr1',tspan,x_ss(:,l),opts); % Time and state outputs

% Parse out the state values
tsv(:,l) = t + tsv(end,l-1); % sec
Ca(:,l) = x(:,1); % M
Cb(:,l) = x(:,2); % M
Ca_star(:,l) = x(:,3); % gmol
Cb_star(:,l) = x(:,4); % gmol

% Initial conditions for the next oscillation
x_ss(:,l+1) = [Ca(end,l);Cb(end,l);Ca_star(end,l);Cb_star(end,l)];
clear t x
end
end

% End dynamic catalysis

% Calculate state values (gmol)
```

```
C_star = u - Ca_star - Cb_star;

% Convert units
Pa = Ca*Rg*TK; % bar
Pb = Cb*Rg*TK; % bar
Theta_A_star = Ca_star/u; % unitless
Theta_B_star = Cb_star/u; % unitless
Theta_star = C_star/u; % unitless

% Measure reactor performance
Yb = (Cb./(Ca + Cb))*100; % mol %

% Preallocate TOF matrix
TOFb = [TOFb(:,1),zeros((te/ti)+1,Nosc-1)]; % 1/sec
TOFb(:,2:end) = Cb(:,2:end)*qdot/u; % 1/sec

% Converge on C yield of B (mol %)
% Data at the end of the run
% Time data (sec)
tdiff = [tsv(:,end-1);tsv(:,end)];
% Yield data (mol %)
Ybdiff = [Yb(:,end-1);Yb(:,end)];

% Data in the middle of the run
% Time data (sec)
tdiff2 = [tsv(:,(end-1)/2);tsv(:,(end-1)/2+1)];
% Yield data (mol %)
Ybdiff2 = [Yb(:,(end-1)/2);Yb(:,(end-1)/2+1)];

% Integrate yield of B over 1 oscillation period
% Preallocate integral matrix (sec*mol %)
Ybint = zeros(size(Ybdiff));
% Integration with midpoint Riemann sum
for m = 2:size(tdiff,1)
   Ybint(m) = (tdiff(m) - tdiff(m-1))*mean([Ybdiff(m-1);Ybdiff(m)]);
End

% Preallocate integral matrix (sec*mol %)
Ybint2 = zeros(size(Ybdiff2));
% Integration with midpoint Riemann sum
for p = 2:size(tdiff2,1)
   Ybint2(p) = (tdiff2(p) - tdiff2(p-1))*mean([Ybdiff2(p-1);Ybdiff2(p)]);
end

% Calculate time-averaged yield of B (mol %)
Ybavg = sum(Ybint)*fosc;
Ybavg2 = sum(Ybint2)*fosc;

% Check for convergence
if abs(Ybavg - Ybavg2) > min([Ybavg,Ybavg2])/100 % Convergence criterion 1
   Nosc = round(2*Nosc) + 1; % Adjust number of oscillations
```

```
    nn = n; % Indicates that criterion 1 was not met
    nn; % Display iteration number
    clear tsv(:,2:end) Ca(:,2:end) Cb(:,2:end) Ca_star(:,2:end) Cb_star(:,2:end) x_ss(:,3:end)
else
    if abs(Ybavg - C) > 0.01 % Convergence criterion 2
        qdot = qdot*Ybavg/C; % Adjust volumetric flowrate
        nq = n; % Indicates that criterion 2 was not met
        nq; % Display iteration number
        clear tsv(:,2:end) Ca(:,2:end) Cb(:,2:end) Ca_star(:,2:end) Cb_star(:,2:end) x_ss(:,3:end)
    else
        % Stop dynamic catalysis timer (sec)
        toc

        break
    end
end
end

% Integrate TOF over 1 oscillation period
TOFbdiff = [TOFb(:,end-1);TOFb(:,end)];
% Preallocate TOF integral matrix (unitless)
TOFbint = zeros(size(TOFbdiff));
% Integration with midpoint Riemann sum
for m = 2:size(tdiff,1)
    TOFbint(m) = (tdiff(m) - tdiff(m-1))*mean([TOFbdiff(m-1);TOFbdiff(m)]);
end
% Calculate the time-averaged TOF (1/sec)
TOFbavg = sum(TOFbint)*fosc;

% Display final results
plot(tsv,Yb) % Visually check for convergence
TOFbavg; % 1/sec
```

Dynamic Catalysis Batch Reactor Shell Code with Square or Triangle Waveform

```
% Remove prior data and runs
clear
clc

% Step test for models - CSTR and Batch Reactor

global Rg R TK Caf Cbf qdot w u delHovr alpha beta gamma delta BEb0 delBEb

% Constants:
% Gas constant
Rg = 8.314459848e-2; % L-bar/K-gmol
R = 8.314459848; % J/K-gmol

% Reactor parameters:
% Temperature
Tc = 150; % deg C
```

```
TK = Tc + 273.15; % K

% Feed pressure (bar)
Paf = 100;
Pbf = 0;
% Feed concentration (M)
Caf = Paf/(Rg*TK);
Cbf = Pbf/(Rg*TK);

% Volumetric flowrate
qsdot = 50; % mL/min
qdot = qsdot/60000; % L/sec

% Steady state initial conditions for the states
Ca_ss = Caf; % M
Cb_ss = Cbf; % M
Ca_star_ss = 0; % gmol
Cb_star_ss = 0; % gmol
x_ss = [Ca_ss;Cb_ss;Ca_star_ss;Cb_star_ss];

% Steady state initial condition for the control
u_ss = 0; % gmol active sites
% Open loop step change
% Catalyst weight (mg)
w = 138;
% Active site density (gmol/g catalyst)
srho = 20e-6;
% Active site calculation (gmol)
u = (w/1000)*srho;

% Reaction parameters:
% Overall heat of reaction for A -> B (J/gmol)
delHovr = 0e3;
% Brønsted-Evans-Polanyi relationship parameters
alpha = 0.6; % unitless
beta = 102e3; % J/gmol
% Binding energy relationship parameters
gamma = 0.5; % unitless
delta = 1.4; % eV

% Volcano plot parameter:
% x-axis zero point (eV)
BEb0 = delta + delHovr/96.485e3;

% Volcano plot peak calculation
% Iterate binding energies of A and B (eV)
is = -delta;
ii = 0.01;
ie = delta;
% Preallocate BEb, TOF, and surface coverage matrices
je = ((ie - is)/ii + 1); % final index
```

```
delBEbv = zeros(round(je),1); % eV
TOFbvf = zeros(round(je),1); % 1/sec
Theta_A_starvf = zeros(round(je),1); % unitless
Theta_B_starvf = zeros(round(je),1); % unitless

% Begin iteration (eV)
for i = is:ii:ie
% Set binding energy of B (eV)
delBEb = i; % eV
% Iterate at each binding energy
for n = 1:inf % index

% Final Time (sec)
tfv = 5e100;
% Generate CSTR data
opts = odeset('RelTol',1e-8,'AbsTol',1e-9);
[tv,xv] = ode15s('cstr1',[0 tfv],x_ss,opts); % Time and state outputs

% Parse out the state values (M)
Cav = xv(:,1);
Cbv = xv(:,2);

% Measure reactor performance
Ybv = (Cbv./(Cav + Cbv))*100; % mol %

% Converge on C yield of B (mol %)
C = 1;
if abs(Ybv(end) - C) > 0.01 % Convergence criterion
   qdot = qdot*Ybv(end)/C; % L/sec
   nv = n; % Indicates that volcano criterion was not met
   nv; % Display iteration count
   clear tv xv Cav Cbv Ybv
else
   % Compute matrix index
   j = ((i - is)/ii) + 1; % unitless

   % Parse out state values (gmol)
   Ca_starv = xv(:,3);
   Cb_starv = xv(:,4);

   % Measure reactor performance
   TOFbv = Cbv*qdot/u; % 1/sec

   % Convert units
   Theta_A_starv = Ca_starv/u; % unitless
   Theta_B_starv = Cb_starv/u; % unitless

   % Store volcano plot results
   delBEbv(round(j)) = i; % eV
   TOFbvf(round(j)) = TOFbv(end); % 1/sec
   Theta_A_starvf(round(j)) = Theta_A_starv(end); % unitless
```

```
    Theta_B_starvf(round(j)) = Theta_B_starv(end); % unitless

    clear tv xv Cav Cbv Ybv Ca_starv Cb_starv TOFbv Theta_A_starv Theta_B_starv
    break
end
end
end

% Extract volcano plot peak information
peakTOF = max(TOFbvf); % 1/sec

% Preallocate relative binding energy matrix (eV)
peakdelBEb = zeros(round(je),1);
% Iterate relative binding energy of B (eV)
for k = 1:je % index
    if abs(TOFbvf(k) - peakTOF) < peakTOF/100 % Convergence criterion
        peakdelBEb(k) = delBEbv(k); % Store relative binding energy
    end
end

% Calculate volcano plot peak position (eV)
peakdelBEb = mean(nonzeros(peakdelBEb));
% Display volcano plot peak results
peakdelBEb; % eV
peakTOF; % 1/sec

% Transition to dynamic catalysis

% Dynamic catalysis parameters
% Oscillation frequency
tau2 = 5e0; % sec
taur = 1.0; % unitless
tau1 = taur*tau2; % sec
fosc = 1/(tau1 + tau2); % Hz
% Number of oscillations (unitless)
Nosc = round(fosc) + 1;
% Set minimum number of oscillations
if Nosc < 11
    Nosc = 11;
end
% Oscillation endpoints (eV)
delBEb0 = peakdelBEb;
delU = 1.50;
UR = delBEb0 + delU/2.0;
UL = UR - delU;

% Static catalysis calculation
% Starting time (sec)
ts = 0;
% Final time (sec)
te = 5e3;
```

```
% Generate batch reactor data
% Static catalysis at volcano plot peak
delBEb = delBEb0; % eV

% Start static catalysis timer (sec)
tic

% Iterate until convergence
for n = 1:inf % index

% Generate time span matrix (sec)
% Time interval
ti = te/40;
% Time span matrix
tspan = ts:ti:te;
[t,x] = ode15s('batch1',tspan,x_ss,opts); % Time and state outputs

% Parse out the state values
Ca(:,1) = x(:,1); % M
Cb(:,1) = x(:,2); % M

% Measure reactor performance
Yb = (Cb./(Ca + Cb))*100; % mol %

% Equilibrium yield calculation (mol %)
Yeq = exp(-delHovr/(R*TK))/(1+exp(-delHovr/(R*TK)))*100;

% Converge on equilibrium yield of B (mol %)
if abs(Yb(end) - Yeq) > 0.01 % Convergence criterion
   te = te*2; % sec
   ns = n; % Indicates that static catalysis criterion was not met
   ns; % Display iteration count
   clear t x Ca Cb Yb
else
   % Stop static catalysis timer (sec)
   toc

   % Store static catalysis results
   tsv(:,1) = t; % sec
   Ca_star(:,1) = x(:,3); % gmol
   Cb_star(:,1) = x(:,4); % gmol

   % Remove static catalysis data and run
   clear t x

   break
end
end

% Begin dynamic catalysis
```

```
% Initial conditions for dynamic catalysis
% Feed pressure (bar)
Pafb = rand*(Paf + Pbf);
Pbfb = rand*(Paf + Pbf);
if (Pafb + Pbfb) > (Paf + Pbf)
   Pbfb = Paf + Pbf - Pafb;
end
% Feed concentration (M)
Cafb = Pafb/(Rg*TK);
Cbfb = Pbfb/(Rg*TK);

% Surface coverage (unitless)
Ca_star_b = rand*u;
Cb_star_b = rand*u;
if (Ca_star_b + Cb_star_b) > u
   Cb_star_b = u - Ca_star_b;
end

x_ss(:,2) = [Cafb;Cbfb;Ca_star_b;Cb_star_b];

% Start dynamic catalysis timer (sec)
tic

% Iterate until convergence
for n = 1:inf % index
% Begin dynamic catalysis
for l = 2:Nosc % index

% Even numbered oscillations
if mod(l,2) == 0
% Operate at strong binding (eV)
delBEb = UR;
% Construct new time span matrix (sec)
% Final time
te = tau1;
% Time interval
ti = te/40;
% Time span matrix
tspan = ts:ti:te;
% Generate batch reactor data
[t,x] = ode15s('batch1',tspan,x_ss(:,l),opts); % Time and state outputs

% Parse out the state values
tsv(:,l) = t + tsv(end,l-1); % sec
Ca(:,l) = x(:,1); % M
Cb(:,l) = x(:,2); % M
Ca_star(:,l) = x(:,3); % gmol
Cb_star(:,l) = x(:,4); % gmol

% Initial conditions for the next oscillation
```

```
x_ss(:,l+1) = [Ca(end,l);Cb(end,l);Ca_star(end,l);Cb_star(end,l)];
clear t x

% Odd numbered oscillations
else
% Operate at weak binding (eV)
delBEb = UL;
% Construct new time span matrix (sec)
% Final time
te = tau2;
% Time interval
ti = te/40;
% Time span matrix
tspan = ts:ti:te;
% Generate batch reactor data
[t,x] = ode15s('batch1',tspan,x_ss(:,l),opts); % Time and state outputs

% Parse out the state values
tsv(:,l) = t + tsv(end,l-1); % sec
Ca(:,l) = x(:,1); % M
Cb(:,l) = x(:,2); % M
Ca_star(:,l) = x(:,3); % gmol
Cb_star(:,l) = x(:,4); % gmol

% Initial conditions for the next oscillation
x_ss(:,l+1) = [Ca(end,l);Cb(end,l);Ca_star(end,l);Cb_star(end,l)];
clear t x
end
end

% End dynamic catalysis

% Calculate state values (gmol)
C_star = u - Ca_star - Cb_star;

% Convert units
Pa = Ca*Rg*TK; % bar
Pb = Cb*Rg*TK; % bar
Theta_A_star = Ca_star/u; % unitless
Theta_B_star = Cb_star/u; % unitless
Theta_star = C_star/u; % unitless

% Measure reactor performance
Yb = (Cb./(Ca + Cb))*100; % mol %

% Converge on steady state yield of B (mol %)
% Data at the end of the run
% Time data (sec)
tdiff = [tsv(:,end-1);tsv(:,end)];
% Yield data (mol %)
Ybdiff = [Yb(:,end-1);Yb(:,end)];
```

```
% Data in the middle of the run
% Time data (sec)
tdiff2 = [tsv(:,(end-1)/2);tsv(:,(end-1)/2+1)];
% Yield data (mol %)
Ybdiff2 = [Yb(:,(end-1)/2);Yb(:,(end-1)/2+1)];

% Integrate yield of B over 1 oscillation period
% Preallocate integral matrix (sec*mol %)
Ybint = zeros(size(Ybdiff));
% Integration with midpoint Riemann sum
for m = 2:size(tdiff,1)
   Ybint(m) = (tdiff(m) - tdiff(m-1))*mean([Ybdiff(m-1);Ybdiff(m)]);
End

% Preallocate integral matrix (sec*mol %)
Ybint2 = zeros(size(Ybdiff2));
% Integration with midpoint Riemann sum
for p = 2:size(tdiff2,1)
   Ybint2(p) = (tdiff2(p) - tdiff2(p-1))*mean([Ybdiff2(p-1);Ybdiff2(p)]);
end

% Calculate time-averaged yield of B (mol %)
Ybavg = sum(Ybint)*fosc;
Ybavg2 = sum(Ybint2)*fosc;

% Check for convergence
if abs(Ybavg - Ybavg2) > 0.01 % Convergence criterion
   Nosc = round(2*Nosc) + 1; % Adjust number of oscillations
   nn = n; % Indicates that dynamic catalysis criterion was not met
   nn; % Display iteration number
   clear tsv(:,2:end) Ca(:,2:end) Cb(:,2:end) Ca_star(:,2:end) Cb_star(:,2:end) x_ss(:,3:end)
else
   % Stop dynamic catalysis timer (sec)
   toc

   break
end
end

% Calculate ddG (kJ/gmol)
ddG = -(log(Ybavg/(100-Ybavg)) - log(Yeq/(100-Yeq)))*R*TK/1000;
% Calculate efficiency (%)
eff = abs(ddG/(delU*96.485))*100;

% Display final results
plot(tsv,Yb) % Visually check for convergence
Ybavg; % mol %
ddG; % kJ/gmol
eff; % %
```

Dynamic Catalysis Batch Reactor Shell Code with Sinusoidal Waveform

```
% Remove prior data and runs
clear
clc

% Step test for models - CSTR and batch reactor

global Rg R TK Caf Cbf qdot w u delHovr alpha beta gamma delta BEb0 delBEb tau UR UL tdel

% Constants:
% Gas constant
Rg = 8.314459848e-2; % L-bar/K-gmol
R = 8.314459848; % J/K-gmol

% Reactor parameters:
% Temperature
Tc = 250; % deg C
TK = Tc + 273.15; % K

% Feed pressure (bar)
Paf = 100;
Pbf = 0;
% Feed concentration (M)
Caf = Paf/(Rg*TK);
Cbf = Pbf/(Rg*TK);

% Volumetric flowrate
qsdot = 50; % mL/min
qdot = qsdot/60000; % L/sec

% Steady state initial conditions for the states
Ca_ss = Caf; % M
Cb_ss = Cbf; % M
Ca_star_ss = 0; % gmol
Cb_star_ss = 0; % gmol
x_ss = [Ca_ss;Cb_ss;Ca_star_ss;Cb_star_ss];

% Steady state initial condition for the control
u_ss = 0; % gmol active sites
% Open loop step change
% Catalyst weight (mg)
w = 138;
% Active site density (gmol/g catalyst)
srho = 20e-6;
% Active site calculation (gmol)
u = (w/1000)*srho;

% Reaction parameters:
% Overall heat of reaction for A -> B (J/gmol)
delHovr = 0e3;
```

```
% Brønsted-Evans-Polanyi relationship parameters
alpha = 0.6; % unitless
beta = 135e3; % J/gmol
% Binding energy relationship parameters
gamma = 2.0; % unitless
delta = 1.4; % eV

% Volcano plot parameter:
% x-axis zero point (eV)
BEb0 = delta + (delHovr/96.485e3);

% Volcano plot peak calculation
% Iterate binding energies of A and B (eV)
is = -delta;
ii = 0.01;
ie = delta;
% Preallocate BEb, TOF, and surface coverage matrices
je = ((ie - is)/ii + 1); % final index
delBEbv = zeros(round(je),1); % eV
TOFbvf = zeros(round(je),1); % 1/sec
Theta_A_starvf = zeros(round(je),1); % unitless
Theta_B_starvf = zeros(round(je),1); % unitless

% Begin iteration (eV)
for i = is:ii:ie
% Set binding energy of B (eV)
delBEb = i; % eV
% Iterate at each binding energy
for n = 1:inf % index
% Final Time (sec)
tfv = 5e100;
% Generate CSTR data
options = odeset('RelTol',1e-8,'AbsTol',1e-9);
[tv,xv] = ode15s('cstr1',[0 tfv],x_ss,options); % Time and state outputs

% Parse out the state values (M)
Cav = xv(:,1);
Cbv = xv(:,2);

% Measure reactor performance
Ybv = (Cbv./(Cav + Cbv))*100; % mol %

% Converge on C yield of B (mol %)
C = 1;
if abs(Ybv(end) - C) > 0.01 % Convergence criterion
   qdot = qdot*Ybv(end)/C; % L/sec
   nv = n; % Indicates that volcano criterion was not met
   nv; % Display iteration count
   clear tv xv Cav Cbv Ybv
else
   % Compute matrix index
```

```
    j = ((i - is)/ii) + 1; % unitless

    % Parse out state values (gmol)
    Ca_starv = xv(:,3);
    Cb_starv = xv(:,4);

    % Measure reactor performance
    TOFbv = Cbv*qdot/u; % 1/sec

    % Convert units
    Theta_A_starv = Ca_starv/u; % unitless
    Theta_B_starv = Cb_starv/u; % unitless

    % Store volcano plot results
    delBEbv(round(j)) = i; % eV
    TOFbvf(round(j)) = TOFbv(end); % 1/sec
    Theta_A_starvf(round(j)) = Theta_A_starv(end); % unitless
    Theta_B_starvf(round(j)) = Theta_B_starv(end); % unitless

    clear tv xv Cav Cbv Ybv Ca_starv Cb_starv TOFbv Theta_A_starv Theta_B_starv
    break
end
end
end

% Extract volcano plot peak information
peakTOF = max(TOFbvf); % 1/sec

% Preallocate relative binding energy matrix (eV)
peakdelBEb = zeros(round(je),1);
% Iterate relative binding energy of B (eV)
for k = 1:je % index
    if abs(TOFbvf(k) - peakTOF) < peakTOF/100 % Convergence criterion
        peakdelBEb(k) = delBEbv(k); % Store relative binding energy
    end
end

% Calculate volcano plot peak position (eV)
peakdelBEb = mean(nonzeros(peakdelBEb));
% Display volcano plot peak results
peakdelBEb; % eV
peakTOF; % 1/sec

% Transition to dynamic catalysis

% Dynamic catalysis parameters
% Oscillation frequency
tau = 1e0; % sec
fosc = 1/tau; % Hz
% Number of oscillations (unitless)
Nosc = fosc;
```

```
if Nosc < 11
   Nosc = 11;
end
% Dynamic time span (sec)
tdyn = tau*Nosc*10;
% Oscillation endpoints (eV)
delBEb0 = peakdelBEb;
delU = 0.6;
UR = delBEb0 + delU/2.0;
UL = UR - delU;

% Equilibrium yield calculation (mol %)
Yeq = exp(-delHovr/(R*TK))/(1+exp(-delHovr/(R*TK)))*100;

% Begin dynamic catalysis

% Start dynamic catalysis timer (sec)
tic

% Batch reactor initial conditions
% Feed pressure (bar)
Pbfb = rand*(Paf + Pbf);
Pafb = Paf + Pbf - Pbfb;
% Feed concentration (M)
Cafb = Pafb/(Rg*TK);
Cbfb = Pbfb/(Rg*TK);

% Surface coverage (gmol)
Ca_star_ssb = rand*u;
Cb_star_ssb = rand*u;
if (Ca_star_ssb + Cb_star_ssb) > u
   Cb_star_ssb = u - Ca_star_ssb;
End

% Initial condition array
x_ssb = [Cafb;Cbfb;Ca_star_ssb;Cb_star_ssb];

% Generate batch reactor data
tdel = rand*tau;

% Iterate until convergence
for n = 1:inf
[t,x] = ode15s('sin_batch1',[0 tdyn],x_ssb,options); % Time and state outputs

% Parse out the state values
Ca = x(:,1); % M
Cb = x(:,2); % M

% Measure reactor performance
Yb = (Cb./(Ca + Cb))*100; % mol %
```

```
% Find convergence point
index = zeros(size(Yb));
for l = 1:size(Yb,1)
   if abs(Yb(end)-Yb(l)) > 0.5
      index(l) = l;
   end
end
index = max(index);

if index > size(Yb,1)/2
   tdyn = 2*tdyn;
else
   break
end
end

% Stop dynamic catalysis timer (sec)
toc

% Parse out the state values
Ca_star = x(:,3); % gmol
Cb_star = x(:,4); % gmol
C_star = u - Ca_star - Cb_star; % gmol

% Convert units
Pa = Ca*Rg*TK; % bar
Pb = Cb*Rg*TK; % bar
Theta_A_star = Ca_star/u; % unitless
Theta_B_star = Cb_star/u; % unitless
Theta_star = C_star/u; % unitless

% Track binding energies
delBEbf = (((UR - UL)/2)*(cos(2*pi()*(t-tdel)/tau))) + ((UR + UL)/2);

% Display final results
plot(t,Yb) % Visually check for convergence
```

**Section S2. ODE Solver Selection and Justification**

Matlab ODE solvers were screened for several different reactor types and catalytic systems under static conditions or using a sinusoidal dynamic catalysis waveform. ODE45 is the recommended solver for general use in Matlab, however, this solver failed to generate solutions for static and dynamic catalysis.

Static Catalysis

Stats for ode15s:
452 successful steps
58 failed attempts
1047 function evaluations
39 partial derivatives
131 LU decompositions
851 solutions of linear systems
Elapsed time is 0.159894 seconds.

Stats for ode23s:
2546 successful steps
1197 failed attempts
20218 function evaluations
2546 partial derivatives
3743 LU decompositions
11229 solutions of linear systems
Elapsed time is 1.949530 seconds.

Stats for ode23t:
1143 successful steps
8 failed attempts
2207 function evaluations
8 partial derivatives
106 LU decompositions
2166 solutions of linear systems
Elapsed time is 0.347212 seconds.

Stats for ode23tb:
1054 successful steps
8 failed attempts
2902 function evaluations
5 partial derivatives
99 LU decompositions
3934 solutions of linear systems
Elapsed time is 0.276370 seconds.

Stats for radau:
72 successful steps
72 failed attempts
1377 function evaluations

147 LU decompositions
397 solutions of linear systems
Elapsed time is 0.210526 seconds.
ODE23t and ODE23tb have the least number of failed attempts, but Radau performed most efficiently in terms of number of steps and ODE15s in terms of time to generate the solution. Therefore, ODE15s was used throughout this manuscript to solve CSTR and Batch Reactor equations under static catalysis conditions.

CSTR with Gamma < 1.0 and Sinusoidal Waveform

ODE23s, ODE23tb, and Radau did not converge on a stable sinusoidal CSTR solution after 8 h of computational time.

Stats for ode15s:
18819 successful steps
3682 failed attempts
46463 function evaluations
1291 partial derivatives
5906 LU decompositions
40007 solutions of linear systems
Elapsed time is 7.945276 seconds.

Stats for ode23t:
51424 successful steps
2625 failed attempts
102764 function evaluations
1671 partial derivatives
8781 LU decompositions
94408 solutions of linear systems
Elapsed time is 17.107914 seconds.

ODE23t and has the least number of failed attempts, but ODE15s performed most efficiently in terms of number of steps and time to generate the solution. Therefore, ODE15s was used throughout this manuscript to solve CSTR and Batch Reactor equations under dynamic catalysis conditions.

**Section S3. Static Catalysis Time on Stream Data**

CSTR at 1 % Yield of B

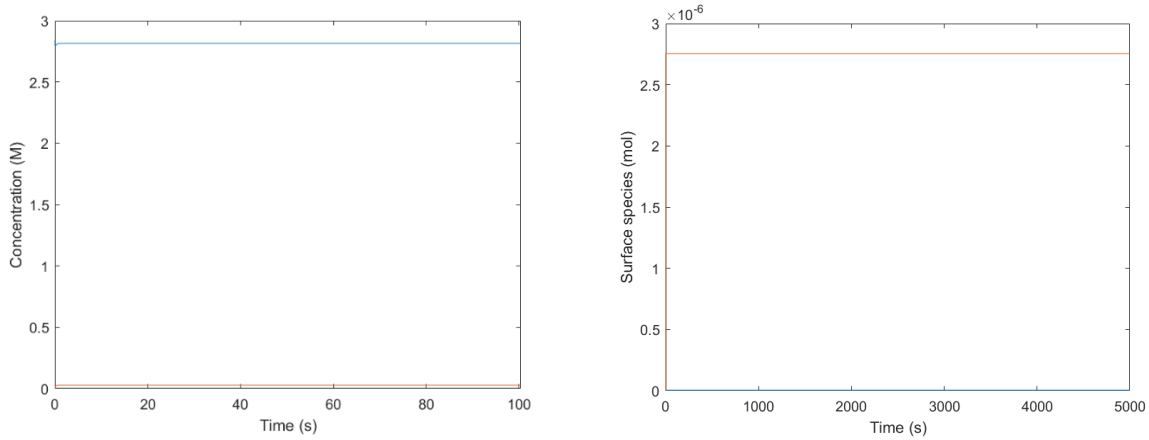


**Figure S1.** Example CSTR time on stream data with **A)** gas phase concentration of A and B and **B)** amount of adsorbed species A* and B*. Conditions: 150 °C, 100 bar, and 1 % yield of B.

Batch Reactor at 50 % Yield of B

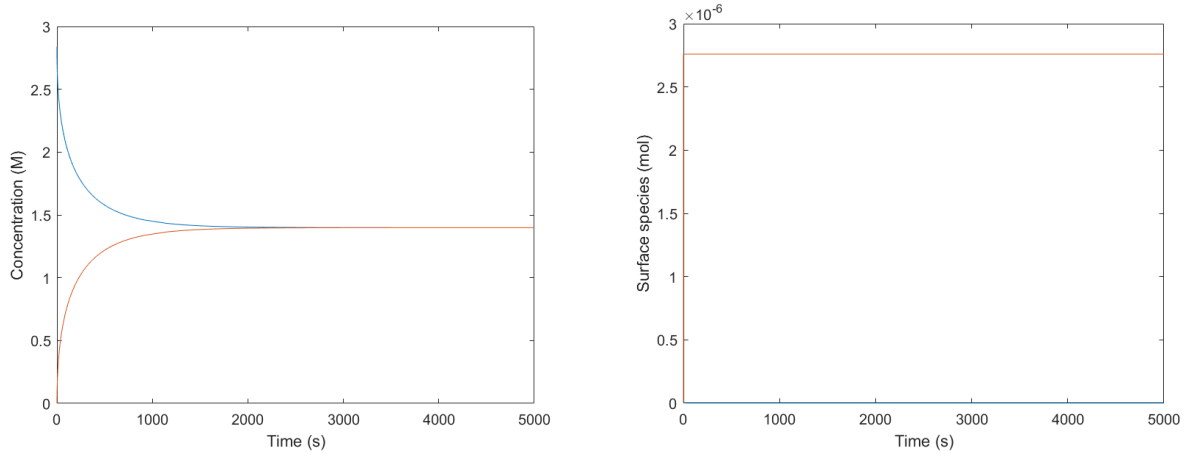


**Figure S2.** Example Batch Reactor time on stream data with **A)** gas phase concentration of A and B and **B)** amount of adsorbed species A* and B*. Conditions: 150 °C, 100 bar, and equilibrium yield of B.

## Section S4. Data from Heatmap Figures

**Table S1.** CSTR TOF (1/s) heatmap data for gamma of 0.5 with varying oscillation endpoints and frequency. Conditions: 100 °C, 100 bar, and 1 % yield of B. Reaction parameters: $\Delta H_{ovr}$ of 0 kJ/mol, alpha of 0.6, beta of 102 kJ/mol, gamma of 0.5, and delta of 1.4 eV. Oscillation amplitude of 1.03 eV.

| | **0** | **-0.10** | **-0.21** | **-0.31** | **-0.41** | **-0.52** | **-0.62** | **-0.72** | **-0.82** | **-0.93** | **-1.03** |
|---|---|---|---|---|---|---|---|---|---|---|---|
| **0.01** | 0.0364 | 0.0256 | 0.0192 | 0.0176 | 0.0188 | 0.0252 | 0.0282 | 0.0281 | 0.0280 | 0.0280 | 0.0280 |
| **0.1** | 0.0364 | 0.0257 | 0.0200 | 0.0187 | 0.0209 | 0.0418 | 0.0644 | 0.0669 | 0.0669 | 0.0669 | 0.0669 |
| **1** | 0.0364 | 0 | 0.0199 | 0.0191 | 0.0315 | 0.1817 | 0.3434 | 0.3620 | 0.3629 | 0.3629 | 0.3629 |
| **10** | 0.0364 | 0 | 0 | 0 | 0.1385 | 1.629 | 3.294 | 3.486 | 3.495 | 3.495 | 3.495 |
| **100** | 0.0364 | 0 | 0 | 0 | 0.7139 | 9.540 | 16.98 | 17.65 | 17.68 | 17.68 | 17.68 |
| **1000** | 0.0364 | 0 | 0 | 0 | 1.020 | 13.88 | 24.02 | 24.84 | 24.88 | 24.88 | 24.88 |
| **10000** | 0.0364 | 0 | 0 | 0 | 0 | 14.51 | 25.00 | 25.83 | 25.87 | 25.87 | 25.87 |
| **100000** | 0.0364 | 0 | 0 | 0 | 0 | 14.55 | 25.06 | 25.89 | 25.93 | 25.93 | 25.93 |

**Table S2.** Batch reactor composition (mol % B) heatmap data for gamma of 2.0 with varying oscillation endpoints and frequency. Conditions: 150 °C, 100 bar, and steady state yield of B. Reaction parameters: $\Delta H_{ovr}$ of 0 kJ/mol, alpha of 0.6, beta of 102 kJ/mol, gamma of 2.0, and delta of 1.4 eV. Oscillation amplitude of 0.5 eV.

| | **-0.2** | **-0.1** | **0.0** | **0.1** | **0.2** | **0.3** | **0.4** | **0.5** | **0.6** | **0.7** | **0.8** |
|---|---|---|---|---|---|---|---|---|---|---|---|
| **0.000001** | 50.00 | 50.00 | 50.00 | 50.00 | 50.01 | 50.01 | 50.02 | 50.01 | 50.00 | 50.00 | 50.00 |
| **0.00001** | 49.98 | 50.00 | 50.00 | 50.01 | 50.02 | 50.09 | 50.22 | 50.14 | 50.07 | 50.04 | 50.01 |
| **0.0001** | 49.99 | 50.00 | 50.00 | 50.01 | 50.06 | 50.66 | 52.61 | 52.73 | 51.24 | 50.44 | 50.21 |
| **0.001** | 49.99 | 50.00 | 50.00 | 50.03 | 50.49 | 55.91 | 69.00 | 69.14 | 63.25 | 57.27 | 53.31 |
| **0.01** | 49.98 | 49.95 | 50.01 | 50.31 | 54.79 | 87.24 | 93.69 | 92.80 | 88.42 | 81.79 | 71.86 |
| **0.1** | 49.99 | 49.92 | 50.10 | 53.06 | 91.80 | 99.02 | 99.18 | 98.79 | 98.29 | 96.97 | 94.09 |
| **1** | 49.17 | 49.26 | 50.44 | 77.73 | 99.65 | 99.84 | 99.79 | 99.61 | 99.52 | 99.34 | 98.61 |
| **10** | 26.00 | 35.62 | 59.77 | 96.98 | 99.78 | 99.95 | 99.94 | 99.91 | 99.88 | 99.88 | 99.90 |
| **100** | 18.43 | 27.60 | 66.32 | 97.21 | 99.79 | 99.96 | 99.97 | 99.97 | 99.97 | 99.97 | 99.97 |

**Table S3.** Batch reactor composition (mol % B) heatmap data for gamma of 2.0 with varying oscillation endpoints and frequency. Conditions: 150 °C, 100 bar, and steady state yield of B. Reaction parameters: $\Delta H_{ovr}$ of 0 kJ/mol, alpha of 0.6, beta of 102 kJ/mol, gamma of 2.0, and delta of 1.4 eV. Oscillation amplitude of 1.0 eV.

| | **0.0** | **0.2** | **0.4** | **0.6** | **0.8** | **1.0** | **1.2** | **1.4** | **1.6** | **1.8** | **2.0** |
|---|---|---|---|---|---|---|---|---|---|---|---|
| **0.000001** | 50.16 | 52.38 | 50.89 | 50.72 | 49.90 | 50.94 | 50.32 | 50.04 | 50.00 | 50.00 | 50.00 |
| **0.00001** | 49.34 | 49.79 | 50.03 | 49.40 | 51.90 | 59.85 | 54.01 | 50.76 | 50.10 | 50.01 | 50.00 |
| **0.0001** | 49.50 | 49.17 | 49.49 | 53.91 | 66.34 | 85.70 | 75.96 | 58.62 | 51.66 | 50.21 | 50.03 |
| **0.001** | 49.23 | 43.99 | 44.88 | 74.52 | 91.44 | 97.69 | 95.55 | 83.97 | 64.31 | 52.56 | 50.62 |
| **0.01** | 45.34 | 22.38 | 37.31 | 92.37 | 99.05 | 99.71 | 98.85 | 97.06 | 90.06 | 72.12 | 56.66 |
| **0.1** | 25.29 | 6.21 | 39.68 | 97.33 | 99.90 | 99.98 | 99.81 | 99.30 | 98.36 | 94.20 | 80.59 |
| **1** | 4.72 | 3.47 | 39.53 | 97.73 | 99.98 | 100.00 | 100.00 | 99.80 | 99.52 | 99.20 | 97.19 |
| **10** | 0.60 | 3.22 | 39.52 | 97.76 | 99.99 | 100.00 | 100.00 | 99.98 | 99.89 | 99.93 | 99.80 |
| **100** | 0.24 | 3.21 | 39.53 | 97.76 | 99.99 | 100.00 | 100.00 | 100.00 | 100.00 | 100.00 | 99.98 |

**Table S4.** Batch reactor composition (mol % B) heatmap data for gamma of 2.0 with varying oscillation endpoints and frequency. Conditions: 150 °C, 100 bar, and steady state yield of B. Reaction parameters: $\Delta H_{ovr}$ of 0 kJ/mol, alpha of 0.6, beta of 102 kJ/mol, gamma of 2.0, and delta of 1.4 eV. Oscillation amplitude of 1.5 eV.

| | **0.0** | **0.3** | **0.6** | **0.9** | **1.2** | **1.5** | **1.8** | **2.1** | **2.4** | **2.7** | **3.0** |
|---|---|---|---|---|---|---|---|---|---|---|---|
| **0.000001** | 49.69 | 49.65 | 50.96 | 50.12 | 47.07 | 51.05 | 50.16 | 50.94 | 50.03 | 50.00 | 50.00 |
| **0.00001** | 49.62 | 49.56 | 59.79 | 53.98 | 50.37 | 47.82 | 52.05 | 59.91 | 50.75 | 50.04 | 50.00 |
| **0.0001** | 49.59 | 47.26 | 83.50 | 84.69 | 57.65 | 52.96 | 66.47 | 84.29 | 58.40 | 50.58 | 50.04 |
| **0.001** | 48.85 | 34.51 | 87.83 | 95.17 | 82.83 | 71.89 | 91.50 | 97.66 | 83.91 | 57.41 | 50.60 |
| **0.01** | 45.46 | 16.37 | 88.55 | 99.29 | 97.63 | 94.39 | 99.11 | 99.53 | 97.37 | 82.14 | 56.66 |
| **0.1** | 25.45 | 11.89 | 88.65 | 99.71 | 99.74 | 99.38 | 99.91 | 99.98 | 99.20 | 97.01 | 80.59 |
| **1** | 4.70 | 11.38 | 88.66 | 99.79 | 99.98 | 99.96 | 99.99 | 100.00 | 99.78 | 99.29 | 97.18 |
| **10** | 0.60 | 11.34 | 88.66 | 99.79 | 99.99 | 99.99 | 100.00 | 100.00 | 99.99 | 99.88 | 99.80 |
| **100** | 0.24 | 11.34 | 88.66 | 99.79 | 100.00 | 100.00 | 100.00 | 100.00 | 100.00 | 100.00 | 99.98 |

**Table S5.** Batch reactor composition (mol % B) heatmap data for gamma of 0.5 with varying oscillation endpoints and frequency. Conditions: 150 °C, 100 bar, and steady state yield of B. Reaction parameters: $\Delta H_{ovr}$ of 0 kJ/mol, alpha of 0.6, beta of 102 kJ/mol, gamma of 0.5, and delta of 1.4 eV. Oscillation amplitude of 0.5 eV.

| | **0.00** | **0.05** | **0.10** | **0.15** | **0.20** | **0.25** | **0.30** | **0.35** | **0.40** | **0.45** | **0.50** |
|---|---|---|---|---|---|---|---|---|---|---|---|
| **0.000001** | 50.00 | 50.00 | 50.00 | 50.00 | 50.00 | 50.00 | 50.00 | 50.00 | 50.00 | 50.00 | 50.00 |
| **0.00001** | 50.00 | 50.00 | 50.00 | 50.00 | 49.99 | 50.00 | 50.00 | 49.99 | 49.99 | 50.00 | 50.00 |
| **0.0001** | 50.02 | 50.01 | 50.00 | 50.00 | 50.00 | 49.98 | 49.93 | 49.89 | 49.88 | 49.91 | 49.93 |
| **0.001** | 50.03 | 50.01 | 50.00 | 50.00 | 49.98 | 49.82 | 49.18 | 48.31 | 47.95 | 48.42 | 49.07 |
| **0.01** | 50.05 | 50.02 | 50.01 | 50.00 | 49.84 | 48.21 | 42.55 | 36.49 | 34.06 | 36.21 | 40.22 |
| **0.1** | 50.05 | 50.02 | 50.01 | 50.00 | 48.39 | 34.44 | 16.94 | 10.54 | 8.884 | 10.47 | 14.46 |
| **1** | 50.06 | 50.02 | 50.01 | 50.00 | 34.60 | 5.573 | 2.340 | 1.447 | 1.363 | 1.663 | 2.249 |
| **10** | 50.06 | 50.02 | 50.01 | 50.00 | 6.778 | 1.030 | 0.5733 | 0.5133 | 0.5231 | 0.5665 | 0.5999 |
| **100** | 73.78 | 75.94 | 74.63 | 49.99 | 5.182 | 0.7511 | 0.4453 | 0.4232 | 0.4231 | 0.4270 | 0.4275 |

**Table S6.** Batch reactor composition (mol % B) heatmap data for gamma of 0.5 with varying oscillation endpoints and frequency. Conditions: 150 °C, 100 bar, and steady state yield of B. Reaction parameters: $\Delta H_{ovr}$ of 0 kJ/mol, alpha of 0.6, beta of 102 kJ/mol, gamma of 0.5, and delta of 1.4 eV. Oscillation amplitude of 1.0 eV.

| | **0.0** | **0.1** | **0.2** | **0.3** | **0.4** | **0.5** | **0.6** | **0.7** | **0.8** | **0.9** | **1.0** |
|---|---|---|---|---|---|---|---|---|---|---|---|
| **0.000001** | 50.23 | 50.09 | 50.01 | 50.00 | 50.00 | 50.00 | 50.00 | 49.99 | 50.00 | 50.00 | 50.00 |
| **0.00001** | 50.38 | 50.34 | 50.18 | 50.04 | 50.00 | 49.98 | 49.93 | 49.83 | 49.95 | 49.99 | 50.00 |
| **0.0001** | 50.39 | 50.39 | 50.42 | 50.53 | 49.92 | 49.67 | 48.74 | 47.04 | 49.16 | 49.80 | 49.94 |
| **0.001** | 50.40 | 50.45 | 51.57 | 55.31 | 48.64 | 45.23 | 37.92 | 29.56 | 40.77 | 46.69 | 49.03 |
| **0.01** | 50.45 | 51.25 | 61.15 | 74.50 | 40.67 | 23.71 | 11.94 | 6.554 | 15.18 | 28.23 | 39.89 |
| **0.1** | 50.98 | 58.15 | 86.67 | 88.18 | 29.33 | 4.267 | 1.654 | 1.140 | 2.470 | 6.000 | 14.06 |
| **1** | 55.70 | 82.71 | 97.77 | 90.43 | 26.52 | 0.7109 | 0.1376 | 0.1313 | 0.6546 | 1.166 | 2.177 |
| **10** | 77.49 | 97.48 | 99.25 | 90.64 | 26.29 | 0.4056 | 0.0190 | 0.0060 | 0.1439 | 0.3561 | 0.3556 |

**Table S7.** Batch reactor composition (mol % B) heatmap data for gamma of 0.5 with varying oscillation endpoints and frequency. Conditions: 150 °C, 100 bar, and steady state yield of B. Reaction parameters: $\Delta H_{ovr}$ of 0 kJ/mol, alpha of 0.6, beta of 102 kJ/mol, gamma of 0.5, and delta of 1.4 eV. Oscillation amplitude of 1.5 eV.

| | **0.0** | **0.1** | **0.2** | **0.3** | **0.4** | **0.5** | **0.6** | **0.7** | **0.8** | **0.9** | **1.0** |
|---|---|---|---|---|---|---|---|---|---|---|---|
| **0.000001** | 50.23 | 50.09 | 50.01 | 50.00 | 50.00 | 50.00 | 50.00 | 49.99 | 50.00 | 50.00 | 50.00 |
| **0.00001** | 50.38 | 50.34 | 50.18 | 50.04 | 50.00 | 49.98 | 49.93 | 49.83 | 49.95 | 49.99 | 50.00 |
| **0.0001** | 50.39 | 50.39 | 50.42 | 50.53 | 49.92 | 49.67 | 48.74 | 47.04 | 49.16 | 49.80 | 49.94 |
| **0.001** | 50.40 | 50.45 | 51.57 | 55.31 | 48.64 | 45.23 | 37.92 | 29.56 | 40.77 | 46.69 | 49.03 |
| **0.01** | 50.45 | 51.25 | 61.15 | 74.50 | 40.67 | 23.71 | 11.94 | 6.554 | 15.18 | 28.23 | 39.89 |
| **0.1** | 50.98 | 58.15 | 86.67 | 88.18 | 29.33 | 4.267 | 1.654 | 1.140 | 2.470 | 6.000 | 14.06 |
| **1** | 55.70 | 82.71 | 97.77 | 90.43 | 26.52 | 0.7109 | 0.1376 | 0.1313 | 0.6546 | 1.166 | 2.177 |
| **10** | 77.49 | 97.48 | 99.25 | 90.64 | 26.29 | 0.4056 | 0.0190 | 0.0060 | 0.1439 | 0.3561 | 0.3556 |

**Table S8.** Batch reactor efficiency (%) heatmap data for gamma of 0.5 with varying oscillation endpoints and amplitudes. Conditions: 150 °C, 100 bar, and steady state yield of B. Reaction parameters: $\Delta H_{ovr}$ of 0 kJ/mol, alpha of 0.6, beta of 102 kJ/mol, gamma of 0.5, and delta of 1.4 eV. Oscillation frequency of 1 Hz.

| | **0.00** | **0.15** | **0.30** | **0.45** | **0.60** | **0.75** | **0.90** | **1.05** | **1.20** | **1.35** | **1.50** |
|---|---|---|---|---|---|---|---|---|---|---|---|
| **0.00** | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 |
| **0.15** | -0.0002 | -0.3224 | -7.612 | -12.61 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 |
| **0.30** | 0.0063 | -0.2547 | -10.52 | -13.65 | -7.409 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 |
| **0.45** | 0.0957 | -0.1519 | -13.02 | -14.85 | -9.846 | -4.949 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 |
| **0.60** | 0.7986 | 1.962 | -12.27 | -13.79 | -10.44 | -7.394 | -3.712 | 0.0000 | 0.0000 | 0.0000 | 0.0000 |
| **0.75** | 1.102 | 10.88 | -3.757 | -15.71 | -11.01 | -9.258 | -5.915 | -2.970 | 0.0000 | 0.0000 | 0.0000 |
| **0.90** | 0.9411 | 11.04 | 6.624 | -10.38 | -13.63 | -9.247 | -7.573 | -4.930 | -2.482 | 0.0000 | 0.0000 |
| **1.05** | 0.7954 | 9.554 | 7.996 | -3.502 | -10.48 | -11.81 | -8.199 | -6.612 | -4.215 | -2.121 | 0.0000 |
| **1.20** | 0.6960 | 8.368 | 7.056 | -2.714 | -7.385 | -9.223 | -10.07 | -7.027 | -5.786 | -3.695 | -1.856 |
| **1.35** | 0.6186 | 7.438 | 6.273 | -2.407 | -7.558 | -6.842 | -8.202 | -8.949 | -5.629 | -5.143 | -3.283 |
| **1.50** | 0.5568 | 6.694 | 5.646 | -2.167 | -7.130 | -8.343 | -6.162 | -7.360 | -8.183 | -5.066 | -4.629 |

**Section S5. Binding Energy Derivation**

In this section, we demonstrate that the binding energies of A and B can be calculated at any point by using the definitions of $\Delta H_{ovr}$, gamma, and delta.

Definitions for gamma and delta are summarized in Equations S1 and S2:

$$\gamma \equiv \frac{\Delta BE_B}{\Delta BE_A} \qquad \text{(S1)}$$

$$when\ BE_A = \delta, BE_B = \delta + \Delta H_{ovr} \quad \text{(S2)}$$

Equation S1 can be integrated with an indefinite integral to obtain Equation S3:

$$BE_B = \gamma BE_A + C \qquad \text{(S3)}$$

After plugging Equation S2 into Equation S3, the constant of integration is obtained:

$$C = (1-\gamma)\delta + \Delta H_{ovr} \qquad \text{(S4)}$$

Equation S4 can therefore be substituted into Equation S3 to define a relationship between the binding energies of A and B at any point.

$$BE_B = \gamma BE_A + (1-\gamma)\delta + \Delta H_{ovr} \quad \text{(S5)}$$

Alternatively, Equation S5 may be rearranged to calculate the binding energy of A from a known binding energy of B.

$$BE_A = (BE_B - (1-\gamma)\delta - \Delta H_{ovr})/\gamma \qquad \text{(S6)}$$