

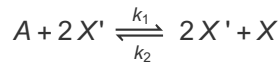
12.C. The Schlogl Model

The Schlogl model is of interest because it exhibits a 1st order phase transition as described by the van der Waals equation. It consists of a chain of two chemical reactions



where X is an auto-catalysis in reaction (12.43a).

As in Ex.12.1, we treat (12.43a) as



to get

$$J_1^c = \frac{d c_X}{d t} = \left(k_1 c_A c_X^2 - k_2 c_X^2 c_X \right)_{c_X = c_X} = k_1 c_A c_X^2 - k_2 c_X^3 \quad (12.43c)$$

$$= -\frac{d c_A}{d t} = -\left(-k_1 c_A c_X^2 + k_2 c_X^2 c_X \right)_{c_X = c_X} = -\left(-k_1 c_A c_X^2 + k_2 c_X^3 \right) \quad (12.43d)$$

and

$$J_2^c = \frac{d c_B}{d t} = k_3 c_X - k_4 c_B \quad (12.43e)$$

$$= -\frac{d c_X}{d t} = -\left(-k_3 c_X + k_4 c_B \right) \quad (12.43f)$$

The (unconstrained) steady states are given by

$$J_\alpha^c = 0 \quad \forall \alpha$$

i.e.,

$$k_1 c_A c_X^2 - k_2 c_X^3 = 0 \quad \text{and} \quad k_3 c_X - k_4 c_B = 0 \quad (12.44)$$

The solutions to (12.44) are

$$c_X^{\text{eq}} = 0 \quad c_B^{\text{eq}} = 0 \quad (12.44a)$$

and

$$c_X^{\text{eq}} = \frac{k_1}{k_2} c_A^{\text{eq}} \quad c_B^{\text{eq}} = \frac{k_3}{k_4} c_X^{\text{eq}} = \frac{k_3}{k_4} \frac{k_1}{k_2} c_A^{\text{eq}} \quad (12.44b)$$

where, for both cases,

$$c_A^{\text{eq}} = \text{arbitrary} \quad (12.44c)$$

Since steady state (12.44a) does not support any chemical reactions, it is of no interest to us.

Assuming ideal gases, the affinities for steady state (12.44b) are [see (12.30g)],

$$A_1^{\text{eq}} = R T \ln \left(\frac{k_2}{k_1} \frac{(c_X^{\text{eq}})^3}{c_A^{\text{eq}} (c_X^{\text{eq}})^2} \right) \quad [\text{For reaction (12.43a).}] \quad (12.44d)$$

$$= R T \ln \left(\frac{k_2}{k_1} \frac{c_X^{\text{eq}}}{c_A^{\text{eq}}} \right) = 0 \quad [(12.44b) \text{ used.}]$$

$$A_2^{\text{eq}} = R T \ln \left(\frac{k_4}{k_3} \frac{c_B^{\text{eq}}}{c_X^{\text{eq}}} \right) \quad [\text{For reaction (12.43b).}]$$

$$= 0 \quad [(12.44b) \text{ used. }]$$

Hence, (12.44b) is the state of thermodynamic equilibrium. The ratio of the concentrations are therefore constants given solely by the rate constants. For example,

$$R_{AB}^{\text{eq}} = \frac{c_A^{\text{eq}}}{c_B^{\text{eq}}} = \frac{k_2 k_4}{k_1 k_3} \quad [(12.44b) \text{ used. }] \quad (12.45)$$

As in Exercise 12.1, we allow only the concentration c_X of the auto-catalysis to vary freely and hold c_A and c_B fixed at some non-equilibrium values

$$c_A = c_A^0 \quad c_B = c_B^0 \quad (12.46a)$$

Since both reactions cause changes in c_X , the total change rate of c_X is the sum of (12.43c) & (12.43f), giving

$$\frac{d c_X}{d t} = k_1 c_A^0 c_X^2 - k_2 c_X^3 - k_3 c_X + k_4 c_B^0 \quad (12.46)$$

The steady states are therefore solutions to the cubic equation

$$c_X^3 - \frac{k_1}{k_2} c_A^0 c_X^2 + \frac{k_3}{k_2} c_X - \frac{k_4}{k_2} c_B^0 = 0 \quad (12.47a)$$

Setting

$$a = k_1 c_A^0 \quad b = k_4 c_B^0 \quad (12.47b)$$

(12.46 & 47a) become

$$\frac{d c_X}{d t} = -k_2 c_X^3 + a c_X^2 - k_3 c_X + b \quad (12.47c)$$

$$c_X^3 - \frac{a}{k_2} c_X^2 + \frac{k_3}{k_2} c_X - \frac{b}{k_2} = 0 \quad (12.47d)$$

Since the signs of the coefficients in (12.47d) are the same as those in the van der Waals equation [see (3.41) of §3.D.4], they share the same qualitative behavior. The Schlogl model thus contains a 1st order phase transition, as advertised previously.

Comparing (12.47) with (3.41) leads to the correspondence

$$k_2 \leftrightarrow P \quad c_X \leftrightarrow v$$

The $v(P)$ diagram in Fig.3.9 thus corresponds to the $c_X(k_2)$ plot of (12.47a) for given values of $(k_1, k_3, k_4, c_A^0, c_B^0)$, as shown in Fig.12.1 below.

Comment: Since all reaction rates and concentrations must be real and non-negative, the pair of variables (c_X, b) used by Reichl are inappropriate for our purposes since they become negative in the region that exhibits 1st order phase transition. Furthermore, keeping a & κ constant in Reichl's (12.47) means that (c_X, b) is equivalent to (c_X, c_B) , which is clearly not a conjugate pair like (v, P) . On the other hand, since (c_X, A_1) is a conjugate pair, so is (c_X, k_2) [c.f. (12.44d)].

Solving the cubic equation (12.47d) for c_X , we obtain 3 branches of the multi-valued function $c_X(k_2)$. Since the coefficients are all real, complex roots of (12.47d) must occur in complex conjugate pairs. Therefore, either 1 or all 3 branches of $c_X(k_2)$ can be real.

A typical 3-branch scenario is shown in Fig.12.1 [c.f. Fig.3.9 of §3.D.4]. As will be proved later [see (12.49c-d)], steady states on the branch (in green) with $c_X^- < c_X < c_X^+$ are unstable while those on the other two branches (in green and blue) are stable. Transition between states of the same k_2 but differ-

ent stable branches is 1st order because c_X is changed discontinuously. The region $k_2^- < k_2 < k_2^+$ or $c_X^- < c_X < c_X^0$ is the coexistence region where steady states on both stable branches can coexist. This means for a given k_2 in the interval (k_2^-, k_2^+) , c_X can be any value in the interval (c_X^-, c_X^0) . The actual value of c_X depends on how (or history) the system is prepared. The system thus exhibits hysteresis behavior.

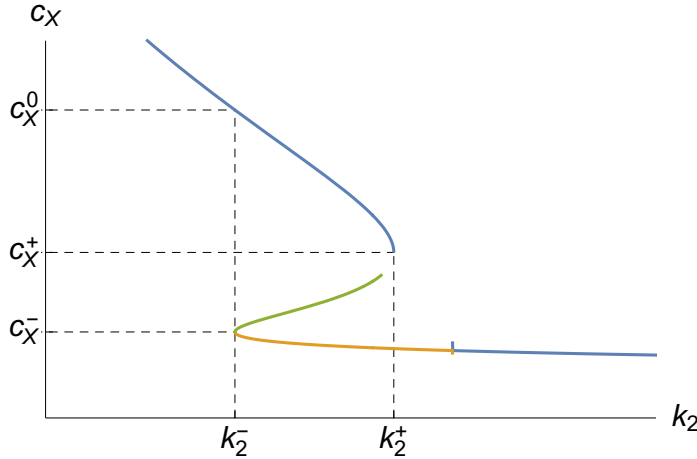


Fig.12.1. $c_X(k_2)$ in the 3 branches regime. Steady states on the branch (in green) with $c_X^- < c_X < c_X^+$ are unstable. The interval (c_X^-, c_X^0) marks the coexistent region.

Mathematically, it is easier to study the function

$$k_2(c_X) = \frac{a}{c_X} - \frac{k_3}{c_X^2} + \frac{b}{c_X^3} \quad (12.48a)$$

since it is single-valued. The extrema of $k_2(c_X)$ are roots of the equation

$$\frac{dk_2}{dc_X} = -\frac{a}{c_X^2} + 2\frac{k_3}{c_X^3} - 3\frac{b}{c_X^4} = 0 \quad (12.48b)$$

$$\text{i.e., } c_X^\pm = \frac{1}{a} \left(k_3 \pm \sqrt{k_3^2 - 3ab} \right) \quad (12.49a)$$

Since all quantities are real and non-negative, $k_2(c_X)$ has two extrema, which means $c_X(k_2)$ is 3-valued, only if

$$k_3^2 \geq 3ab \quad \rightarrow \quad k_3^2 \geq 3k_1k_4c_A^0c_B^0 \quad [(12.47b) \text{ used. }] \quad (12.49b)$$

which is also the criteria for hysteresis behavior.

For a given value of $ab = k_1k_4c_A^0c_B^0$, we can map out the hysteresis region in a plot of $k_2^\pm = k_2(c_X^\pm)$ vs k_3 , as shown in Fig.12.2.

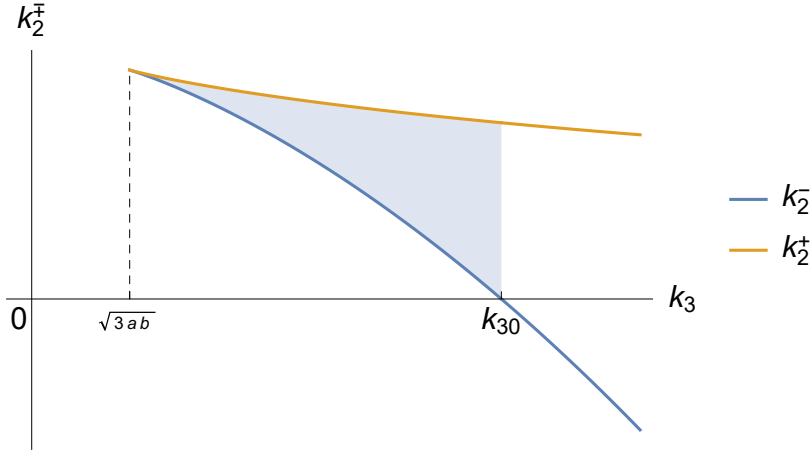


Fig.12.2. Hysteresis region (shaded region) is bounded by the curves $k_2^\pm \geq 0$. k_{30} is given by $k_2^-(k_{30}) = 0$. A plot of $k_2(c_X)$ is shown in Fig.12.1a.

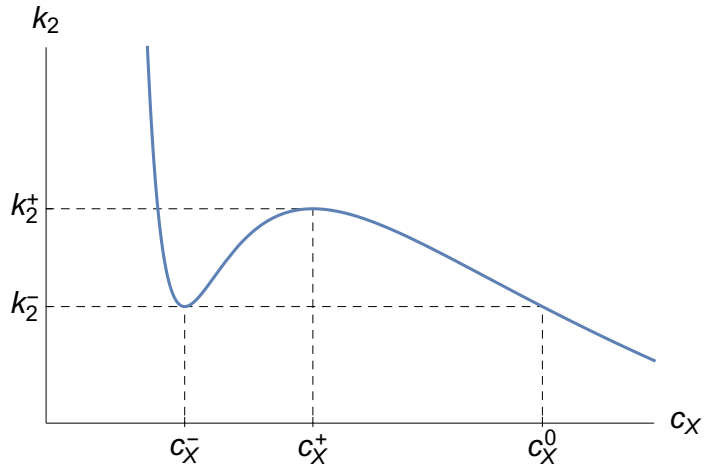


Fig.12.1a. $k_2(c_X)$ in the two extrema regime. The interval (c_X^-, c_X^0) is the coexistent region.

Stability of the steady states can be established using the linear stability theory. Setting

$$c_X = \bar{c}_X + \epsilon \quad k_2 = \bar{k}_2$$

where \bar{c}_X is a steady state, (12.47c) becomes, to $O(\epsilon)$,

$$\begin{aligned} \frac{d\epsilon}{dt} &= (-3\bar{k}_2\bar{c}_X^2 + 2a\bar{c}_X - k_3)\epsilon \\ &\equiv \beta\epsilon \end{aligned}$$

where

$$\begin{aligned} \beta &= -3k_2\bar{c}_X^2 + 2a\bar{c}_X - k_3 \\ &= -3\left(\frac{a}{\bar{c}_X} - \frac{k_3}{\bar{c}_X^2} + \frac{b}{\bar{c}_X^3}\right)\bar{c}_X^2 + 2a\bar{c}_X - k_3 \\ &= -a\bar{c}_X + 2k_3 - 3\frac{b}{\bar{c}_X} \\ &= \bar{c}_X^3 \frac{dk_2}{d\bar{c}_X} \end{aligned}$$

[(12.48b) used.]

$$= -\frac{1}{\bar{c}_X} (\bar{c}_X - c_X^+) (\bar{c}_X - c_X^-) \quad [(12.49a) \text{ used. }]$$

Hence,

$$\begin{aligned} \beta < 0 & \text{ for } \bar{c}_X > c_X^+ \text{ or } \bar{c}_X < c_X^- \rightarrow \text{steady state is stable (12.49c)} \\ \beta > 0 & \text{ for } c_X^- < \bar{c}_X < c_X^+ \rightarrow \text{steady state is unstable (12.49d)} \end{aligned}$$

Code

```
In[1]:= K2[cX_] := a/cX - k3/cX^2 + b/cX^3
```

```
In[2]:= solp = Solve[K2'[cX] == 0, cX];
cxE = cX /. solp
```

```
Out[3]= { (k3 - sqrt(-3 a b + k3^2))/a, (k3 + sqrt(-3 a b + k3^2))/a }
```

```
In[4]:= K2''[cX] /. solp // Simplify
```

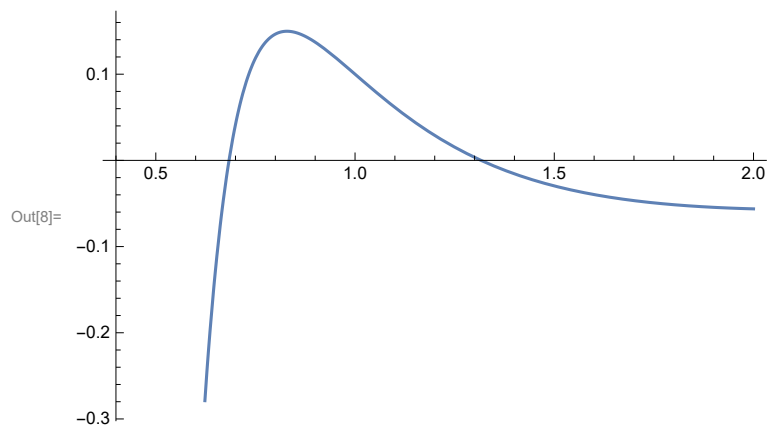
```
Out[4]= { (2 a^4 (-3 a b + k3 (k3 - sqrt(-3 a b + k3^2)))) / ((-k3 + sqrt(-3 a b + k3^2))^5), - (2 a^4 (-3 a b + k3 (k3 + sqrt(-3 a b + k3^2)))) / ((k3 + sqrt(-3 a b + k3^2))^5) }
```

```
In[5]:= par = {a -> 1, k3 -> 1, b -> .3};
cxE /. par
```

```
Out[6]= {0.683772, 1.31623}
```

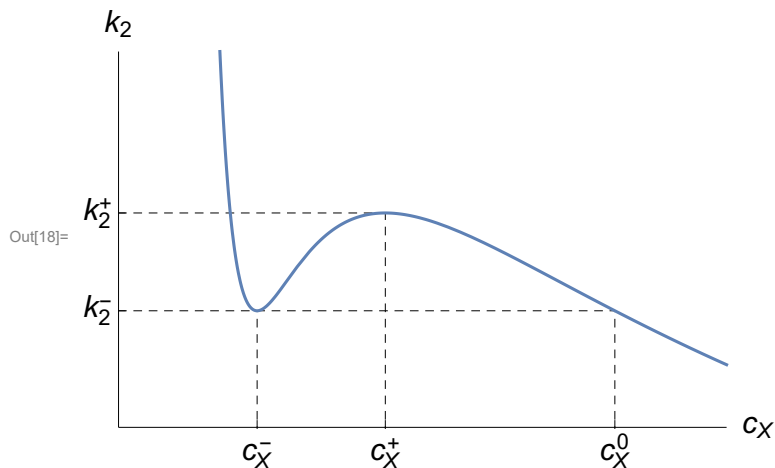
```
In[7]:= fp = K2'[cX] /. par
Plot[fp, {cX, .4, 2}]
```

```
Out[7]= -0.9/cX^4 + 2/cX^3 - 1/cX^2
```



```
In[9]:= eq := cx3 -  $\frac{a}{k_2}$  cx2 +  $\frac{k_3}{k_2}$  cx -  $\frac{b}{k_2}$  == 0;
sol = Solve[eq, cx] // Simplify;
cxL = cx /. sol;
lst = cxL /. par;
```

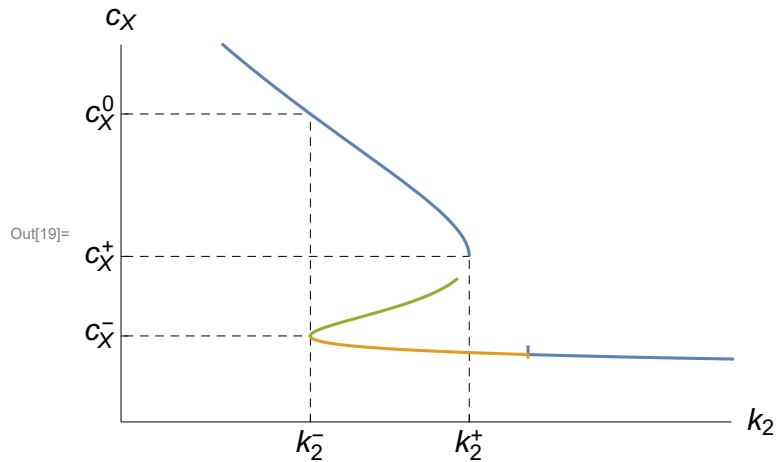
```
In[13]:= f = K2[cX] /. par;
lst = cxL /. par;
cx0 = lst[[1]] /. k2 -> K2[cxE[[1]]] /. par;
tic = {{cxE[[1]], "CX-"}, {cxE[[2]], "CX+"}, {cx0, "CX0"}} /. par;
tick = {{K2[cxE[[1]]], "k2-"}, {K2[cxE[[2]]], "k2+"}} /. par;
Plot[f, {cX, .2, 3}, PlotRange -> {{0, 3}, {0.2, .4}},
  AxesLabel -> {"CX", "k2"}, Ticks -> {tic, tick},
  Prolog -> {Dashed, Line[{{cxE[[1]], 0}, {cxE[[1]], f /. cX -> cxE[[1]]}] /. par],
  Line[{{cxE[[2]], 0}, {cxE[[2]], f /. cX -> cxE[[2]]}] /. par],
  Line[{{0, K2[cxE[[1]]]}, {cx0, K2[cxE[[1]]]}] /. par],
  Line[{{0, K2[cxE[[2]]]}, {cxE[[2]], f /. cX -> cxE[[2]]}] /. par],
  Line[{{cx0, 0}, {cx0, K2[cxE[[1]]]}] /. par]
}]
```



```

In[19]:= Plot[lst, {k2, .2, .5}, PlotRange -> {{.2, .4}, {0, 3}},
  AxesLabel -> {"k2", "cX"}, Ticks -> {tick, tic},
  Prolog -> {Dashed, Line[{{0, cxE[[1]]}, {f /. cX -> cxE[[1]], cxE[[1]]} /. par],
    Line[{{0, cxE[[2]]}, {f /. cX -> cxE[[2]], cxE[[2]]} /. par],
    Line[{{K2[cxE[[1]]], 0}, {f /. cX -> cxE[[1]], cx0} /. par],
    Line[{{K2[cxE[[2]]], 0}, {f /. cX -> cxE[[2]], cxE[[2]]} /. par],
    Line[{{0, cx0}, {K2[cxE[[1]]], cx0} /. par]}]

```



```

In[115]:= k30 = k3 /. (NSolve[K2[cxE[[1]]] == 0 /. par0, k3] // Flatten)

```

Out[115]= 1.09545

```

In[317]:= par0 = {a → 1, b → 0.3};
k3E =  $\sqrt{3 a b}$  /. par0;
g = (K2[#1] &) /@ cxE /. par0;
gE = g[[1]] /. k3 → k3E;
ticx = {{k3E, " $\sqrt{3 a b}$ "}, {k30, "k30"}; ticy = {{gE, "k30"};
p1 = Plot[g // Evaluate, {k3, 0.91, k30}, Filling → {1 → {2}}, PlotLegends → {"k2-", "k2+"}];
p2 = Plot[g, {k3, k30, 1.05 k30}];
p3 = Graphics[{Dashed, Line[{{k3E, 0}, {k3E, gE}}],
Text["0", {.905, -.03}]}];
Show[{p1, p2, p3}, PlotRange → All, AxesLabel → {"k3", "k2±"}, Ticks → {ticx, None}]

```

