

Phase-Plane Analysis

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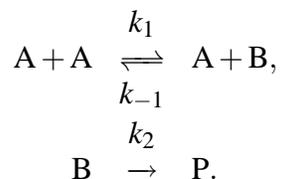
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1 Introduction

Phase-plane analysis is a set of techniques for analyzing the behavior of a dynamical system described by a pair of ordinary differential equations (ODEs). This sounds a bit limiting, but the fact is that there are quite a few dynamical systems which can be described this way, either directly or because they can be reduced to a pair of ODEs using methods which we will discuss later. Furthermore, the ideas we develop here will form a foundation for analyzing higher-dimensional systems.

2 The Lindemann mechanism

Phase-plane analysis is much easier to handle by example than any other way. We will therefore immediately consider an example, namely the Lindemann mechanism for gas-phase unimolecular reactions (e.g. isomerizations and decompositions):



In this reaction, A is the reactant, B is an energized molecule of A (usually denoted A^* in kinetics textbooks) and P is the product of the reaction.

Our objective is to study the dynamics of this mechanism. Over time, I have developed a notation which I think is quite helpful in treating abstract reaction

mechanisms. I simply denote the concentration of a species by the equivalent upper-case letter. Thus A is the concentration of A, which chemists would normally write $[A]$. Note that concentrations and pressures are proportional to each other, so that we don't have to distinguish these. One obvious advantage of this notation is that it saves us writing a lot of square brackets. The other will become clear in due course.

According to the law of mass action, the rate equations for this mechanism are

$$\frac{dA}{dt} = -k_1A^2 + k_{-1}AB, \quad (1a)$$

$$\frac{dB}{dt} = k_1A^2 - k_{-1}AB - k_2B, \quad (1b)$$

$$\frac{dP}{dt} = k_2B. \quad (1c)$$

This is a dynamical system. The differential equations give the rule for evolving this system forward in time. The state space is the concentration vector (A, B, P) . However, we don't need all three of these concentrations to fully define the state of the system. Why? Note that

$$\frac{dA}{dt} + \frac{dB}{dt} + \frac{dP}{dt} = 0.$$

Since

$$\frac{dA}{dt} + \frac{dB}{dt} + \frac{dP}{dt} = \frac{d}{dt}(A + B + P),$$

we can conclude that $A + B + P$ is a constant. Since we normally start experiments with just pure A, this constant is the initial amount of A, usually denoted A_0 :

$$A + B + P = A_0. \quad (2)$$

We can therefore eliminate (say) P from our set of equations. This is a convenient choice since the product-forming step is treated as irreversible¹ so that P doesn't appear in any of our ODEs. If this were not the case, we would just solve equation 2 for P and substitute the result into the ODEs for A and B . In any event, our original dynamical system therefore reduces to just two equations, namely equations

¹This is a good approximation for many reactions, but is inconsistent with the law of microscopic reversibility.

1a and 1b. If at some point we want to calculate P , we can get it from equation 2. In other words, the minimum number of variables required to describe the behavior of the Lindemann mechanism is two, which are most conveniently chosen to be A and B . The subsystem of the original Lindemann equations 1 consisting of the corresponding two-component state vector and of its equations is itself a dynamical system. This is the system which we will study here.

We were able to eliminate P because of mass conservation. We wrote the Lindemann mechanism assuming a single product. The mechanism as we wrote it therefore describes an isomerization. The conservation equation 2 is just a statement that all the atoms of A eventually end up in P after passing through the intermediate form B . Since mass conservation is a universal law, it is always possible to eliminate some variables using this principle. In general, there are as many independent concentrations in a mechanism as there are chemical steps. In the Lindemann mechanism, there are two chemical steps, so we have two independent concentrations. There can be additional variables. For instance, if the reaction is not held at constant temperature, the temperature is also a variable.

3 Dimensionless variables

We could work with equations 1a and 1b exactly as they are. However, it's generally a good idea to rescale the variables. We will talk about rescaling in much more detail later. For now, all we need to know is that rescaling involves a change of measurement scales based on quantities contained within the equations themselves. The result is a set of equations in which all the remaining quantities are dimensionless. There can be many different reasons to rescale equations, and different scalings are appropriate to different purposes. For now, we'll focus on one benefit of scaling: It can reduce the number of parameters (constants) in our equations. This makes analysis a great deal easier.

A scaling analysis starts by writing down the units of all quantities appearing in the equations. The pressures of A and B might be measured in bar, and time could be measured in seconds. (It doesn't actually matter what we pick as our "initial" measurement units.) Then we have

$$\begin{array}{ll} A, B: \text{bar} & t: \text{s} \\ k_1, k_{-1}: \text{bar}^{-1}\text{s}^{-1} & k_2: \text{s}^{-1} \end{array}$$

Next, we try to make up some combinations which define new dimensionless variables. Given our current purpose, it doesn't matter which of several arbitrary

choices we make. In order to make it easier to read the equations I'm deriving, I usually use lower-case letters for the dimensionless variables, and something reasonably obvious (e.g. τ) for the dimensionless time. Here are my choices:

$$\begin{aligned} a &= k_1 A / k_2, \\ b &= k_1 B / k_2, \\ \tau &= k_2 t. \end{aligned}$$

Next, we substitute our new variables into the original ODEs. For instance, equation 1a becomes

$$\begin{aligned} \frac{d\left(\frac{k_2 a}{k_1}\right)}{d(\tau/k_2)} &= -k_1 \left(\frac{k_2 a}{k_1}\right)^2 + k_{-1} \left(\frac{k_2 a}{k_1}\right) \left(\frac{k_2 b}{k_1}\right). \\ \therefore \frac{da}{d\tau} &= -a^2 + \frac{k_{-1}}{k_1} ab. \end{aligned}$$

Note that k_{-1}/k_1 is also a dimensionless parameter. Let's give it a name:

$$\alpha = k_{-1}/k_1.$$

The evolution equation for a is therefore

$$\frac{da}{d\tau} = -a^2 + \alpha ab.$$

We can do the same thing with equation 1b:

$$\frac{db}{d\tau} = a^2 - \alpha ab - b.$$

We started out with a system with three parameters (the three rate constants). We're down to one parameter. The number of parameters eliminated is usually equal to the number of different measurement scales in the original equations. In this case, we had pressure and time as our basic units, so we lost two parameters.

Borrowing a notation frequently seen in mechanics, we typically denote the time rate of change of a quantity by a dot. Here, I will use dots to denote the derivative with respect to τ . Thus we have

$$\dot{a} = -a^2 + \alpha ab, \tag{3a}$$

$$\dot{b} = a^2 - \alpha ab - b. \tag{3b}$$

4 The vector field

At any time t , the state can be represented by a point $\mathbf{x} = (a, b)$. Imagine that we plot the state of the system in the (a, b) plane, a space which we will call the system's **phase space** or, in the two-dimensional case under consideration, the **phase plane**.² At any given time, the state is a point in this plane. If we draw the sequence of points through which the system passes as it evolves, we will draw out a continuous curve called a **trajectory** or **orbit**.

Now suppose that we just wanted to roughly sketch the trajectories. We could proceed as follows: Equations 3 give us the magnitude and direction of change of our two variables at any point in the phase plane. In other words, we can think of the vector $\mathbf{v} = (\dot{a}, \dot{b})$ as a kind of velocity vector for our dynamical system. All we have to do is to follow where these vectors lead us, and we should be able to determine what the trajectory looks like starting from a particular point in the phase plane. Better yet, if we draw a whole bunch of these velocity vectors in our phase plane, we might get a general idea of what all the possible trajectories look like as a set. If we imagine putting a velocity vector at every point in phase space—clearly, we can't do that, but just imagine that we can—then we have the **vector field** corresponding to our dynamical system. The set of all trajectories implied by this vector field is the **flow**.

We started out with a dynamical system, which by definition involves a time evolution. Talking about the shapes of trajectories in the phase plane in some sense takes time out of the picture. Why would we want to do that? It turns out that a lot of the properties of **autonomous** differential equations (ones which don't have an explicit t in their right-hand sides) are much easier to understand if we focus on the flow in phase space rather than on the time evolution.

Our vector field has an **equilibrium point**, also known as a **stagnation point** or **steady state**. These terms are all interchangeable and refer to a point where the velocity vector vanishes and where the system can therefore be at rest. We can find the equilibrium point by solving the equations $\dot{a} = \dot{b} = 0$. In this case however, we can recognize the equilibrium point by inspection: It is the point $(0,0)$. Identifying equilibria (there can be more than one in some types of systems, although not in closed chemical systems) is an important part of the analysis.

It's fairly easy to draw a representative set of the velocities of our vector field. This can be done using software, but let's try it out by hand to get used to the

²These terms are borrowed from mechanics. I've never seen an explanation of how the word "phase" got associated with this concept, although I can imagine how it might have happened.

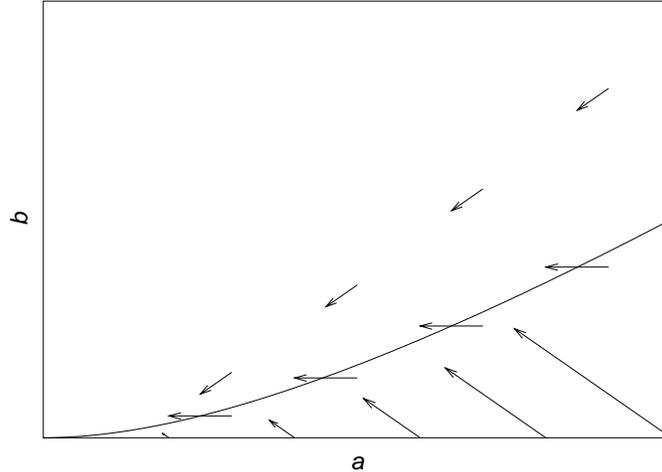


Figure 1: First details of the phase plane behavior of the Lindemann mechanism. The solid curve is the b nullcline.

ideas.

Suppose that we start with a set of points along the a axis, i.e. points for which $b = 0$. The velocity vector along this axis reduces to $\mathbf{v} = (-a^2, a^2)$, i.e. it points up and to the left. If I follow this vector, a will decrease and b will increase. Eventually (equations 3), the positive and negative terms in \dot{b} will balance and \dot{b} will equal zero. This has to happen before \dot{a} becomes zero, because \dot{b} has an extra negative term. The trajectory will become momentarily horizontal, while a continues to decrease. The time derivative \dot{b} will then become negative, and the velocity vector will therefore point down and to the left. The curve which separates vectors with the sign pattern $(-, +)$ from those with sign pattern $(-, -)$ and on which $\dot{b} = 0$ can be calculated in the obvious way from equation 3b. We use the subscript \mathcal{B} to denote this special curve:

$$b_{\mathcal{B}} = \frac{a^2}{\alpha a + 1}.$$

This curve is called the b **nullcline**. The root “cline” has to do with slopes. The meaning of this word is thus clear: It is the curve on which b (in this case) has a zero slope. Figure 1 shows the arrows we have described so far, along with the b nullcline. Note that I didn’t bother to draw all the arrows to scale. In principle,

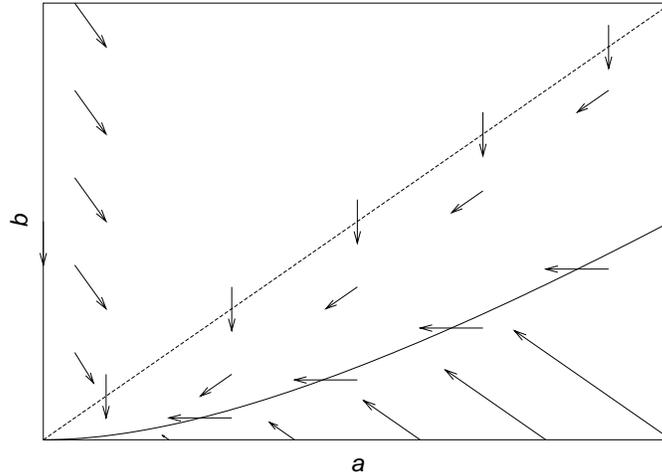


Figure 2: Rough vector field for the Lindemann mechanism. The solid curve is the b nullcline while the dashed curve is the a nullcline.

we should, but in practice it's usually good enough just to have them pointing in the right directions.

What happens if we consider a point on the b axis? Since $a = 0$ there, the velocity vector is $(0, -b)$. In other words, if you're right on the b axis, you move straight down. This doesn't tell us much. Imagine instead starting just *off* the b axis, with a small value of a . Then, $\mathbf{v} \approx (\alpha ab, -\alpha ab - b)$, i.e. it points to the right and down. The a^2 terms which we are neglecting will grow as the system moves away from the b axis. Given the physical interpretation of the model, the variable a can't grow forever. Eventually, the term $-a^2$ in equation 3a will balance the positive term αab . At that point, $da/d\tau$ will pass through zero, which corresponds to a momentarily vertical trajectory segment, and then a will start to decrease. This will happen when the trajectory crosses the a nullcline, which we obtain by setting the right-hand side of equation 3a equal to zero. Again, we use \mathcal{A} to indicate the nullcline:

$$b_{\mathcal{A}} = a/\alpha.$$

We can now complete our velocity vector field, shown in figure 2.

We're now almost ready to sketch the trajectories. We just need one more simple idea from the theory of differential equations before we proceed, namely that trajectories can't cross. This is easy to see: At each point in the phase plane,

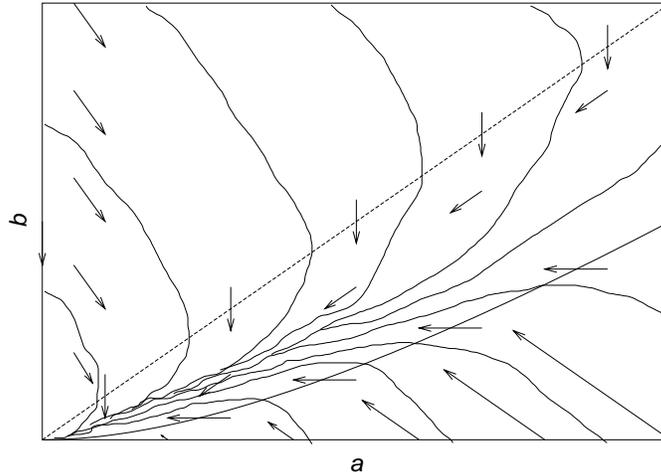


Figure 3: Completed phase-plane sketch for the Lindemann mechanism. The roughly drawn lines are approximate trajectories. Note that, no matter where we start from, the trajectories are funneled into the region between the two nullclines.

there is a unique velocity vector determined by the differential equations. Suppose that it were possible for two trajectories to cross. This would mean that there would be points in the plane from which it was possible to go in two directions, i.e. that the velocity vector was *not* uniquely defined by the coordinates in phase space. Since this isn't the case, trajectories can't cross. All we have to do now is to follow the arrows while avoiding trajectory crossings. A rough sketch of the trajectories produced by this method is shown in figure 3. It is clear from our sketch that, no matter where we start from, the trajectories end up between the two nullclines.³ Moreover, they must end up at the equilibrium point. In other words, we have determined that the equilibrium point is a **stable attractor**, i.e. a point which, once reached, the system can never leave, even if we allow for small disturbances which might occasionally push the system away from equilibrium. In fact, the equilibrium point in this mechanism is clearly an attractor for the entire positive quadrant. (We haven't analyzed the behavior in the negative quadrant since it isn't physically relevant.)

³Some authors refer to the region between the two nullclines as a **funnel** which drains into the equilibrium point.

Note that this qualitative picture is independent of the value of the parameter α . This is one of the real strengths of phase-plane analysis: We can sometimes make general qualitative statements about the way in which the system will behave without doing much mathematics.