

Changing the Speed Does Not Change the Destination

— A Catalyst Multiplies the Rate by 10^7 and Leaves the Equilibrium Constant Unmoved to Eight Decimals —

And Le Chatelier Is Not a Theorem: the Turning Point Is $1/2$, Whatever K Is — [Paper 257]

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— *From thinking to syncing.* —

Abstract

A catalyst makes a reaction faster. Can it also change where the reaction ends up?—the answer is no. This paper asks why not—the answer is that a catalyst lowers two barriers by the same amount, because the difference between them is a state function. And the principle that is supposed to say which way the destination moves, that of Le Chatelier, is not a theorem. No new mathematical theorem and no new law is claimed. First, write down what fixes the destination. It is $K = \exp(-\Delta G^\circ/RT)$, and the catalyst never appears on the right— ΔG° is a function of the start and the end alone (Section 2). Second, this is the core of the paper. Even when a catalyst multiplies the rate by 1.02×10^7 , the equilibrium constant stays at 5.549162×10^{-6} , unmoved to eight decimal places—because forward and reverse speed up by the same factor (Section 3). Third, the speed side changes violently. Lowering the activation energy by 25 kJ/mol alone gives 2.3978×10^4 , and by 75 kJ/mol gives 1.3786×10^{13} —what can be changed and what cannot are separated by orders of magnitude (Section 4). Fourth, Le Chatelier is not a theorem. Adding nitrogen to an ammonia synthesis does not raise the yield without end; beyond a point it begins to fall—by 50 mol the ammonia is down to $1/1.9147$ of the peak (Section 5). Fifth, the turning point is a single number. The direction reverses the moment the mole fraction of nitrogen passes 0.5000 (Section 5). Sixth, that $1/2$ does not move. Moving K from 10^{-3} to 10^2 , a factor of 10^5 , and changing the amount of hydrogen, leaves the turning point at 0.5000 —the stoichiometry alone fixes it (Section 6).

Scope of this paper (scope note): No new mathematical theorem and no new law is claimed—that $K = \exp(-\Delta G^\circ/RT)$, the Arrhenius expression, the transition-state picture, and the existence of counterexamples to Le Chatelier's principle are all standard. No chemistry is built—what is used is one exponential, one equilibrium condition, and bisection. No reaction mechanism is discussed—not one account of how a particular catalyst works is given. What this paper treats is only the sorting of what can and cannot be changed. No kinetics is built—the Arrhenius expression is used as a guide, with the temperature dependence of the pre-exponential factor neglected. The factors in Section 4 are values for seeing orders of magnitude. No real catalyst is evaluated—the 25 kJ/mol lowering in Section 3 is a value that has been posited, not a measurement on a particular catalyst. Non-ideality is not treated—Sections 5 and 6 are solved with ideal-gas partial pressures and no activity coefficients. The turning point of 1/2 is a result inside that idealisation. Le Chatelier's principle is not denied—stated properly, with the constraints made explicit, it holds. The counterexample here is aimed at the naive reading, that a system moves so as to oppose the change. The impossibility of perpetual motion of the second kind is not proved—the second law is used as a premise. Relation to earlier papers: Paper 232 counted four different claims written with the same equals sign—this paper separates two different things named by the same verb, to move: moving the speed and moving the destination. Reversibility appears in 21 papers and the second law in 5, and this paper uses them as premises—no new thermodynamics is built. Paper 190 measured rare on a logarithmic scale—this paper likewise writes the change in speed in orders of magnitude and the change in destination as the number of digits that do not move. What is added is setting the catalytic speed-up from 1 to 1.02×10^7 against K and showing it unmoved to eight decimals, placing what can be changed (the rate, 10^{13}) and what cannot (the constant, no digits at all) in one table, solving the counterexample to Le Chatelier explicitly and locating its peak, and confirming that the turning point stays at 0.5000 when K is moved by a factor of 10^5 .

1. Notation and Placement

Setting: consider a reversible reaction. **Speed** is carried by the forward and reverse rate constants k_f and k_r ; **destination** is carried by the equilibrium constant $K = k_f/k_r$.

Question: which of the two can a catalyst move?

The answer is the speed alone. k_f and k_r move by the same factor, and their ratio K does not move.

A second question: when the destination does move, can one say which way? Le Chatelier's principle is supposed to answer that—but the naive reading has counterexamples.

This paper sets two things side by side: what cannot be moved (Sections 2 to 4) and what moves in a direction one cannot name (Sections 5 and 6).

2. What Fixes the Destination

Setting: the equilibrium constant is fixed by the free-energy difference alone.

$$K = \exp\left(-\frac{\Delta G^\circ}{RT}\right)$$

Check 2.1: computed at $T = 298.15$ K, where $RT = 2478.9570$ J/mol.

ΔG° [kJ/mol]	K
-40.0	1.017881×10^7
-20.0	3.190424×10^3
0.0	1.000000
+20.0	3.134380×10^{-4}
+40.0	9.824336×10^{-8}

Observation 2.2

the catalyst never appears on the right. ΔG° is a function of the start and the end alone and does not depend on the road between—a catalyst changes the road, not the endpoints.

Observation 2.3

if a catalyst could change K , then two vessels with different catalysts could circulate matter and yield work with nothing else changed—the second law of thermodynamics forbids it. What forbids it is not chemistry but the level above it.

3. The Core: A Catalyst Lowers Both Barriers by the Same Amount

Setting: the heat of reaction is the difference of the two activation energies, $\Delta H = E_{a,f} - E_{a,r}$. ΔH is a state function and cannot move—so if a catalyst lowers $E_{a,f}$, then $E_{a,r}$ falls by exactly as much.

Check 3.1: from $E_{a,f} = 75$ and $E_{a,r} = 45$ kJ/mol (so $\Delta H = +30$ kJ/mol), lower both by the same amount, at $T = 298.15$ K.

Lowering [kJ/mol]	$E_{a,f}$	$E_{a,r}$	Speed-up	$K = k_f/k_r$
0	75	45	1.0000	5.549162×10^{-6}
10	65	35	5.64838×10^1	5.549162×10^{-6}
25	50	20	2.39779×10^4	5.549162×10^{-6}
40	35	5	1.01788×10^7	5.549162×10^{-6}

Observation 3.2

while the speed-up moves through 7 orders of magnitude, from 1 to 1.02×10^7 , K does not move in eight decimal places.

Observation 3.3

the reason is one line. If the lowering is δ , then k_f and k_r are each multiplied by $\exp(\delta/RT)$ —and in the ratio that factor cancels. A catalyst is multiplying numerator and denominator by the same number.

Observation 3.4

the separator—what has to be changed for these to become different things. Whether $E_{a,f}$ and $E_{a,r}$ can be moved separately. Anything that moves them separately is not a catalyst—it is changing the reaction itself.

4. The Speed Side Changes Violently

Check 4.1: the same exponential tells on the speed side in orders of magnitude, at $T = 298.15$ K.

Lowering of the activation energy [kJ/mol]	Factor on the rate
10	5.6484×10^1
25	2.3978×10^4
50	5.7494×10^8
75	1.3786×10^{13}

Check 4.2: temperature enters through the same exponential. Raise it by the 10 K from 300 to 310.

E_a [kJ/mol]	Factor over 10 K
25	1.3817
50	1.9091
75	2.6378
100	3.6446

Observation 4.3

at $E_a = 50$ kJ/mol the factor over 10 K is 1.9091—the rule of thumb that ten degrees roughly doubles a rate is this value.

Observation 4.4

the same $\exp$ makes 10^{13} on the speed side and no digits at all on the side of K . The difference is only whether it cancels.

Observation 4.5

a point to state honestly—Section 4 treats the pre-exponential factor as constant. It depends weakly on temperature, so the factors here are values for seeing orders of magnitude, not precise predictions.

5. Le Chatelier Is Not a Theorem

Setting: solve $\text{N}_2 + 3\text{H}_2 \rightleftharpoons 2\text{NH}_3$ at constant temperature and constant pressure. Hold the hydrogen at 3.000 mol and add nitrogen alone. The naive reading says that adding a reactant raises the product.

Check 5.1: with the dimensionless equilibrium group set to 0.10, solved by bisection.

N_2 added [mol]	$x(\text{N}_2)$	NH_3 [mol]	Direction
0.500	0.115076	0.252608	—
1.000	0.228543	0.316169	rising
2.000	0.392335	0.355950	rising
3.000	0.500000	0.362527	peak
4.000	0.575294	0.359339	falling
10.000	0.775904	0.314420	falling
50.000	0.944986	0.189341	falling

Observation 5.2

a reactant is being added and the product falls. By 50 mol it is down to 1/1.9147 of the peak—the naive reading gets the direction wrong here.

Observation 5.3

the reason is dilution. The pressure is held fixed, so adding nitrogen raises the total number of moles and lowers the partial pressures of everything else. The partial pressure of H_2 enters cubed, so the loss from dilution wins first over the gain from more nitrogen.

Observation 5.4

say exactly what the counterexample is against—it is against the naive reading, that a system moves so as to oppose the change. Under a properly stated formulation, with the constraints written out, the principle holds—the principle is not wrong; using it without writing the conditions is.

6. The Turning Point Does Not Depend on K

Check 6.1: locate the peak by ternary search, then move K and the amount of hydrogen.

Dimensionless K	H ₂ [mol]	$x(\text{N}_2)$ at the peak	NH ₃ at the peak
0.001	3.0	0.5000	0.045984
0.010	3.0	0.5000	0.136473
0.100	3.0	0.5000	0.362527
1.000	3.0	0.5000	0.772603
100.000	3.0	0.5000	1.595039
0.100	5.0	0.5000	0.604212
100.000	5.0	0.5000	2.658398

Observation 6.2

moving K from 10^{-3} to 10^2 , a factor of 10^5 , and changing the hydrogen from 3 to 5 mol, leaves the turning point at **0.5000**. The height of the peak moves from 0.045984 to 2.658398, a factor of **57.8**, while the position alone does not move.

Observation 6.3

what fixes the turning point is the stoichiometry alone. K decides how much is formed, and the stoichiometry decides the boundary of which way it moves—two different offices.

Observation 6.4

a point to state honestly—this $1/2$ is a result inside the ideal-gas idealisation. With activity coefficients the turning point can move—what this paper states is only that inside the idealisation it does not depend on K .

7. Roll Call: What Moves and What Does Not

Quantity	Moved by a catalyst?	Range of movement
Forward rate k_f	yes	10^{13}
Reverse rate k_r	yes	the same 10^{13}
Equilibrium constant $K = k_f/k_r$	no	no digits at all
ΔG°	no	it is a state function
Time taken to arrive	yes	orders of magnitude
Composition on arrival	no	fixed by K

Observation 7.1

a catalyst touches the top three rows alone. The lower three lie beyond its reach.

Observation 7.2

where a knob is not connected, turning it moves nothing. The knob called a catalyst is connected to the speed alone—turn it hard and the speed answers up to 10^{13} , while the destination does not answer by one graduation.

8. Roll Call and Closing

1. The destination is fixed by ΔG° alone (Check 2.1): $K = \exp(-\Delta G^\circ/RT)$, with no catalyst in it.
2. Were it otherwise, perpetual motion (Observation 2.3): what forbids it is the second law.

3. Both barriers fall together(Check 3.1): because $\Delta H = E_{a,f} - E_{a,r}$ is a state function.
4. 10^7 and K still does not move(Check 3.1): 5.549162×10^{-6} to eight decimals.
5. The factor cancels(Observation 3.3): the same $\exp(\delta/RT)$ above and below.
6. The rate moves by 10^{13} (Check 4.1): 1.3786×10^{13} for a lowering of 75 kJ/mol.
7. Ten degrees gives 1.9091(Check 4.2): at $E_a = 50$ kJ/mol.
8. Adding a reactant lowers the product(Check 5.1): at 50 mol, 1/1.9147 of the peak.
9. The turning point is $x = 0.5000$ (Check 5.1): the direction reverses there.
10. The $1/2$ does not depend on K (Check 6.1): 0.5000 across a factor of 10^5 in K .
11. Only the height moves, by 57.8(Observation 6.2): position and height have different offices.

Closing: a catalyst is said to move a reaction. But the one verb, to move, was naming two different things—the speed and the destination. A catalyst can multiply the speed by 10^{13} and cannot shift the destination in eight decimal places. It is multiplying numerator and denominator by the same number, and that is not a shortfall of ingenuity but cancellation. As for saying which way the destination moves when it does, the naive reading cannot—there is a point at which adding a reactant lowers the product, and the boundary sits at **0.5000**. Move K by a factor of 10^5 and that boundary still does not move—the height is decided by K and the boundary of direction by the stoichiometry. One thing separates them—writing down which knob is connected to what. Write it down, and the occasions for seeking a catalyst separate from the occasions for changing the conditions. Do not write it down, and one goes on seeking a catalyst that moves K .

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