Compensation effect in catalytic oxidation of carbon monoxide

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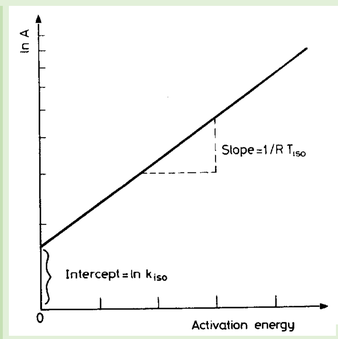
Theory

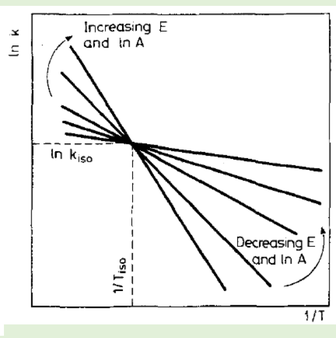
Kinetic correlations

- ✓ **Compensation effect (CE)** is based on the Arrhenius equation, $k = A \cdot exp(-E_a/RT)$, and is defined as the linear relation between *ln A* and E_a for a series of related reactions or for the same reaction carried out in a series of different conditions.
- ✓ In mathematical terms, CE is expressed as: $\ln A = \ln k_{iso} + E_a/RT_{iso}$, k_{iso} = rate constant at the isokinetic temperature, T_{iso} is the isokinetic temperature
- ✓ *CE is divided into two sets: one arising from "chemical" factors (true CE) and the other from computational and experimental artifacts (false CE).*

(a) for *true CE* the plot of *ln A vs.* E_a is linear and the plot of *lnk vs. 1/T* displays a point of concurrence;

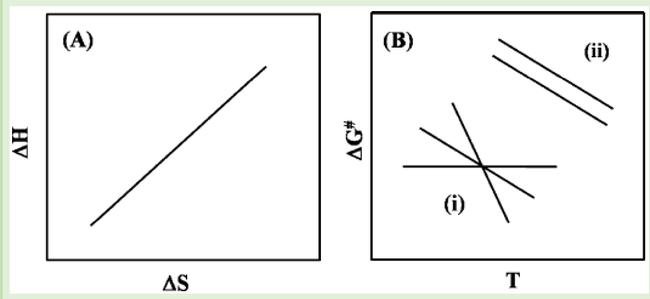
(b) for *false CE* the plot of *ln A vs. Ea* is linear but the plot of *lnk vs. 1/T* does not show a point of concurrence. [1,2]





Thermodynamic correlations

✓ For some closely related processes the enthalpy and entropy changes are often linearly related by the relation, $\Delta H = \alpha + \beta \Delta S$, α and β are constants, and such phenomenon is known as **"enthalpy−entropy compensation" (EEC)** [3].



CE in catalytic oxidation of CO

Table 1. Activation parameter

Catalysts	E_a (kJ/mol)	A (h^{-1})
7 wt. % CuO / Al_2O_3	10.13	$1.12x10^4$
7 wt. % Ni / TiO_2	22.30	$7.93x10^4$
7 wt. % Ni / Al_2O_3	51.06	$5.60x10^8$
Pd/Al_2O_3	198.86	$7.54x10^{22}$

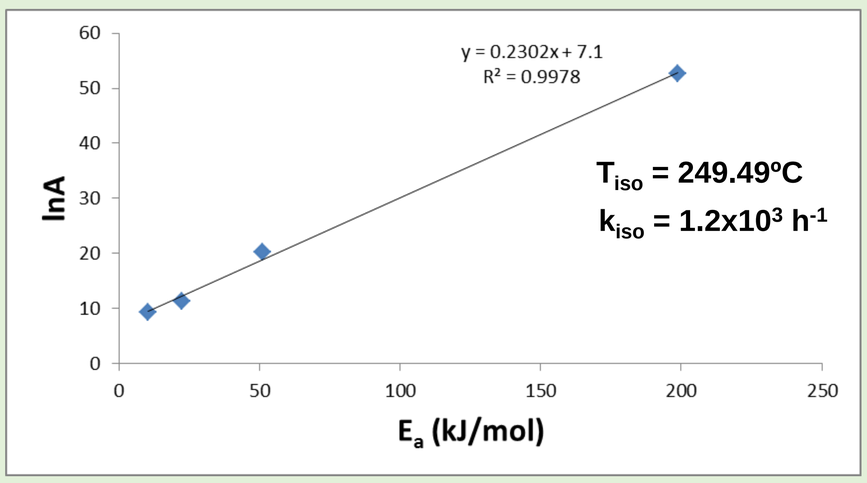


Figure 1. ***ln A vs.*** E_a

Table 2. Reaction rate constant

Temperature (°C)	k (h^{-1})			
	7 wt. % CuO / Al_2O_3	7 wt. % Ni / TiO_2	7 wt. % Ni / Al_2O_3	Pd/Al_2O_3
220	946	343.9	2178	64.1
240	1041.6	425.1	3539.7	425
260	1138.7	517.3	5547.1	2444.2
280	1236.9	620.6	8414.8	12388
300	1335.7	735	12399.2	56060

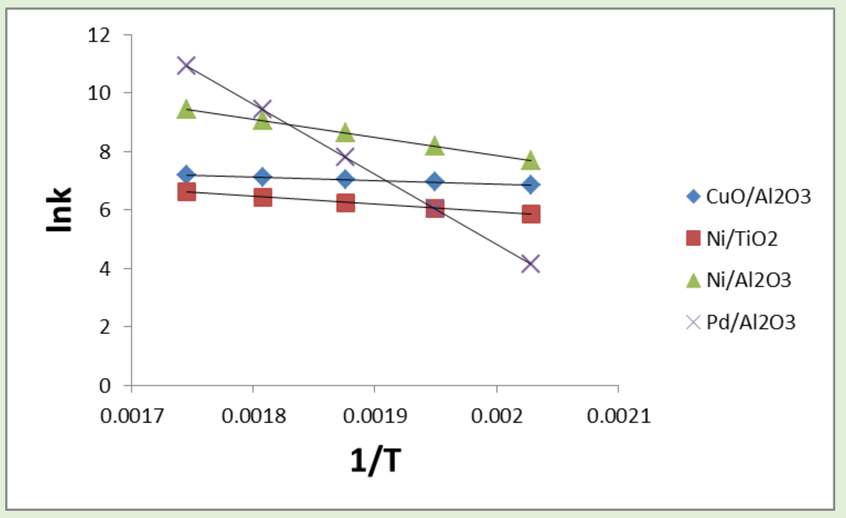


Figure 2. ***lnk vs. 1/T***

Table 3. Thermodynamic parameter

Catalysts	ΔH° (kJ/mol)	ΔS° (J/K·mol)
7 wt. % CuO / Al_2O_3	-178.42	6.69
7 wt. % Ni / TiO_2	-164.47	17.75
7 wt. % Ni / Al_2O_3	-90.47	46.86
Pd/Al_2O_3	180.23	194.59

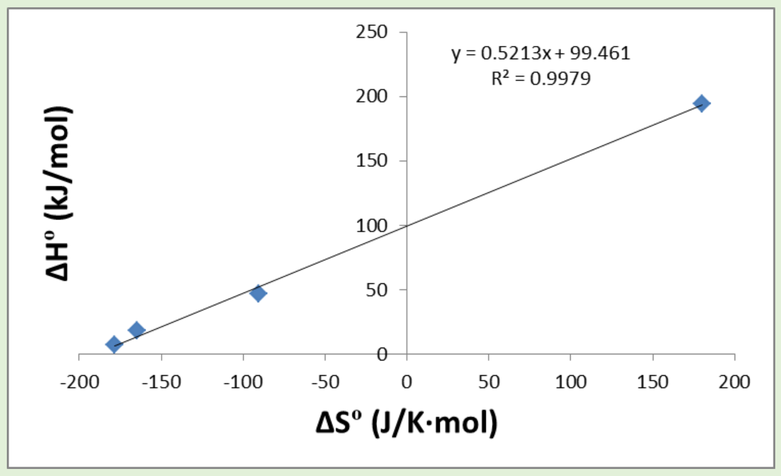


Figure 3. ***ΔH° vs. ΔS°***

Table 4. Gibbs free energy

Temperature (°C)	ΔG° (kJ/mol)			
	7 wt. % CuO / Al_2O_3	7 wt. % Ni / TiO_2	7 wt. % Ni / Al_2O_3	Pd/Al_2O_3
220	87967.75	81101.46	44648.57	-88658.8
240	91536.15	84390.86	46457.97	-92263.4
260	95104.55	87680.26	48267.37	-95868
280	98672.95	90969.66	50076.77	-99472.6
300	102241.35	94259.06	51886.17	-103077

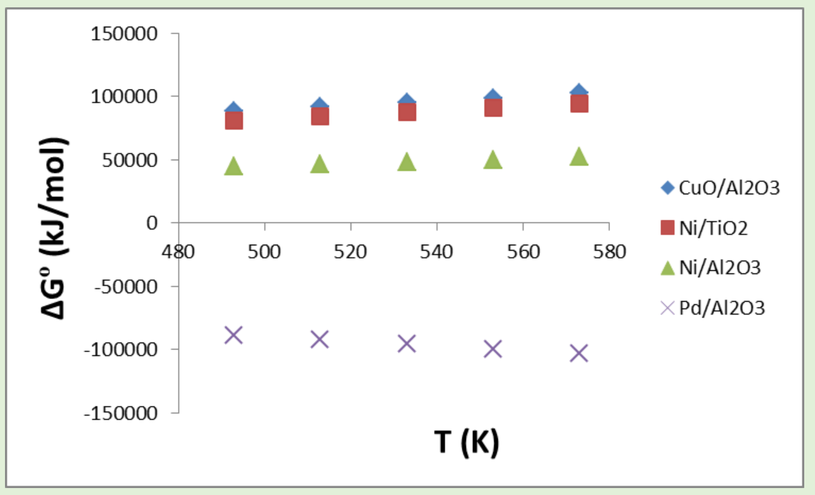


Figure 4. ***ΔG° vs. T***

Conclusion – kinetic and thermodynamic correlations show that CO oxidation is characterized by a false CE

Acknowledgements

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References:

[1] R.K. Agrawal, *The compensation effect: a fact or a fiction*, Journal of Thermal Analysis, 35 (1989) 909-917

[2] R.K. Agrawal, *On the compensation effect*, Journal of Thermal Analysis, 31 (1986) 73-86

[3] A. Pan et al., *Enthalpy−Entropy Compensation (EEC) Effect: A Revisit*, The Journal of Physical Chemistry B, 119 (2015) 15876−15884