Supplementary Materials

Application of thermodynamics at different scales to describe the behaviour of fast reacting binary mixtures in vapour-liquid equilibrium

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S1. Calculation of $\Delta_R G$, the Gibbs energy of reaction

Let us recall that $\Delta_R G$ is defined by eq. **Error! Reference source not found.** reported in the main text. In this study, the chemical potential of component i, $\bar{g}_i$, has been expressed in terms of both a pure-component ideal-gas contribution under the standard pressure $P^\circ = 1\ bar$ ($G_{i,\,\text{pure ideal gas}}^\circ(T)$) – classically called a *reference state* – and a second contribution involving the fugacity $\hat{f}_i$ of component i:

$$\bar{g}_i = G_{i,\,\text{pure ideal gas}}^\circ(T) + RT \ln \frac{\hat{f}_i}{P^\circ} \tag{S1}$$

Eq. **Error! Reference source not found.**, in the main text, thus writes:

$$\Delta_R G = \Delta_R G^\circ(T) + RT \ln \mathscr{P} \quad \text{with:} \quad \begin{cases} \Delta_R G^\circ(T) = \displaystyle\sum_{i=A,B} \nu_i \cdot G_{i,\,\text{pure ideal gas}}^\circ(T) \\ \mathscr{P} = \displaystyle\prod_{i=A,B} \left(\frac{\hat{f}_i}{P^\circ} \right)^{\nu_i} \end{cases} \tag{S2}$$

The reaction equilibrium constant (K) is related to $\Delta_R G^\circ(T)$ by its definition:

$$\ln K(T) \triangleq -\frac{\Delta_R G^\circ(T)}{RT} \tag{S3}$$

As a direct consequence, the numerical value of K is dictated by the choice of the reference state used to express the chemical potential (the pure ideal gas under standard pressure was chosen here). Finally, eq. (S2) becomes:

$$\Delta_R G = -RT \ln\left(\frac{K}{\wp}\right) \tag{S4}$$

and eq. **Error! Reference source not found.** writes:

$$K - \wp = 0 \tag{S5}$$

As shown in eqs. (S6)-(S7), it is important to recall that $\Delta_R G^\circ(T)$ can be straightforwardly calculated from the knowledge of the ideal gas standard enthalpy of formation at 298.15 K ($\Delta_f H^\circ_{i,298.15K}$), the ideal gas standard molar entropy ($S^\circ_{i,298.15K}$) and the ideal gas heat capacity ($c^{ig}_{p,i}(T)$) of each species. A key point is that all these properties can be obtained at the atomic level using ab-initio calculations.

$$\Delta_R G^\circ(T) = \Delta_R H^\circ(T) - T\Delta_R S^\circ(T) \tag{S6}$$

with:
$$\begin{cases} \Delta_R H^\circ(T) = \sum_{i=A,B} \nu_i \cdot \Delta_f H^\circ_{i,298.15K} + \int_{298.15}^{T} \left(\sum_{i=A,B} \nu_i \cdot c^{ig}_{p,i}(T) \right) dT \\ \Delta_R S^\circ = \sum_{i=A,B} \nu_i \cdot S^\circ_{i,298.15K} + \int_{298.15}^{T} \left(\sum_{i=A,B} \nu_i \cdot \frac{c^{ig}_{p,i}(T)}{T} \right) dT \end{cases} \tag{S7}$$

On the other hand, $\wp$ has to be calculated with an equation of state (EoS).

S2. Results from Quantum Mechanics calculations

Table S1. Force field parameters for NO₂ and N₂O₄ used in this work.

Atom	σ [Å]	ε/k [K]	q [e]
N_N₂O₄	3.24	50.36	0.588
O_N₂O₄	2.93	62.51	-0.294
N_NO₂	3.24	50.36	0.146
O_NO₂	2.93	62.51	-0.073

Table S2. Optimal coordinates of the molecule NO₂. QM (Gaussian) result obtained in this work.

Atom	x	y	z
O_NO₂	-0.4971	1.7461	-0.4984
N_NO₂	0.2256	0.7842	-0.4984
O_NO₂	1.42	0.6393	-0.4984

Table S3. Optimal coordinates of the molecule N$_2$O$_4$. QM (Gaussian) result obtained in this work.

Atom	x	y	z
O_N$_2$O$_4$	0	-1.104	1.3516
N_N$_2$O$_4$	0	0	0.891
O_N$_2$O$_4$	0	1.104	1.3516
O_N$_2$O$_4$	0	-1.104	-1.3516
N_N$_2$O$_4$	0	0	-0.891
O_N$_2$O$_4$	0	1.104	-1.3516

Table S4. Input to the calculation of partition functions of NO$_2$ and of N$_2$O$_4$, obtained by Quantum Mechanics.

Property	NO$_2$	N$_2$O$_4$
Atomization energy [kJ/mol]	$D_0 = 927.7$	$D_0 = 1908.6$
Rotational temperatures [K]	$\Theta_{rot,1} = 11.19159$ $\Theta_{rot,2} = 0.61889$ $\Theta_{rot,3} = 0.58646$	$\Theta_{rot,1} = 0.31106$ $\Theta_{rot,2} = 0.17435$ $\Theta_{rot,3} = 0.11173$
Vibrational temperatures [K]	$\Theta_{vib,1} = 1077.91$ $\Theta_{vib,2} = 2019.82$ $\Theta_{vib,3} = 2475.42$	$\Theta_{vib,1} = 136.95$ $\Theta_{vib,2} = 330.47$ $\Theta_{vib,3} = 431.14$ $\Theta_{vib,4} = 624.03$ $\Theta_{vib,5} = 720.59$ $\Theta_{vib,6} = 980.52$ $\Theta_{vib,7} = 1088.21$ $\Theta_{vib,8} = 1206.75$ $\Theta_{vib,9} = 1914.44$ $\Theta_{vib,10} = 2102.84$ $\Theta_{vib,11} = 2634.17$ $\Theta_{vib,12} = 2673.10$
Electronic degeneracy [-]	2	1
Symmetry number [-]	2	4

Table S5. Cosine series coefficients used in Brick for N$_2$O$_4$ torsion,
$U_{torsion} = c_0 + c_1(1+\cos\phi) + c_2(1-\cos 2\phi) + c_3(1+\cos 3\phi)$, *optimised from Gaussian's Quantum Mechanics results.*

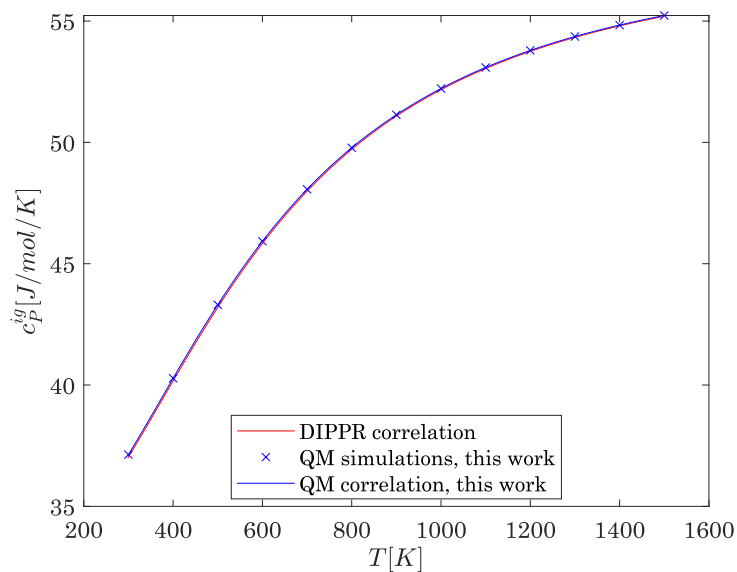| C_0 [K]	C_1 [K]	C_2 [K]	C_3 [K]
-40.046	-9.196	1826.432	10.335

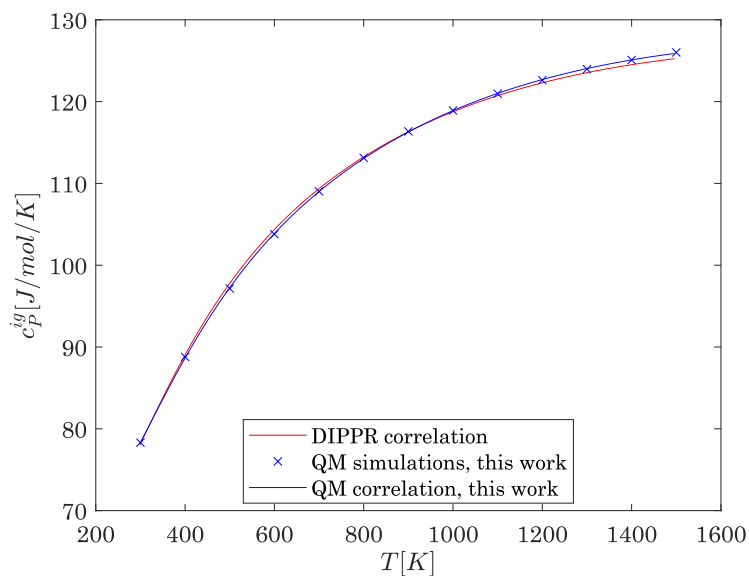*Figure S1. Isobaric specific heat capacity of NO_2 in the ideal gas phase.*

Figure S2. Isobaric specific heat capacity of N_2O_4 in the ideal gas phase.

S3. Thermodynamic correlations

Table S6. Optimised coefficients of the P^{sat}-T correlation (P in Pascal) n. (27) of the main text.

i	MC code from which P^{sat}-T data have been obtained	α_i [-]	β_i [T]
NO_2	MC Brick-CFCMC	21.411091	-1602.068176
N_2O_4	MC Brick-CFCMC	22.633860	-3436.816418
NO_2	MC GIBBS	21.460130	-1624.593796
N_2O_4	MC GIBBS	22.862732	-3492.620373