**Title: A systematic error exists in the current use of the Johnson et al. (1942) modified Arrhenius function due to a missing term – a broken paradigm**

Author: Joseph R. Stinziano1,\*, Sandra M. Kerbler2, Bridget Murphy3

Affiliations: 1Department of Biology, University of New Mexico, Albuquerque, NM, USA;   
2Max Planck Institute for Molecular Plant Physiology, Potsdam-Golm, Germany

3Department of Biology, University of Western Ontario, London, ON, Canada

\* Corresponding author; Email: [jstinziano@unm.edu](mailto:jstinziano@unm.edu)

Article Type: Opinion

Word Count: 1,540  
Number of Figures: 2

**Abstract**

Understanding biological temperature responses is crucial to predicting global carbon fluxes. The current approach to modeling photosynthetic temperature responses in large scale modeling efforts uses a modified Arrhenius equation. We rederived the modified Arrhenius equation from the source and uncovered a missing term that was dropped between 1942 and 2002. We compare fitted temperature response parameters between the new and old derivation of the modified Arrhenius equation. We find that most parameters are minimally affected, though small errors still exist. Such errors could propagate uncertainties in carbon fluxes on a global scale, potentially biasing predictions of global carbon fluxes. We therefore argue that it is time to move beyond the modified Arrhenius paradigm since the current implementation is categorically incorrect and use more thermodynamically-grounded temperature response equations.

*Keywords: Arrhenius, temperature, photosynthesis, gas exchange, modeling*

**Background**

Globally, photosynthesis and autotrophic respiration are the largest biological carbon fluxes, with photosynthesis removing ~120 Gt C year-1 and autotrophic respiration releasing ~60 Gt C year-1 (Amthor, 2000; Ciais et al., 2013). Given the temperature sensitivity of these large carbon fluxes, understanding how photosynthesis and respiration respond on acute, acclimatory, and adaptive timescales is crucial for predicting vegetative and carbon cycle responses to future global climates (Rogers et al., 2017; Stinziano et al. 2018). Biological temperature responses including photosynthesis and respiration are typically assumed to be exponential or peaked (Way and Yamori, 2014; Smith & Dukes, 2017; Kumarathunge et al., 2019). Exponential responses are usually modelled based on an Arrhenius-type curve (Arrhenius, 1915):

Equation 1

Equation 2

where f(T) is the rate of the process at temperature, A is a pre-exponential factor, T in K, k25 is the rate of the process at 298.15 K, Ea is the activation energy in J mol-1, R is the universal gas constant of 8.314 J mol-1 K-1, and 298.15 is the reference temperature in K. As for peaked responses, while a few options are available (Kruse et al., 2008; Hobbs et al., 2013; Heskel et al., 2016), the most commonly implemented version is the modified Arrhenius model of Johnson et al. (1942) as presented in Medlyn et al. (2002):

Equation 3

where Hd is the deactivation energy in J mol-1, and ΔS is the entropy of the process in J mol-1.

Equation 3 is used for modeling the temperature responses of photosynthetic capacity (based on Farquhar et al., 1980): maximum carboxylation capacity of rubisco, Vcmax, maximum electron transport capacity, Jmax, and related kinetics as well as Sharkey (1985) and Harley & Sharkey (1991) in their calculation of triose phosphate utilization capacity (TPU) in ecophysiological studies to understand thermal acclimation of photosynthesis (see Kattge & Knorr, 2007; Smith & Dukes, 2017; and Kumarathunge et al., 2019 for examples). Furthermore, this equation is also used in terrestrial biosphere models to predict the future state of the Earth system (e.g. Rogers et al., 2017).

Due to its ubiquity, we revisited the original Johnson et al. (1942) modified Arrhenius function to rederive Equation 3. In the process of this rederivation, we uncovered a term that was dropped sometime between Johnson et al. (1942) and Medlyn et al. (2002) that causes a systematic error in the application of Equation 3 in calculations covering individual species (e.g. Medlyn et al., 2002) to global scale processes (e.g. Rogers et al., 2017). We then use a freely available dataset and code (Kumarathunge et al., 2019), modified to fit the new derivation of the modified Arrhenius model, to re-interpret the updated acclimation functions reported in Kumarathunge et a. (2019).

**Materials & methods**

**Rederivation of the modified Arrhenius response**

Johnson et al. (1942, equation 24) describe the temperature response of the light intensity of a luciferase reaction as:

Equation 4

where I is the intensity of the luciferase reaction, c’’ is not explicitly defined in Johnson et al. (1942), but presumably represents a second derivative of the rate, T is the temperature in K, R is the universal gas constant of 8.314 J mol-1 K-1, ΔH‡ is the activation energy in J mol-1, ΔH is the deactivation energy in J mol-1, and ΔS is the entropy in J mol-1. We can relativize the equation to a reference temperature:

Equation 5

Equation 6

Equation 7

Equation 8

Equation 9

Harmonizing the notation scheme to that typically used in plant ecophysiology:

Equation 10

Note the difference between Equations 3 and 10: the term T / 298.15 is missing from Equation 3. This introduces multiple systematic errors:

1. fitted parameters Ea, Hd, and ΔS;
2. scaling the rate variable using the wrong equation;
3. acclimation of Ea, Hd, and/or ΔS as errors due to 1) at each acclimation temperature.

**Data analysis**

Using data from Kumarathunge et al. (2019), available from Kumarathunge et al. (2018), we fit Equations 3 and 10 to the data, both setting Hd to 200,000 J mol-1 and allowing Hd to be fit. This allows us to explore the impact of the missing term on the output data under a typical fitting scenario (Hd is fixed) and under the full fitting scenario.

**Modeling**

We modelled the impact of the equations X and Y on daily net plant carbon balance. Data for leaf area, root and shoot masses, as well as Vcmax, Jmax and dark respiration at 25 °C were taken from Stinziano & Way (2017), while stomatal conductance model parameters were calculated with the gas exchange data reported in Stinziano & Way (2017). All data were taken from the control treatment

**Results**

*Fixed Hd of 200,000 J mol-1*

Incorporating the missing term into Equation 3 to produce Equation 10 caused small differences in the fitting of Ea for Vcmax, with a slope of 0.997 ± 0.001 and intercept of -2.162 ± 0.119 kJ mol-1 (*F*1,90 = 4.56 ∙ 105, *R2* = 0.9998, *P* < 2.2 ∙ 10-16) (Fig. 1b). For ΔS, the slope was 0.991 ± 0.003 and an intercept of 0.005 ± 0.002 kJ mol-1 (approximately 1% of fitted ΔS) (*F*1,90 = 1.23 ∙ 105, *R2* = 0.9993, *P* < 2.2 ∙ 10-16) (Fig. 1f). Meanwhile Vcmax25 was identical between both approaches with a slope of 1.000 ± 1.1 ∙ 10-5 (intercept not significant; *F*1,91 = 8.2 ∙ 109, *R*2 = 1.000, *P* < 2.2 ∙ 10-16) (Fig. 2b). For Jmax, there were small differences in the fitting of Ea for Jmax, with a slope of 0.998 ± 0.002 and intercept of -2.230 ± 0.108 kJ mol-1 (*F*1,91 = 3.3 ∙ 105, *R2* = 0.9997, *P* < 2.2 ∙ 10-16) (Fig. 1d). For ΔS, the slope was 0.962 ± 0.003 and an intercept of 0.025 ± 0.002 kJ mol-1 (approximately 5% of fitted ΔS) (*F*1,90 = 1.1 ∙ 105, *R2* = 0.9992, *P* < 2.2 ∙ 10-16) (Fig. 1h). Meanwhile Vcmax25 was identical between both approaches with a slope of 1.000 ± 1.2 ∙ 10-5 (intercept not significant; *F*1,92 = 6.7 ∙ 109, *R*2 = 1.000, *P* < 2.2 ∙ 10-16) (Fig. 2d).

*Variable Hd*

Incorporating the missing term into Equation 3 to produce Equation 10 caused small differences in the fitting of Ea for Vcmax, with a slope of 0.966 ± 0.026 (intercept not significant; *F*1,74 = 3005, *R2* = 0.976, *P* < 2.2 ∙ 10-16) (Fig. 1a). For ΔS, the slope was 0.989 ± 0.017 (intercept not significant; *F*1,74 = 3339, *R2* = 0.9783, *P* < 2.2 ∙ 10-16) (Fig. 1e), while Hd had a slope of 0.992 ± 0.019 (intercept not significant; *F*1,74 = 2812, *R*2 = 0.9744; *P* < 2.2 ∙ 10-16) (Fig. 2e). Meanwhile Vcmax25 was nearly identical between both approaches with a slope of 0.9996 ± 0.004 (intercept not significant; *F*1,74 = 7.98 ∙ 106, *R*2 = 1.000, *P* < 2.2 ∙ 10-16) (Fig. 2a). For Jmax, there were small differences in the fitting of Ea for Jmax, with a slope of 1.000 ± 0.005 and an intercept of -3.119 ± 1.089 kJ mol-1 (*F*1,80 = 3.6 ∙ 104, *R2* = 0.9978, *P* < 2.2 ∙ 10-16) (Fig. 1c). ΔS was identical, the slope was 1.000 ± 0.004 (intercept not significant; *F*1,81 = 6.4 ∙ 104, *R2* = 0.9987, *P* < 2.2 ∙ 10-16) (Fig. 1g), while Hd was identical with a slope of 1.000 ± 0.004 (intercept not significant; *F*1,81 = 5.2 ∙ 104, *R*2 = 0.9985; *P* < 2.2 ∙ 10-16) (Fig. 2f). Jmax25 was identical between both approaches with a slope of 1.000 ± 0.001 (intercept not significant; *F*1,81 = 5.8 ∙ 107, *R*2 = 1.000, *P* < 2.2 ∙ 10-16) (Fig. 2c).

**Discussion**

We sought to determine whether the missing term in Equation 3 had a meaningful impact on fitted temperature response parameters due to its prevalence in photosynthetic temperature response data and vegetation modeling (Kattge & Knorr, 2007; Duursma & Medlyn, 2012; Rogers et al., 2017; Smith & Dukes, 2017; Stinziano et al., 2018; Stinziano et al., 2019; Kumarathunge et al., 2019). Our present analysis suggests that there is no large impact on the fitted temperature response parameters for Vcmax and Jmax. In general, fitting Equation 10 instead of Equation 3 results in slightly reduced values for Ea and ΔS, with essentially no impact for k25 and Hd when Hd is fit. When Hd is fixed, there are no meaningful differences in the fits except for ΔS for Jmax, where Equation 10 values are ~4% lower than Equation 3 values, and intercepts in the Ea regressions of ~ -2 kJ mol-1, which represents <5% differences between the two equations in most instances. These findings are promising in that one of the parameters to which modelled carbon gain is particularly sensitive, Hd (Stinziano et al., 2018), is minimally affected by the missing term.

Based on the above analysis, we conclude that the impact of the missing term in the modified Arrhenius equation is negligible. It is possible that the few small differences we observed could accumulate to relatively large carbon flux errors across large spatial and temporal scales with fluctuating temperatures; however, uncertainties in the determinations of the values for Vcmax and Jmax are likely to overwhelm any errors due to the missing term. Since Equation 3 is incorrect, there are three arguments for moving beyond the modified Arrhenius paradigm: 1) there are new approaches to modeling biological temperature responses that are better grounded in thermodynamics (e.g. Macromolecular Rate Theory; Hobbs et al., 2013; Liang et al., 2018); 2) uncertainties in model outputs may accumulate due to the missing term across large spatial and temporal scales, and 3) the modified Arrhenius model as implemented is categorically incorrect due to a missing term. Therefore, we argue that future modeling efforts should move beyond this incorrect paradigm.

**Acknowledgments**

**References**

Amthor JS. 2000. Direct effect of elevated CO2 on nocturnal in situ leaf respiration in nine temperate deciduous tree species is small. Tree Physiology 20: 139–144.

Arrhenius S. 1915. Quantitative laws in biological chemistry. Bell:London.

Ciais P, Sabine C, Bala G, Bopp L, Brovkin V, Canadell J, Chhabra A, DeFries R, Galloway J, Heimann M. 2013. Carbon and Other Biogeochemical Cycles. In: Heinze C, Tans P, Vesala T, eds. Climate Change 2013: The Physical Science Basis. Cambridge, UK, and New York, NY, USA: Cambridge University Press.

Duursma RA, Medlyn BE. 2012. MAESPA: a model to study interaction between water limitation, environmental drivers and vegetation function at tree and stand levels, with an example application to [CO2] x drought interactions. Geoscientific Model Development 5:919-940.

Elzhov TV, Mullen KM, Spiess A-N, Bolker B. 2016. minpack.lm: R Interface to the Levenberg-Marquardt nonlinear least-squares algorithm found in MINPACK, plus support for bounds. R package version 1.2-1. https://CRAN.R-project.org/package=minpack.lm

Farquhar GD, et al. 1980. A biochemical model of photosynthetic CO2 assimilation in leaves of C3 species. Planta 149: 78-90.

Harley PC, Sharkey TD. 1991. An improved model of C3 photosynthesis at high CO2: reversed O2 sensitivity explained by lack of glycerate re-entry into the chloroplast. Photosynthesis Research 27:169-178.

Heskel MA, O’Sullivan OS, Reich PB, Tjoelker MG, Weerasinghe LK, Penillard A, Egerton JJG, et al. 2016. Convergence in the temperature response of leaf respiration across biomes and plant functional types. Proceedings of the National Academy of Sciences USA 113: 3832-3837.

Hobbs JK, Jiao W, Ester AD, Parker EJ, Schipper LA, Arcus VL. 2013. Change in heat capacity for enzyme catalysis determines temperature dependence of enzyme catalyzed rates. ACS Chemical Biology 8:2388-2392.

Johnson FH, Eyring H, Williams RW. 1942. The nature of enzyme inhibitions in bacterial luminescence: sulfanilamide, urethane, temperature and pressure. Journal of Cellular and Comparative Physiology 20:247-268.

Kattge J, Knorr W. 2007. Temperature acclimation in a biochemical model of photosynthesis: a reanalysis of data from 36 species. Plant, Cell & Environment 30:1176-1190.

Kruse J, Hopmans P, Adams MA. 2008. Temperature responses are a window to the physiology of dark respiration: differences between CO2 release and O2 reduction shed light on energy conservation. Plant, Cell Environment 31: 901-914.

Kumarathunge DP, Medlyn BE, Drake JE, Tjoelker MG, Aspinwall MJ, Battaglia M, Cano FJ, Carter KR, Molly AC, Lucas AC, et al. 2019. Acclimation and adaptation components of the temperature dependence of plant photosynthesis at the global scale. New Phytologist 222:768-784.

Kumarathunge DP, Medlyn BE, Drake JE, Tjoelker MG, Aspinwall MJ, Battaglia M, Cano FJ, Carter KR, Molly AC, Lucas AC, et al. 2018. ACi-TGlob\_V1.0: a global dataset of photosynthetic CO2 response curves of terrestrial plants. doi: 10.6084/m9.figshare.7283567.v1.

Liang LL, Arcus VL, Heskel MA, O’Sullivan OS, Weerasinghe LK, Creek D, Egerton JJG, et al. 2018. Macromolecular rate theory (MMRT) provides a thermodynamics rationale to underpin the convergent temperature response in plant leaf respiration. Global Change Biology 24:1538-1547.

Medlyn BE, Dreyer E, Ellsworth D, Forstreuter M, Harley PC, Kirschbaum MUF, Le Roux X, et al. 2002. Temperature responses of parameters of a biochemically based model of photosynthesis. II. A review of experimental data. Plant, Cell & Environment 25:1167-1179.

R Core Team. 2018. R: A language and environment for statistical computing. R Foundation for Statistical Computing, Vienna, Austria. URL https://www.R-project.org/.

Rogers A, Medlyn BE, Dukes JS, Bonan G, von Caemmerer S, Dietze MC, Kattge J, et al. 2017. A roadmap for improving the representation of photosynthesis in Earth system models. New Phytologist 213:22-42.

Sharkey TD. 1985. Photosynthesis in intact leaves of C3 plants – physics, physiology and rate limitations. Botanical Review 51:53-105.

Smith NG, Dukes JS. 2017. Short-term acclimation to warmer temperatures accelerates leaf carbon exchange processes across plant types. Global Change Biology 23:4840-4853.

Stinziano JR, Way DA, Bauerle WL. 2018. Improving models of photosynthetic thermal acclimation: which parameters are most important and how many should be modified? Global Change Biology 24:1580-1598.

Stinziano JR, Bauerle WL, Way DA. 2019. Modelled net carbon gain responses to climate change in boreal trees: impacts of photosynthetic parameter selection and acclimation. Global Change Biology 25:1445-1465.

Way DA, Yamori W. 2014. Thermal acclimation of photosynthesis: on the importance of adjusting our definitions and accounting for thermal acclimation of respiration. Photosynthesis Research 119:89-100.

**Figures**

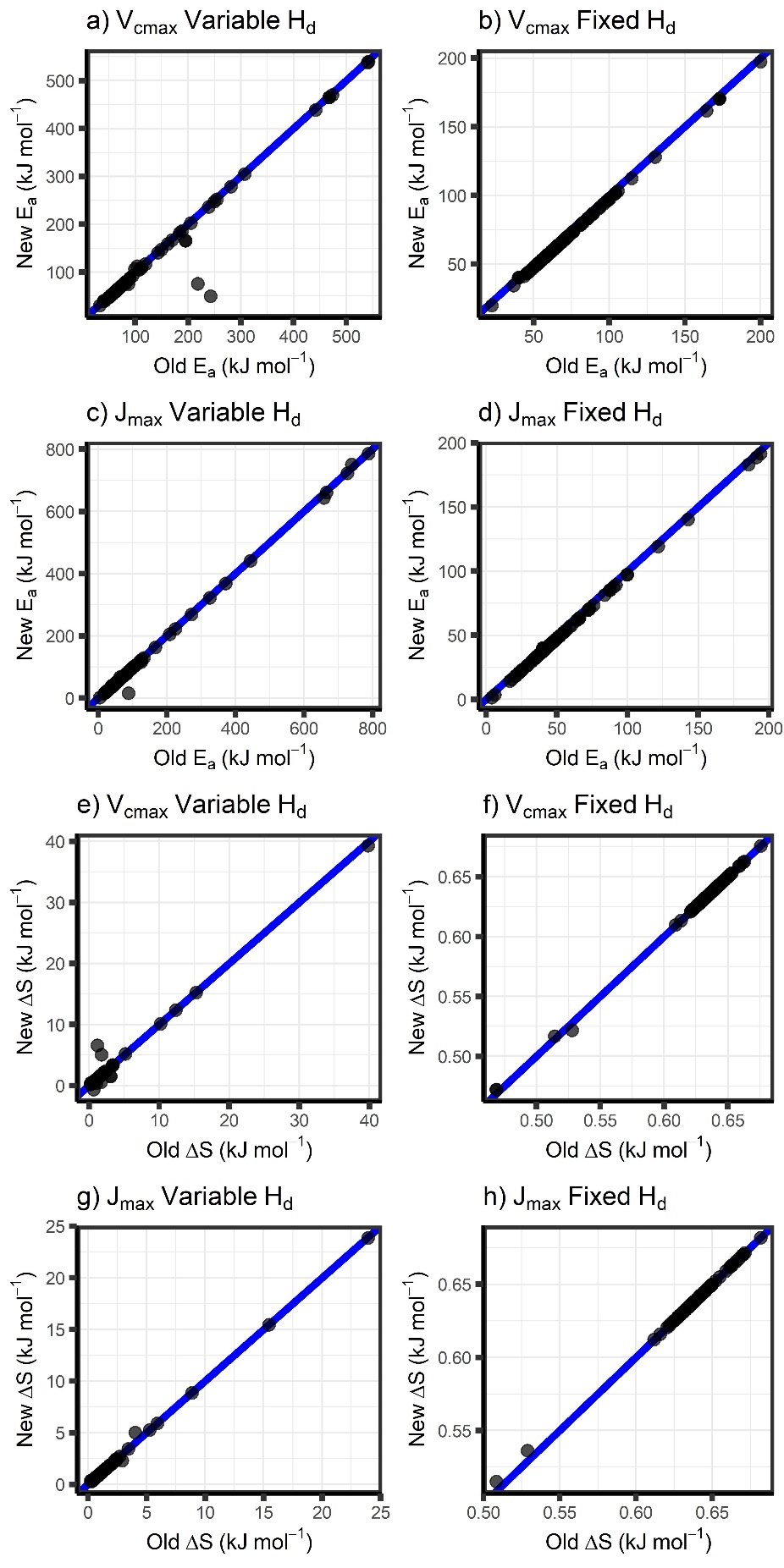


Figure 1 – The modified Arrhenius equation with the missing term (Equation 10) gives

similar temperature response parameters as Equation 3 for Ea (a-d) and ΔS (e-h) for both Vcmax (a, b, e, f) and Jmax (c, d, g, h) under scenarios where Hd is allowed to vary (a, c, e, g) and is fixed to 200 kJ mol-1 (b, d, f, h). “New” indicates Equation 10, “Old” indicates Equation 3. Ea: activation energy, ΔS: entropy parameter, Hd: deactivation energy, Vcmax: maximum capacity of rubisco carboxylation, Jmax: maximum rate of electron transport. Blue line indicates 1:1 line.

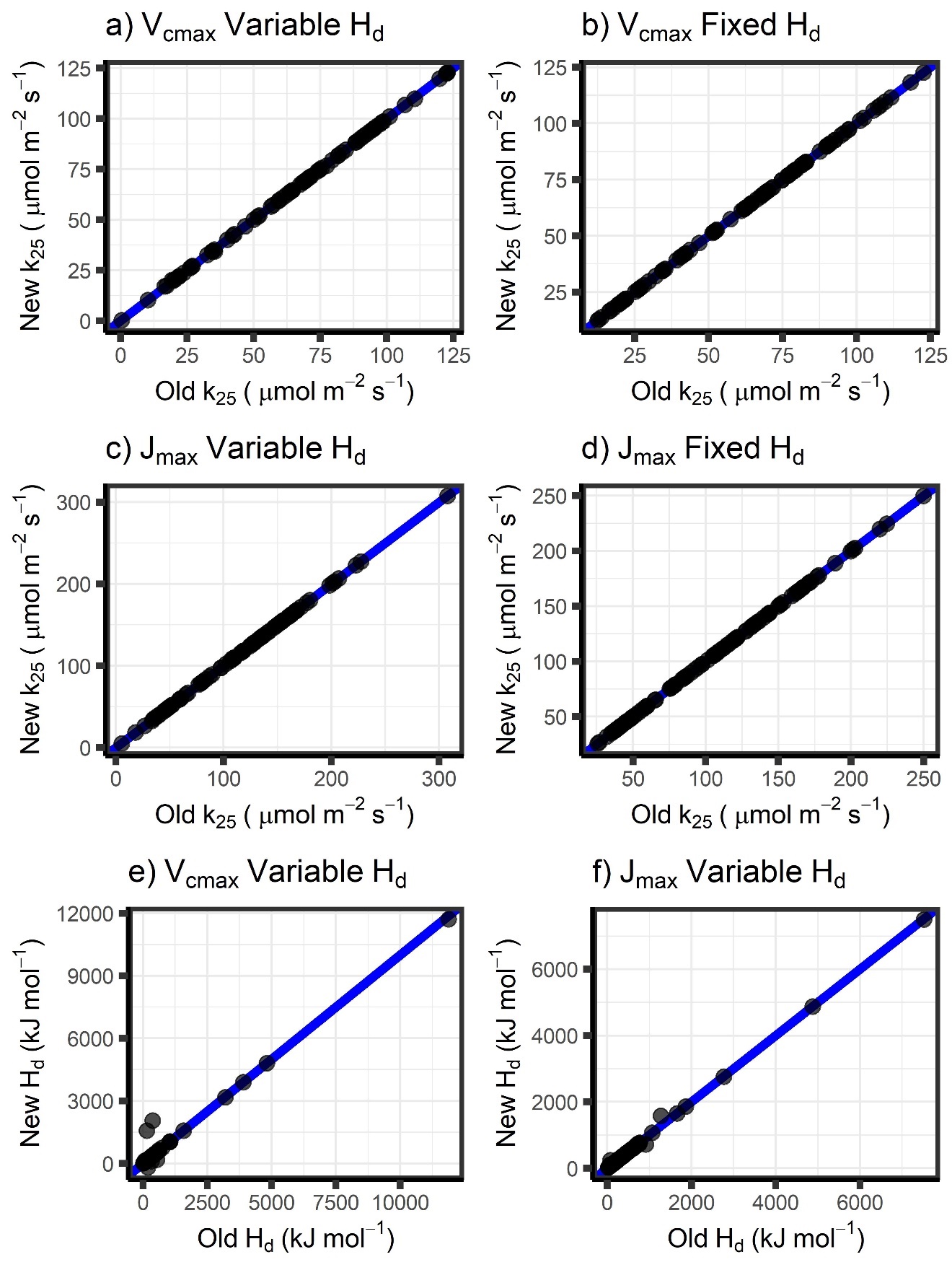


Figure 2 – The modified Arrhenius equation with the missing term (Equation 10) gives

similar temperature response parameters as Equation 3 for k25 (a-d) and Hd (e, f) for both Vcmax (a, b, e) and Jmax (c, d, f) under scenarios where Hd is allowed to vary (a, c, e, f) and is fixed to 200 kJ mol-1 (b, d). “New” indicates Equation10, “Old” indicates Equation 3. k25: rate of the process at 25 °C, Hd: deactivation energy, Vcmax: maximum capacity of rubisco carboxylation, Jmax: maximum rate of electron transport. Blue line indicates 1:1 line.