# Thermodynamics, Kinetics, Thermal History and Petroleum System Modelling

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## ABSTRACT

All natural (macro-) systems, i.e. those with sizes >$10^{-9}$ m and velocities > $10^{-8}$ m.$s^{-1}$, obey the laws of classical (sometimes called Newtonian) mechanics. The laws in physical chemistry, e.g. kinetics and thermodynamics, are also consistent with classical mechanics. The processes within geological basins therefore also obey classical mechanics, and any attempt to model processes within basins must also obey those laws. The widespread use of basin and petroleum system modeling (BPSM) to predict petroleum generation in geological basins, must mean that geoscientists undertaking BPSM projects are confident that the current approach can at least yield usable results. An argument often used in favour of BPSM is that they are only models that contain many uncertainties such as the amount of erosion at unconformities, although the uncertainties can be evaluated using multiple scenario testing. A counter-argument is that if the methodology in BPSM incorrectly implements some basic laws of classical mechanics, then regardless of the quality of the geological or geochemical models, the model results will always be incorrect.

The effect of using thermodynamically modified thermal modelling equations is that they predict high maturities and petroleum generation when using conventional temperature-time (T-t) kinetic models. The petroleum system modeller when attempting to simulate the petroleum generation of a well generally uses calibration to ensure that the modelled data, e.g. vitrinite reflectance, TOC, temperature, porosity, etc., matches the available data. Calibration entails adjusting the model so that the simulated maturity values match those measured in samples at varying depths in the well. The higher heat flows required during tectonic events, e.g. extension, produces predicted maturities that exceed the measured values, but the heat flow cannot be reduced because the enormous amount of work being undertaken in the crust or mantle produces elevated heat flows for the reasons already described. The main reason for the failure of the T-t kinetic models to predict values that match the measured values, is the absence of the conservation of energy within the kinetic models. As already discussed, endothermic reactions, e.g. petroleum generation, etc. convert thermal energy into pV, with the amount of pV being controlled by the volumes generated and the pore pressure. At present, kinetics derived from hydrous and hydrous pyrolysis contain ~10 kJ/mol of total pV, with pV being contained within the activation energy. Using the volumes of petroleum generated from a source rock with type I kerogen and 10% TOC in the overpressured Bohai Bay Basin, the total pV can rise to values >400 kJ/mol. Note that total pV refers to all of the mechanical work during the entire kerogen conversion from TR 0 to 1.0. As the pV has to be added to the activation internal energy and RT to give the $E_a$, this would suggest that total $E_a$ > 600 kJ/mol, although this drops to ~350 kJ/mol in a hydrostatically pressure basin. Such enormous numbers may daunt experienced petroleum system modellers, but can be accounted for by elevated heat flows, and by earlier onset, but extended durations of petroleum generation when pressures are lower, with the consequential reduction in the required pV values. The end result is a temperature-pressure-time (T-P-t) kinetic model that is consistent with the thermodynamically controlled heat flow histories.