SYNERGIES BETWEEN SULFUR REMOVAL AND AROMATIC FORMATION AND/OR MITIGATION IN THE DEVELOPMENT OF "CARBON-SAVER FUELS" FROM HEAVY OIL.

W. V. Steele, Nuclear Science and Technology Division, Oak Ridge National Laboratory (ORNL) Oak Ridge, TN 37831-6273, U.S.A.

Physical Properties Research Facility, Chemical Engineering Department, 327 Dougherty Engineering Bldg., 1512 Middle Drive, University of Tennessee, Knoxville, TN 37996-2200, U.S.A.

Introduction

General comments on sulfur in fossil fuels

Carbon, hydrogen, and sulfur are the three major constituents of sedimentary organic matter making the latter a major concern when combustion reactions are considered. The organic sulfur content of fossil fuels is highly variable ranging from less than 0.05 wt% to upwards of 14 wt% [1]. Sinninghe Damste and de Leeuw [2] pointed out that "the sulfur content of crude oils and bitumens is much too high to be accounted for by the sulfur content of biochemical molecules". In addition the structures of sulfur-containing biochemical molecules are markedly different from the organic sulfur compounds identified in crude oils, bitumens, and kerogens. Some 30 years ago Ivlev *et al.* [3] proposed, based on thermodynamic considerations, that at least some of the sulfur-containing compounds are produced by the action of hydrogen sulfide (H_2S) on olefinic bonds in the biologic precursors of sedimentary organic matter. This is now currently accepted among organic geochemists. Significant early work defining many

thermodynamic properties for the range of sulfur compounds present in mature crude oils was accomplished at Bartlesville during the American Petroleum Institute (API) Research Project 48 [4]. Compounds identified included thiols, sulfides, disulfides, and thiophenic entities. In more recent years emphasis has shifted from these species of smaller molecular weight to aromatic sulfur-containing molecules, *i.e.*, alkylated benzothiophenes and dibenzothiophenes. The change in distribution of organic sulfur-containing compounds from bitumens to crude oils with increasing maturity is, at best, only partially understood. Further insights may be deduced using theoretical calculations for which thermodynamic properties will form the foundation.

Quality of crude runs to US refineries

Whether it is an East Coast refinery importing crude oil from Nigeria, or a U.S. Gulf Coast refinery importing crude oil from Saudi Arabia, or even a U.S. West Coast refinery operating on Alaskan North Slope crude, over the decade (1988-97), the quality of the crude oil processed by refineries had declined. If the decline in the quality of crude processed in U.S. refineries is denoted in terms of the API gravity, the gravity had decreased by an average of 0.11 degree per year in the decade 1988-97 [5a]. Furthermore, the decline appeared to have accelerated back to the rate applicable in the early 1990's. Measured as a five-year average (1989-93), the API gravity had declined by 0.22 degree per year. After leveling at 31.3 degrees for the next four years, in 1996 it was back on the line pointing to a value of 30.5 degrees for the API gravity in the year 2000. If the decline is denoted in terms of the sulfur content, the trend over the decade was more complicated. Over the years 1987-1991 the average increase was 0.16 wt% per year. However, that rate has slowed by a factor of ten in the last 5 years (average 0.016 wt%, 1992-1997). In 1997, the absolute average sulfur content of all crudes refined in the U.S. was 1.25 wt% S. As the API gravity of crude oil falls, the aromatic content (carbon content) increases and the optimum processing conditions derived for the light crudes no longer hold. The shift away from optimization is well documented in the literature and in the industry (the increase in coke formation). New or revised process conditions are

necessary for continued high thermal efficiency in the refining of present and future crudes.

In his most recent update Swain [5b] notes the gravities of crude oils processed in US refineries have slowed from a previous rapid decrease in quality to a decrease of 0.07 degree per year over the decade ending in 2002. During the same period, there was a moderate increase in sulfur content of the lower-quality crudes, about 0.032 wt% per year. In Table 1 of the report Swain lists a gravity of 30.99 degrees for the year 2000 with the corresponding sulfur wt% of 1.34.

Sulfur removal and EPA regulations

In the refining industry hydrodesulfurization (HDS) is an important aspect of the hydroprocessing of petroleum crudes. HDS has long been one of the major catalytic operations in the petroleum industry [6, 7, 8, 9, 10, 11 and 12]. In HDS, sulfur-containing compounds are generally converted to hydrocarbons and hydrogen sulfide. In the past, the major reason for this conversion was to prevent the poisoning of the sulfur-sensitive catalysts used in subsequent operations in the refinery (e.g., platinum-containing catalysts used in reforming). A secondary reason was to avoid major atmospheric pollution. Most fuels leaving the refinery still contained appreciable amounts of sulfur. For example, before 1991, diesel fuel in the USA contained up to 0.5 mass fraction of sulfur [13]. This sulfur was bound in structures resistant to the HDS reaction conditions – a temperature range of $560<(T/\mathrm{K})<670$ and a hydrogen pressure range of $7.6<(p/\mathrm{MPa})<15.2$ – and did not poison the platinum catalysts. The resilient structural types were all aromatic thiophenic compounds including benzothiophene, dibenzothiophene, thianthrene, and phenoxathiin. Effective October 1993, the Environmental Protection Agency (EPA) of the United States mandated reduction of the sulfur content of highway diesel fuels sold in the contiguous 48 states to less than 0.05 mass fraction [14]. Although the exact matrix of sulfur-containing compounds present in a diesel fuel produced in a given refinery is somewhat dependent on the crude oil, it is probable that the remaining compounds at the

0.25 mass fraction level and below are benzothiophenes, dibenzothiophenes, and benzonapthothiophenes [11, 12 and 15].

The advent of the 21st century has seen even more stringent mandates for sulfur levels in diesel. Recently, the US EPA promulgated regulations in the Federal Register of January 18th 2001 [16] that state that refiners will be required to start producing diesel fuel for use in highway vehicles with a sulfur content of no more than 15 parts per million (ppm), beginning June 1, 2006. The European Commission has gone even further proposing to make the use of "zero sulfur" fuel mandatory in every member state by 2011 [17]. The Commission is still to make a final decision on what is "zero sulfur" with a consensus growing for a value near the 5 ppm sulfur level.

Stringent sulfur-level mandates and other regulations also exist for gasoline. Reduced levels of Volatile Organic Compounds (VOC) and ozone have demonstrated the recent success of gasoline reformulation in the United States. Significantly since 1997 the Los Angles Basin has experienced the cleanest environment it has seen since the late 1940s. Reformulation of gasoline in the US has resulted in major changes in gasoline composition in those areas with the highest levels of ozone and carbon monoxide. The Clean Air Act Amendments of 1990 have called for oxygenated gasoline, reformulated gasoline (RFG), Simple Model and now Complex Model requirements [14]. California has its own formulation called CARB (Californian Air Resources Board) gasoline. Certain other states have called for low RVP (Reid Vapor Pressure) formulations.

In the United States, the EPA has mandated that the sulfur content of gasoline be slashed from an average of 300 ppm to 30 ppm for all states except California [18]. The regulations are complicated with a shifting cap and average. Beginning in 2004 refiners and importers can make or sell gasoline containing a range of sulfur levels provided all of their production is capped at 300 ppm and their corporate sulfur level averages 120 ppm during the calendar year. In 2005, the refinery average will be set at 30 ppm, with a production cap of 300 ppm, and a corporate average of 90 ppm. In 2006, refiners must meet a 30 ppm average sulfur level with a cap of 80 ppm. To complicate the regulations

even more, some of the average standards can be met with the use of credits. Additionally, small refiners (less than 155,000 barrels/day of processing capacity company wide) will be given to 2010 to meet the final standards, if they can demonstrate a severe economic hardship.

New technologies

Most US refineries marketing gasoline outside of California will need to add a new desulfurization scheme. Some of the refineries already equipped with hydroprocessing units will need to modify their operating conditions to reach the new sulfur targets. Others will employ new technologies to meet the new sulfur levels. Examples of the new technologies include the BP OATS (British Petroleum Olefinic Alkylation of Thiophenic Sulfur) [19] process where thiophenes and benzothiophenes are transalkylated to produce compounds with boiling points above the gasoline cut-off point; Phillips S-Zorb sulfur removal technology [20] a new adsorption technique using zero-valence transition metals to adsorb thiophenes and benzothiophenes from the fluidized catalytic cracker (FCC) gasoline feed and/or product under reducing conditions; and Uni Pure's ASR-2 desulfurization process [21], an aqueous oxidation-extraction process to remove sulfur-containing compounds such as sulfones. Biodesulfurization [22] is an example of a "new technology" that does not appear to be advanced far enough to be applicable to solve the short-term problem. Other options include refining only sweet or low-sulfur crudes and reducing gasoline production by decreasing the gasoline cut-off point.

Thermodynamic limitations in sulfur removal

The hydrodesulfurization of thiols (mercaptans), sulfides, and disulfides is exothermic and there is no thermodynamic limitation under industrial reaction conditions where the equilibrium constants all decrease with an increase in temperature and have values greater than unity [23]. In contrast, the equilibrium constant for hydrogenation of thiophene to tetrahydrothiophene is less than unity above 600 K, indicating that a HDS pathway via the hydrogenation of the thiophene ring may be restricted under industrial

reaction conditions because of the low equilibrium concentration of tetrahydrothiophene. Prior to the results published here no corresponding analysis for the hydrogenation of the thiophenic ring in benzothiophene and dibenzothiophene could not be made without some form of estimation of the properties of the hydrogenated species.

Recent publications by our Thermodynamics Group have detailed measurements leading to the standard thermodynamic properties of gaseous benzothiophene [24], dibenzothiophene [25], thianthrene and phenoxathiin [26], and diphenylsulfide [27]. In FY2003 and subsequently in FY2004 publication of detailed measurements leading to the standard thermodynamic properties of gaseous 2,3-dihydrobenzothiophene [28], and 1,2,3,4-tetrahydrodibenzothiophene [29], has ensured that a detailed analysis for the hydrogenation of the thiophenic ring in benzothiophene and dibenzothiophene could be made without having to estimate any of the properties of the hydrogenated species. Details of the analysis are reported below.

Aromatics in gasoline and diesel

High aromatic content in diesel fuel has been recognized both to lower the quality of the fuel and to contribute significantly to the formation undesired emissions in exhaust gases. Because of the health hazards associated with these emissions, environmental regulations governing the composition of diesel fuels are being tightened in both Europe and the US, leading to limitations on aromatics. For example in Sweden Class I diesel receives a tax incentive because it contains less than 5%wt aromatics. In California a limit of 10% wt has been in force for some time. In gasolines aromatics are a major constituent. Unleaded gasoline satisfies octane requirements through the use of catalytic reforming, which unfortunately produces high concentrations of benzene and other aromatics which are good sources of octane but are also highly toxic and benzene is a known carcinogen. Reformulated gasolines added certain oxygenates such as methyl tert-butyl ether MTBE to boost octane and allow reduction of the aromatics content which was as high as 32% wt in the late 1980s. As a result, the benzene level was regulated down and now stands at 1% wt in the general US (California <0.8% wt). However, aromatics levels remain high

at 25% wt. MTBE is "under fire" and will be band in many states across the US within the next few years.

Aromatics and CO_2 reduction

Fossil fuels continue to supply greater than 85 percent of the energy needs of the United States, and their combustion accounts for greater than 90 percent of the greenhouse gas (GHG) emissions in the contiguous 48 states [30]. In a recent article in Environmental Progress, Klara and Srivastava [31].note, "The Energy Information Administration within the U.S. Department of Energy (DOE) projects U.S. consumption of coal, oil, and natural gas to increase by 40 percent and carbon emissions to rise by 33 percent over the next 20 years." If these projections are correct, carbon sequestration then becomes very important, if GHG emissions are to be contained. One can visualize some means of carbon sequestration when considering reduction of CO_2(g) emissions from power plants and other industrial entities. Klara and Srivastava [31]. list five such technologies (separation and capture; geological sequestration; terrestrial sequestration; oceanic sequestration; and novel sequestration systems) that are being pursued within the DOE's Office of Fossil Energy's (FE) carbon sequestration effort. However, when total U.S. carbon emission sources are considered, 33 percent of the total arises from transportation. It is difficult to envision any of the five technologies listed above resulting in significant carbon sequestration in the transportation sector. Implementation of technologies resulting in capture of the CO_2(g) would, in turn, lower fuel efficiency with the excess weight of the capture system accounting for most of the decrease.

Decreasing the GHG emissions in the transportation sector can be accomplished by increased engine efficiency, lighter materials for vehicle construction, etc., and by fuel changes. As noted above modern gasolines have aromatic contents in the range of 25 to 35 volume percent. Diesel fuels have similar aromatic contents made up of one, two, and even three-ring systems (alkylbenzenes, alkylnapththalenes and alkylphenanthrenes). Increasing the content of napthenes (saturated rings) in these fuels via hydrogenation of the aromatic systems would result in products with an increased energy of combustion: "Carbon-Saver Gasoline" and "Carbon-Saver Diesel Fuel." These "Carbon-Saver" fuels

would have increased miles per unit of CO_2(g) production. In addition, studies by CARB (California Air Resources Board) [32] have shown that reduction of aromatics in gasoline engines leads to a cooler-burning engine with less benzene and NO_X formation and engine deposits. Similarly, reducing diesel aromatics from 30 percent to 10 percent reduces NO_X formation by greater than 5 percent. Reductions in polyaromatic hydrocarbon (PAH) content results in significant decreases in particulate (soot) content. Also, toxic PAH emissions in the exhaust are directly related to the amount of PAH in the fuel [33].

Thermodynamic limitations in aromatics reduction

The equilibrium constant for hydrogenation of benzene to tcyclohexane is less than unity above 550 K, (537°F) indicating that a HDS pathway via the hydrogenation of the benzene ring may be restricted under industrial reaction conditions because of the low equilibrium concentration of cyclohexane. Prior to the results published here, no corresponding analysis for the hydrogenation of an aromatic ring in either naphthalene or phenanthrene could not be made without some form of estimation of the properties of the hydrogenated species.

Recent publications by our Thermodynamics Group have detailed measurements leading to the standard thermodynamic properties of gaseous tetralin [34], and 9.10-dihydrophenanthrene and 1,2,3,4-tetrahydrophenanthrene [35]. Results from those DOEFE NTIS documents has ensured that a detailed analysis for the hydrogenation of an aromatic ring in naphthalene and phenanthrene could be made without having to estimate any of the properties of the hydrogenated species. [Results for both the hydrogenated phenanthrenes and naphthalenes are being prepared for publication the readily available scientific literature, further milestones in this project.] Details of the analysis of the conditions for the hydrogenation of the aromatics are reported below.

Experimental and Results

Thermodynamic equilibria

For the general reaction

"aromatic" + n H2 "naphthene"

the equilibrium constant, K, can be defined as

$$K = [\text{naphthene}] / ([\text{aromatic}] \,.\, [p_{H2} / p°]^n)$$

A pseudo-equilibrium constant, K', can be defined as

$$K' = K \,.\, [p_{H2} / p°]^n$$

K' gives the ratio of concentrations of naphthene to aromatic. The relationship between the Gibbs energy of reaction and the equilibrium constant is

$$\Delta G = -RT \ln K$$

Therefore

$$\ln K' = -\Delta G / RT + [n \,.\, \ln(p_{H2} / p°)]$$

where p° is the standard-state pressure 1 atmosphere.

If ln K' is plotted versus 1/ T, nearly linear curves are produced and extrapolations to higher temperatures can be made reliably. To obtain maximum utilization of the thermodynamic data the above procedures for extrapolation to process conditions have been applied in the following sections.

Graphical representation of thermodynamic limitation

For the hydrogenation of benzene to form cyclohexane the available literature Gibbs energies of formation [36], can be used to obtain the following equation representing the results over a large temperature range:

$$\ln K' = 25630 / T - 46.311 + [3 \,.\, \ln(p_{H2} / p°)]$$

Substituting values for T (in Kelvin) and a value for K' (the ratio of concentrations of naphthene to aromatic) allows calculation of the corresponding hydrogen pressure. This was done for each system studied at values corresponding to 99.9% conversion, 99% conversion and 90% conversion. Results were plotted and compared with the conditions corresponding to those in the typical hydrodesulfurization (HDS) unit in an average refinery reaction conditions – a temperature range of $560<(T/\mathrm{K})<670$ and a hydrogen pressure range of $7.6<(p/\mathrm{MPa})<15.2$. Figure 1 is an example of the results. Note the temperature scale is given in the much used in engineering °F and not Kelvin. In the Figure the blue curve represents 99.9% conversion, the red curve 99% conversion and the green curve 90% conversion to hydrogenated product. The box represents the boundaries of the typical HDS conditions. As noted across the top of the figure, towards the left of the figure the hydrogenation is under kinetic control and to the right thermodynamic control takes over (thermodynamic limitation is in effect). A, B, and C are marked in the figure as representative points. A represents a point on the 99.9% conversion curve at 620°F and 120 atmospheres hydrogen pressure. B at 650°F and 100 atmospheres hydrogen pressure is a position where conversion is between 99.9% and 99% under thermodynamic control. C at 800°F and 25 atmospheres hydrogen pressure has much less than 90% conversion and is under thermodynamic control (limitation).

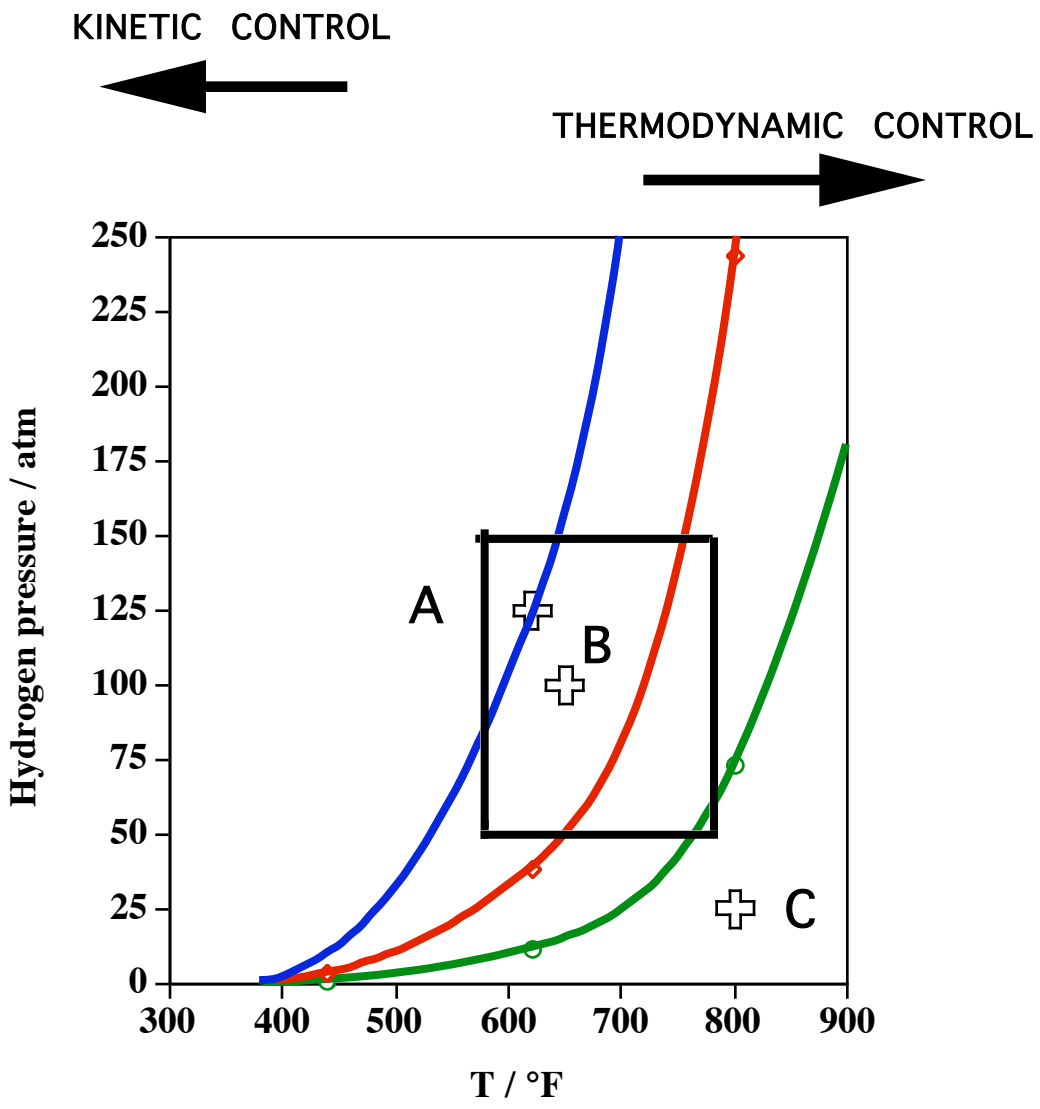

FIGURE 1. **Representative figure defining kinetic and thermodynamic control, ranges for typical HDS reactions, curves for 99.9%, 99%, and 90% conversion (hydrogenation), and three representative conditions. See text for details.**

Equilibria equations and figures

Figure 2 shows the results for the hydrogenation of thiophene to form tetrahydrothiophene. Using the available Gibbs energies of formation [23], the following equation was derived and represents the results over a large temperature range:

$$\ln K' = 18450 / T - 29.57 + [2 \,.\, \ln(p_{H2} / p°)].$$

Figure 3 shows the results for the hydrogenation of benzothiophene to form 2,3-dihydrobenzothiophene. Using the available Gibbs energies of formation [24,28], the following equation was derived and represents the results over a large temperature range:

$$\ln K' = 7480 / T - 14.105 + [\ln(p_{H2} / p°)].$$

Figure 4 shows the results for the hydrogenation of dibenzothiophene to form 1,2,3,4-tetrahydrodibenzothiophene. Using the available Gibbs energies of formation [25,29], the following equation was derived and represents the results over a large temperature range:

$$\ln K' = 13940 / T - 28.92 + [2 \,.\, \ln(p_{H2} / p°)].$$

Figure 5 shows the results for the hydrogenation of benzene to form cyclohexane. Using the available Gibbs energies of formation [37], the following equation was derived and represents the results over a large temperature range:

$$\ln K' = 25630 / T - 46.311 + [3 \,.\, \ln(p_{H2} / p°)]$$

Figure 6 shows the results for the hydrogenation of naphthalene to form tetralin. Using the available Gibbs energies of formation [34,37,38], the following equation was derived and represents the results over a large temperature range:

$$\ln K' = 15490 / T - 28.51 + [2 \,.\, \ln(p_{H2} / p°)].$$

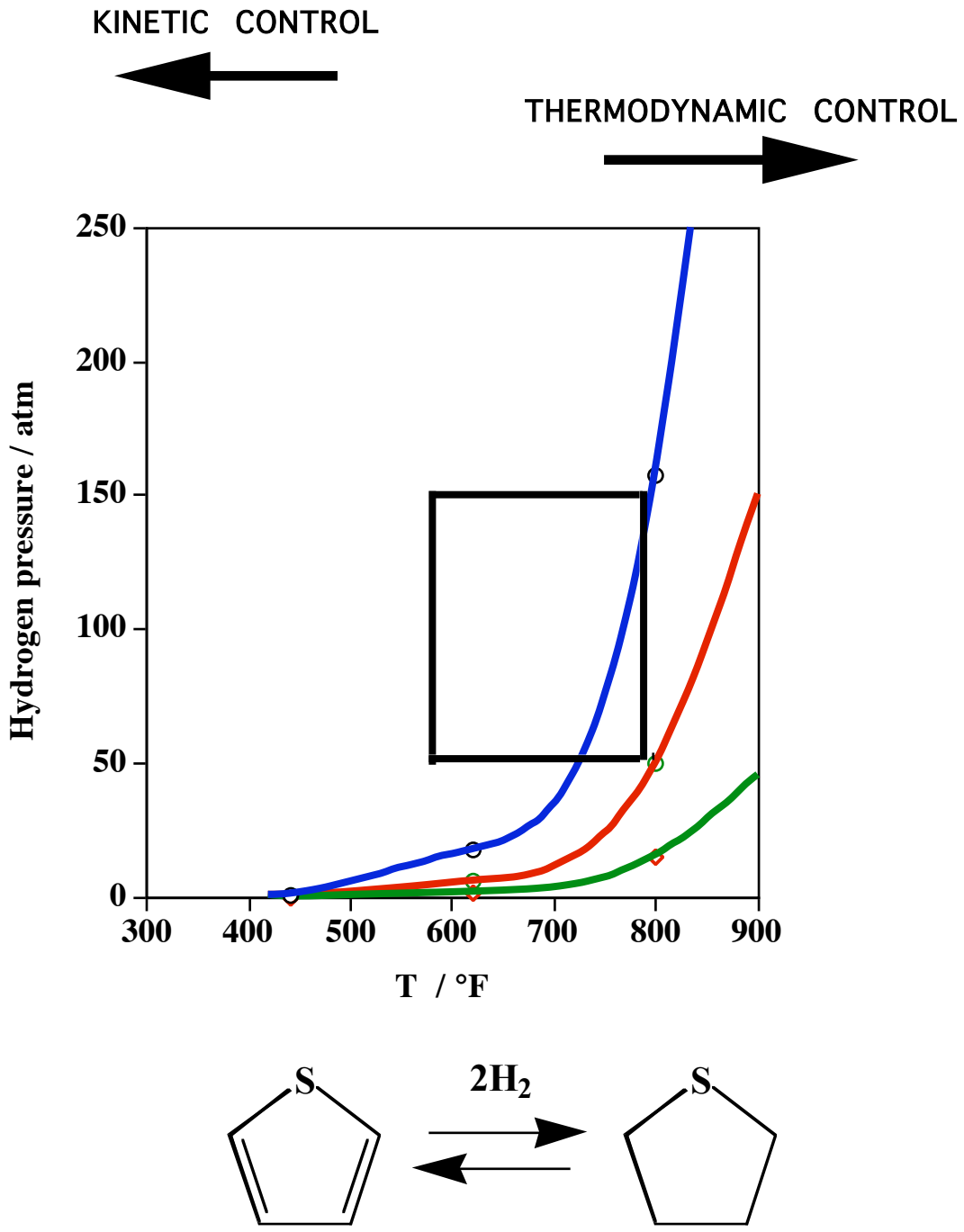

Figure 2 Thiophene / tetrahydrothiophene equilibria.

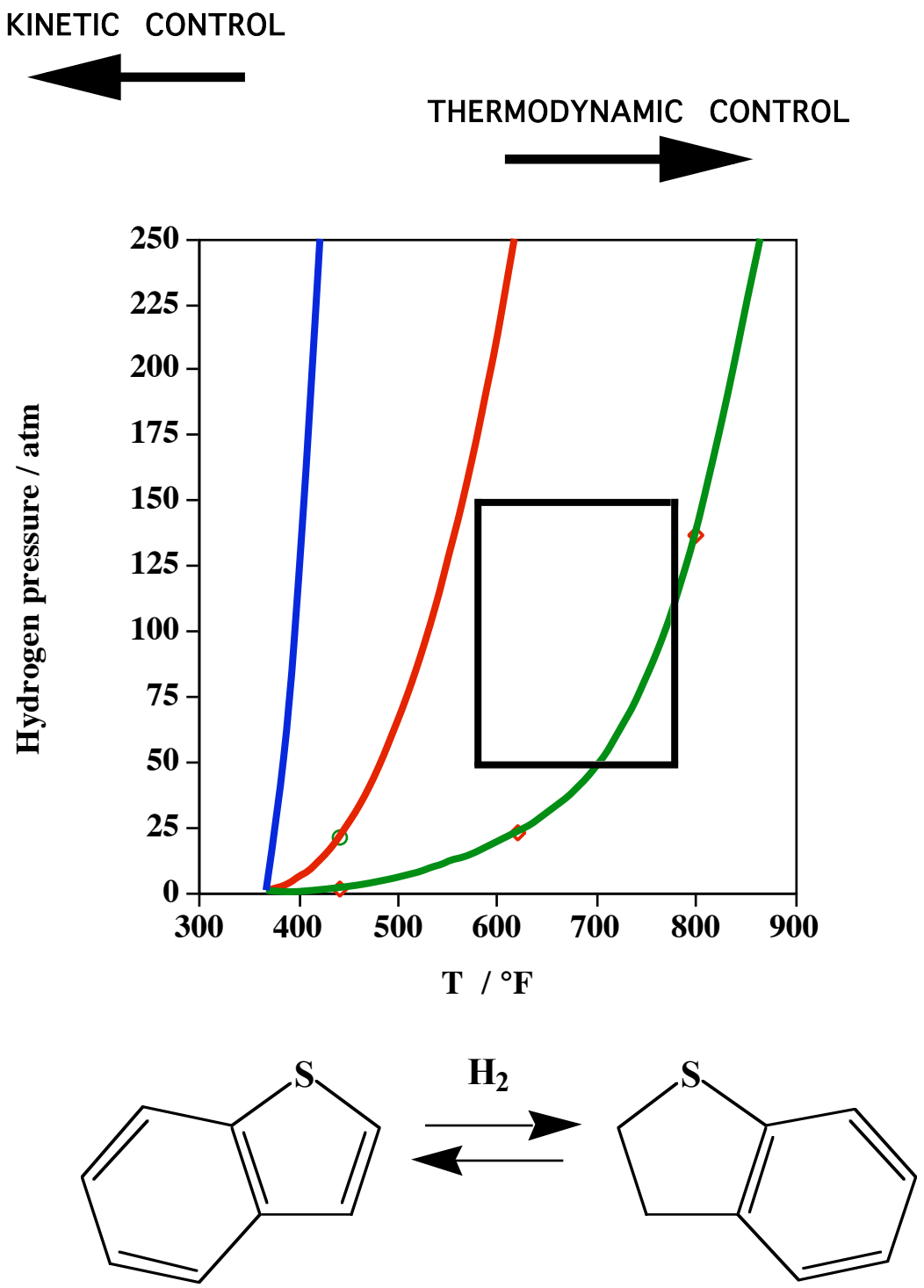

Figure 3 Benzothiophene / 2,3-dihydrodibenzothiophene equilibria.

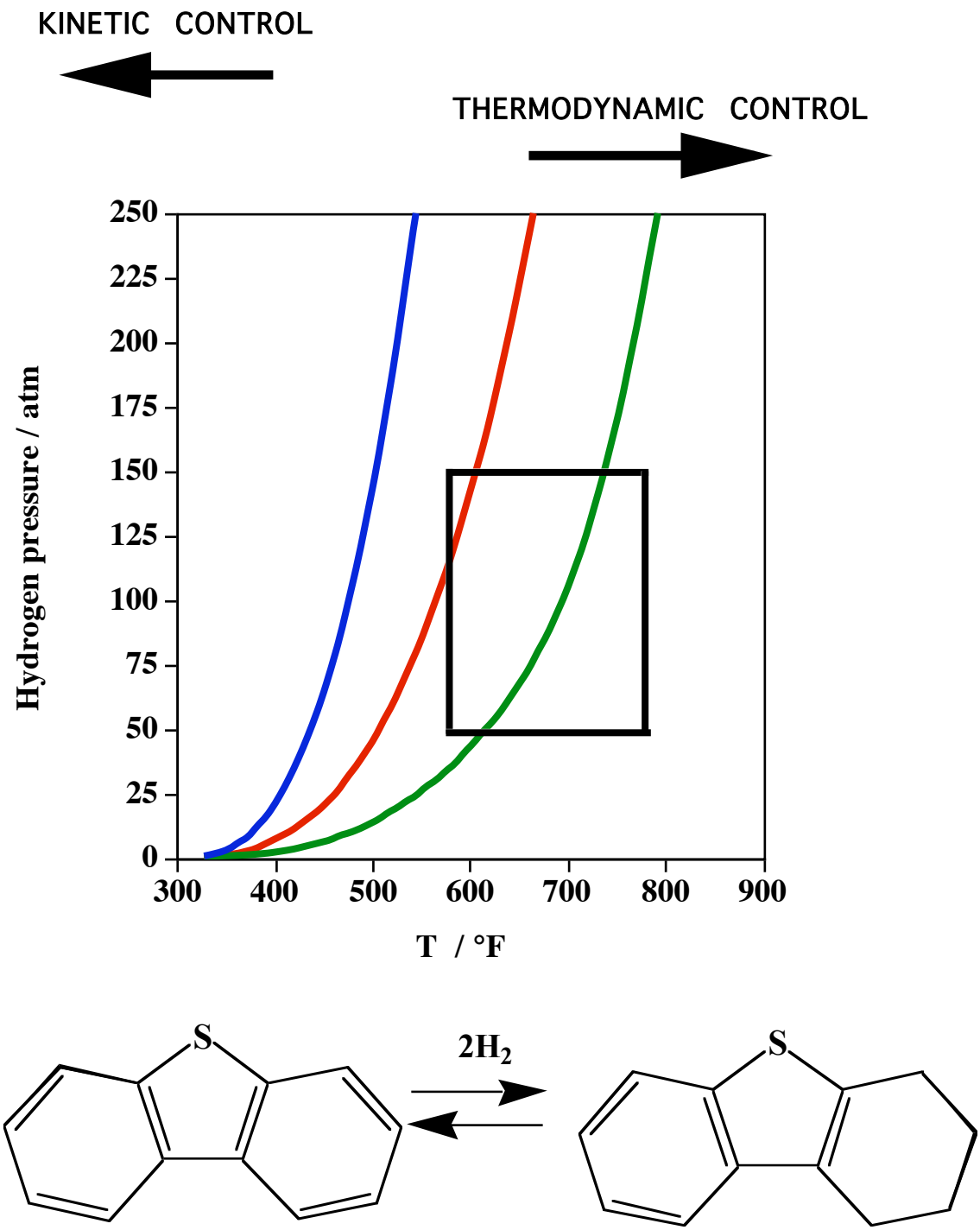

Figure 4 Dibenzothiophene / 1,2,3,4-tetrahydrodibenzothiophene equilibria.

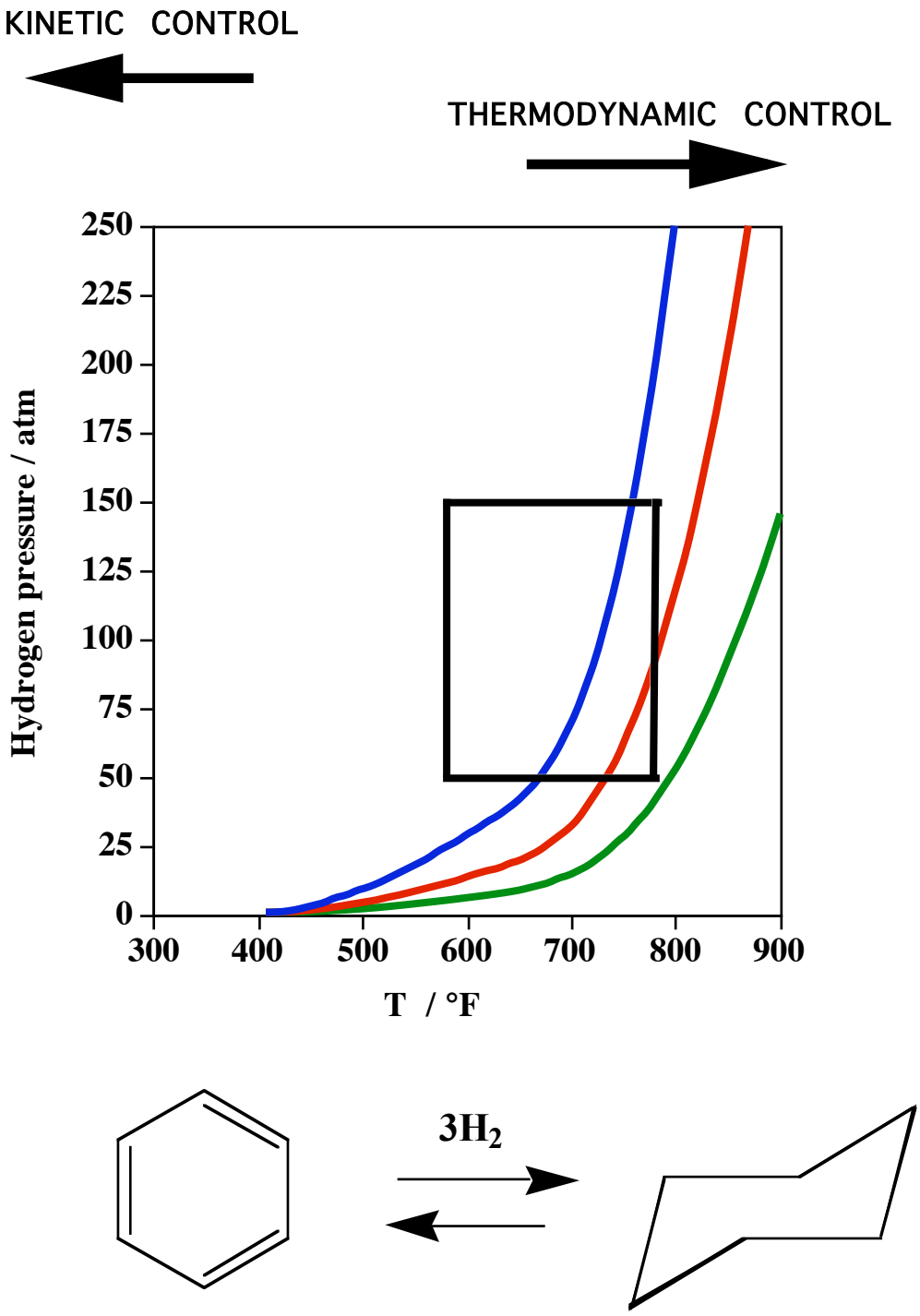

Figure 5 Benzene / cyclohexane equilibria

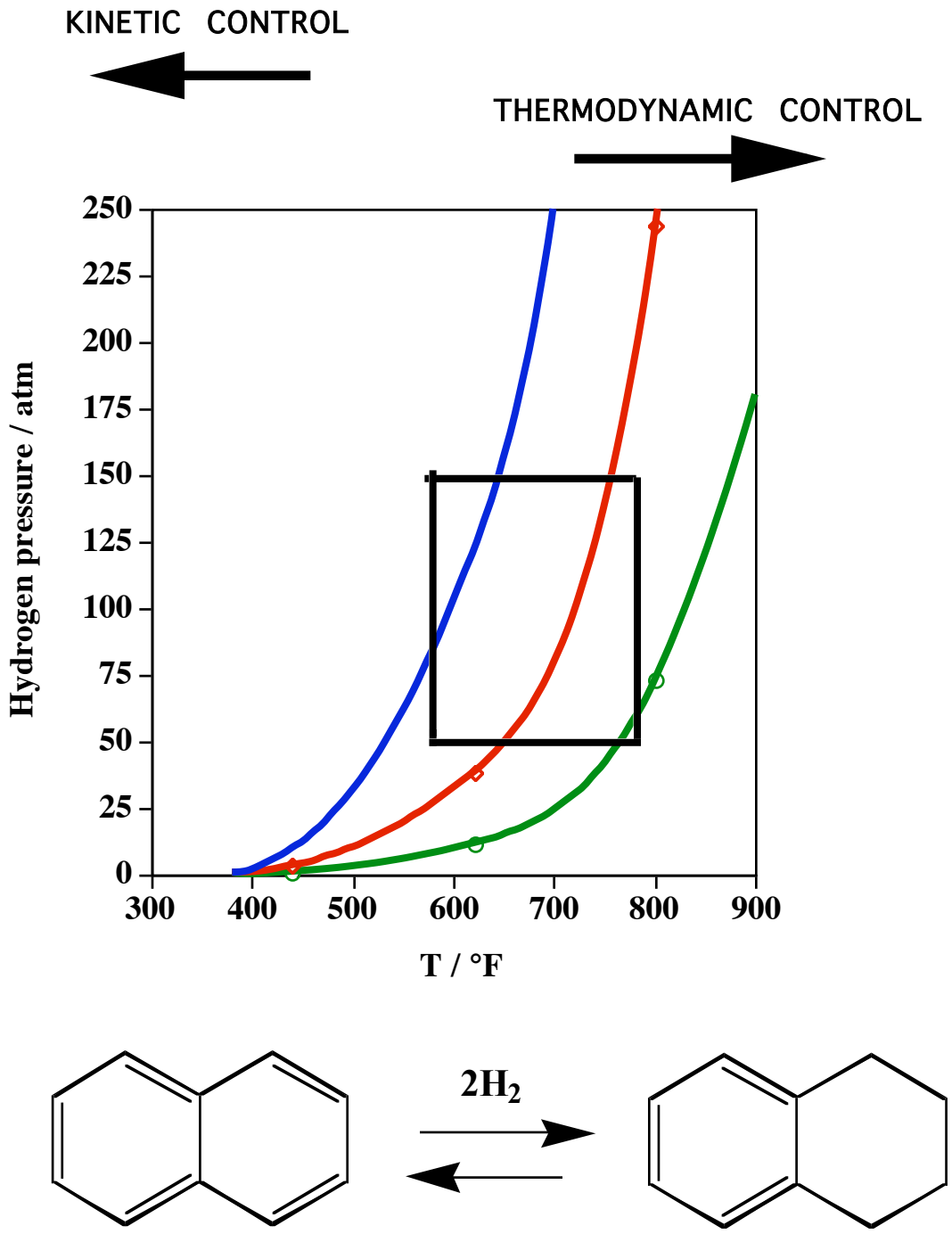

Figure 6 Naphthalene / tetralin equilibria

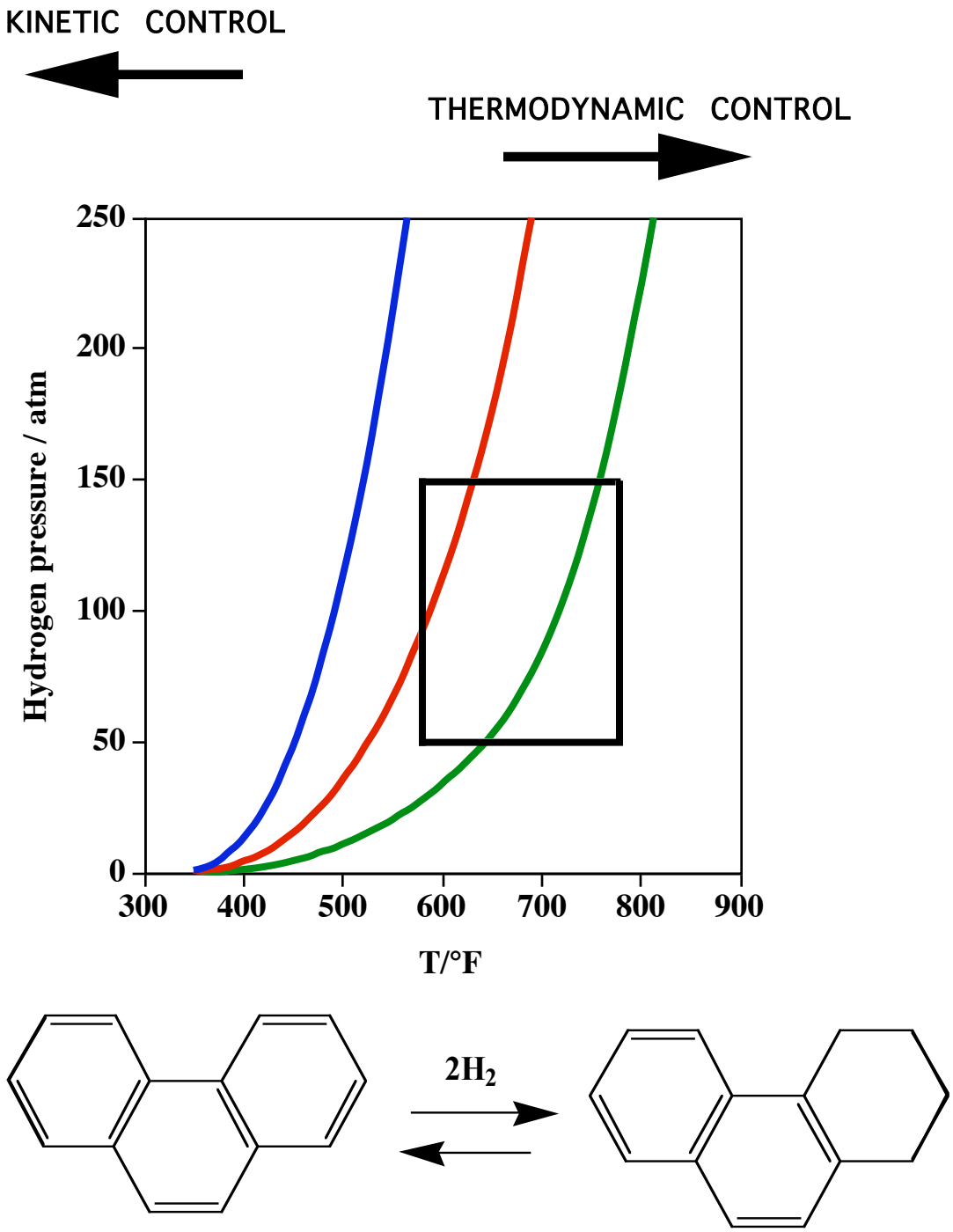

Figure 7 Phenanthrene / 1,2,3,4-tetrahydrophenanthrene equilibria

Figure 7 shows the results for the hydrogenation of phenanthrene to form 1,2,3,4-tetrahydrophenanthrene. Using the available Gibbs energies of formation [35], the following equation was derived and represents the results over a large temperature range:

$$\ln K' = 14380 / T - 29.16 + [2 \cdot \ln(p_{H2} / p^{\circ})].$$

Summary and future research

From figure 2 it can be seen that for >99.9% conversion the initial reaction leading to the HDS of thiophenes is under kinetic control and no thermodynamic limitations exist. Therefore, provided the HDS catalyst has a high-activity and no major impediments such as bulky substituents on the ring adjacent to the sulfur are present attainment of low sulfur levels is very possible.

For both benzothiophene and dibenzothiophene (figures 3 and 4) attainment of >99% conversion to hydrogenated product is not possible under the defined conditions. These are examples of the temperature "wall" effect. There is a temperature beyond which the rate of sulfur removal begins to decrease. Figure 3 of reference [39] is an example from the recent literature where the wall effect limited the sulfur removal level to 30 ppm from and initial feedstock level of 0.41% wt. The results reported here confirm this effect.

The result depicted in figures 5,6, and 7 confirm the review of Stanislaus and Copper of Haldor Topsoe, Lyngby, Denmark [40]. Further more detailed analysis is required to combine the results reported here with literature kinetic studies reported by Stanislaus and Copper. What must be emphasized here is that detailed analyses for the hydrogenation reactions have now been made without having to estimate **any** of the properties of the hydrogenated species.

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Appendix Further comments

Just a sentence to emphasize that the reduction of the aromatic content of diesel in particular would result in a new fuel with more miles per gallon for the SAME amount of carbon dioxide production. Just think that the energy of combustion of 1-methylnaphthalene is 41.353 kJ/g and that of 1-methyltetralin is 42.889 kJ/g 5 percent greater. Larger ring systems have correspondingly larger increase in energies of combustion.

Further analysis of the papers by Swain [5A and 5B] shows trends that differ across the 5 PADD areas of the US. In particular PADD 1 increased the use of foreign oil to 98% in 2001 from a low of just over 80% in the early 1980s. East coast refiners are users of light, sweet crudes (sulfur level dropped from 1.01% wt in 1992 to 0.89% wt in 2001) and have little coking capacity (See Swain Oil & Gas Journal, November 3, 2003: pp. 54-57). Therefore the East coast is very susceptible to the political situation in the World. Talks on the situation with the majors seem necessary ASAP??