

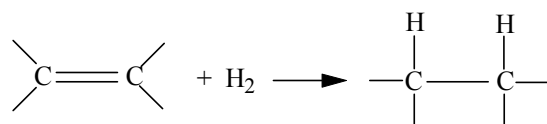
## Chapter 1

# Hydrogen Thermochemistry

Historically, experimental heats of hydrogenation have had an importance far out of proportion to the small number of research groups engaged in their measurement. Much of our quantitative understanding of such concepts as resonance, conjugation, aromaticity and antiaromaticity, molecular strain, and the more subtle aspects of molecular stability arose from hydrogenation experiments. For examples from the work of the six principal research groups in the field, see Conant and Kistiakowsky (1937), Williams (1942), Skinner (1959), Turner *et al.* (1973), Roth *et al.* (1991), and Rogers *et al.* (1998).

### 1.1 Definitions

When hydrogen is added across a carbon-carbon double or triple bond

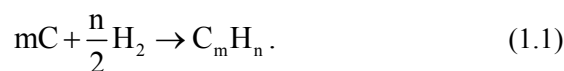


a measurable amount of heat is given off to the surroundings owing to a decrease in energy and enthalpy of the system. For a reaction carried out at constant pressure, the heat out is equal and opposite to the enthalpy change of the system  $\Delta H$ . From the vast field of hydrogenation chemistry, we shall concentrate almost exclusively on the thermochemistry of simple hydrogen addition to unsaturated hydrocarbons in this work. Hydrogenation of unsaturated hydrocarbons always gives off heat, hence the molar enthalpy change of hydrogenation  $\Delta_{\text{hyd}}H_{298}$  is always negative.

The molar enthalpy of formation  $\Delta_f H$  of any substance is the change in enthalpy that takes place when elements combine to form one mol of that substance by a formation reaction, real or hypothetical

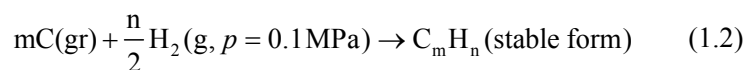
Elements  $\rightarrow$  Compound

In the case of hydrocarbons, the formation reaction is



It is possible to determine the energy change of any well defined chemical reaction  $\Delta_r U$  carried out at constant volume by measuring the heat given off to or absorbed from the surroundings by suitable calorimetric means. (Heat absorbed increases the energy of the system making  $\Delta_r U$  positive.) If a substance is burned at constant volume  $V$ , one speaks of its “heat” of combustion  $\Delta_c U$  and if a hydrogenation is run at constant pressure  $P$ , one speaks of its heat of hydrogenation, meaning its  $\Delta_{\text{hyd}} H_{298}$ . Energy and enthalpy are related by the well-known definition  $H \equiv U + PV$ .

If the reactants and products of a formation reaction are in their standard states, the enthalpy change is a *standard* enthalpy of formation  $\Delta_f H_{298}^\circ$



where (gr) designates the graphitic form of carbon and the stable form of the hydrocarbon is a gas (g), liquid (l) or a solid (s) according to the temperature. The unit of pressure is the pascal  $\text{Pa} = \text{Nm}^{-2}$ , where  $10^5 \text{ Pa} = 1 \text{ bar} \cong 1 \text{ atmosphere}$ . If the reaction is carried out at or corrected to a standard temperature of 298 K (strictly defined as 298.15 K) the symbol  $\Delta_f H_{298}^\circ$  is used. See Klotz and Rosenberg (2000), especially Table 4.1 for a more detailed discussion of standard states. An enthalpy change measured at or corrected to 298 K but not under strict standard state conditions is denoted  $\Delta H_{298}$ . Each enthalpy change,  $\Delta_f H_{298}^\circ$  and  $\Delta_{\text{hyd}} H_{298}$ , is a special case of the less restricted  $\Delta H_{298}$ .

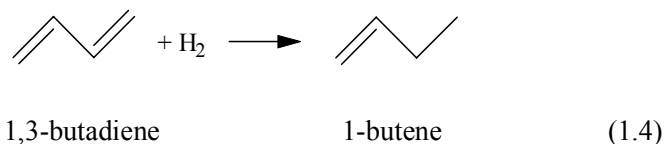
A reliable  $\Delta_{\text{hyd}} H_{298}$  and a reliable enthalpy of formation  $\Delta_f H_{298}^\circ$  of either the reactant or the product of hydrogenation leads to  $\Delta_f H_{298}^\circ$  of the

other participant in the reaction because  $\Delta_f H^\circ(H_2) = 0$  at 298 K and  $10^5$  Pa by definition.

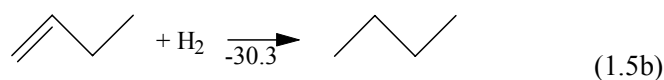
$$\Delta_{\text{hyd}} H_{298} = \Delta_f H_{298}(\text{product}) - \Delta_f H_{298}(\text{reactant}) - \underbrace{\Delta_f H_{298}^\circ(H_2)}_0. \quad (1.3)$$

Frequently, the  $\Delta_f H_{298}$  of an alkane is accurately known but  $\Delta_f H_{298}$  values of one or more of the several alkenes or alkynes that can be hydrogenated to it are not known. The hydrogenation experiment then yields  $\Delta_f H_{298}(\text{alkene or alkyne})$  by Eq. (1.3). A simple example is that of the isomeric linear hexenes, hexadienes, and 1,3,5-hexatriene, all of which can be hydrogenated to give *n*-hexane. Conditions are usually such that  $\Delta_f H$  calculated from hydrogenation data is very close to the enthalpy of formation of the alkene in the standard state  $\Delta_f H_{298}^\circ$ . A less usual situation is determination of the  $\Delta_f H_{298}$  of the product alkane by combining  $\Delta_{\text{hyd}} H_{298}$  with the known  $\Delta_f H_{298}$  of an alkene.

Partial heats of hydrogenation that are not directly measurable can be obtained from total heats of hydrogenation by an indirect calculation.



The hydrogenation of 1,3-butadiene to 1-butene cannot be carried out quantitatively but we know the total heats of hydrogenation at 355 K of both components to give *n*-butane as the product (Conant and Kistiakowsky, 1937).



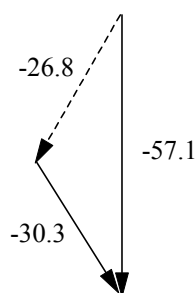


Fig. 1.1 A thermochemical cycle of hydrogenation reactions.

These results (both in  $\text{kcal mol}^{-1}$ , Chap. 2) permit one to construct a thermochemical cycle with one unknown  $\Delta_{\text{hyd}}H$ , shown in Fig. 1.1 as a dashed arrow. By the first law of thermodynamics, the closed path around the cycle has  $\Delta H = 0$ , so

$$\Delta_{\text{hyd}}H_{355}(\text{1,3-butadiene}) = -57.1 - (-30.3) = -26.8 \text{ kcal mol}^{-1}. \quad (1.6)$$

It is not always necessary to have an accurate  $\Delta_{\text{f}}H_{298}$  for the product alkane. For example, if the  $\Delta_{\text{f}}H_{298}$  (alkane) in Fig. 1.1 were unknown or thought to be unreliable, calculation of  $\Delta_{\text{f}}H_{298}$  (1,3-butadiene) and  $\Delta_{\text{f}}H_{298}$  (1-butene) would be suspect but  $\Delta_{\text{hyd}}H_{298}$  of the difference between them, which is the partial reaction of 1,3-butadiene to 1-butene, would still be valid. In this way Kistiakowsky (Conant and Kistiakowsky, 1937) found the enthalpy of isomerization of *cis*- to *trans*-2-butene to be negative (*trans* more stable than *cis*) and to have  $\Delta_{\text{isom}}H_{355} = -0.95 \pm 0.14 \text{ kcal mol}^{-1}$ . See also Turner and Garner (1957) for an analogous determination of the enthalpy difference between *exo*- and *endo*-cyclic double bonds.

No one has ever claimed that hydrogen thermochemistry will replace combustion thermochemistry but, as Kistiakowsky pointed out in his first paper on the subject (Kistiakowsky *et al.*, 1935), reaction thermochemistry, despite its lack of generality, is a powerful tool because it can be expected to yield more accurate enthalpies of formation than combustion thermochemistry for some molecules under some circumstances. Reaction thermochemistry, especially hydrogen

thermochemistry, is particularly well suited for determination of small energy differences between large molecules.

Hydrogenation thermochemistry has been effective in quantitative evaluation of quantum mechanical effects and molecular strain, for example, resonance stabilization of aromatic compounds, conjugative stabilization of linear polyenes and polyynes, and steric effects in *cis*- and *trans*- isomers. Kistiakowsky's measurement of  $\Delta_{\text{hyd}}H$  of benzene (Conant and Kistiakowsky, 1937) gave the first experimental, quantitative value of the resonance energy of benzene, long known qualitatively through its reluctance to add bromine across the presumed double bonds of its Kekule structure, and given a quantum mechanical rationale by Huckel in 1931 and by Pauling in 1933. The first quantitative measure of conjugation, hyperconjugation, and strain in organic molecules arose from Kistiakowsky's determination of the differences in  $\Delta_{\text{hyd}}H$  among alkenes and between monoalkenes and dienes (Conant and Kistiakowsky, 1937).

Recent advances in computational chemistry have made it possible to calculate enthalpies of formation from quantum mechanical first principles for rather large unsaturated molecules, some of which are outside the practical range of combustion thermochemistry. Quantum mechanical calculations of molecular thermochemical properties are, of necessity, approximate. Composite quantum mechanical procedures may employ approximations at each of several computational steps and may have an empirical factor to correct for the cumulative error. Approximate methods are useful only insofar as the error due to the various approximations is known within narrow limits. Error due to approximation is determined by comparison with a "known" value, but the question of the accuracy of the "known" value immediately arises because the uncertainty of the comparison is determined by the combined uncertainty of the approximate quantum mechanical result and the standard to which it is compared.

Once the validity of a quantum mechanical procedure has been established by its ability to reproduce various *accurate* experimental results, the way is clear to calculate unknown thermochemical values of unstable or explosive compounds, unsuited to classical thermochemical methods, or to calculate thermochemical properties of molecules, radicals, or ions of fleeting existence (e.g., Zavitsas, Matsunaga, and

Rogers, 2005). Herein lies a major advantage of the accuracy inherent hydrogen thermochemical results and a reason for renewed interest in the diverse but scattered literature devoted to hydrogen thermochemistry. Parts 1 and 2 of this work are devoted to experimental hydrogen thermochemistry while part 3 treats the emerging field of computational hydrogenation thermochemistry.

## 1.2 History

In 1935, Kistiakowsky's group (Kistiakowsky *et al.*, 1935) published the first of a series of papers on the experimental determination of  $\Delta_{\text{hyd}}H$  of 51 hydrocarbons containing from 2 to 10 carbon atoms. They pointed out that, while experimental measurement of the energy of combustion  $\Delta_{\text{c}}U$  is generally more *precise* than  $\Delta_{\text{hyd}}H$  measurement, arriving at the desired enthalpy of formation  $\Delta_{\text{f}}H_{298}$ , through  $\Delta_{\text{hyd}}H_{298}$  may be more *accurate* because  $\Delta_{\text{hyd}}H_{298}$  is much the smaller number. Thus  $\Delta_{\text{c}}U$  values increase monotonically with the number of carbons and the molecular weight but  $\Delta_{\text{hyd}}H_{298}$  for monoalkenes, for example, do not.

At the time of Kistiakowsky's first paper, many extant thermochemical results had been measured in the nineteenth century and are now of archival interest only. Using these data, Kistiakowsky observed that it was impossible to calculate the magnitude or, in some cases, even the sign of energy differences resulting from small changes in molecular structure. This motivated an investigation into hydrogen thermochemistry by which the Kistiakowsky group determined  $\Delta_{\text{hyd}}H_{298}$  at a level of precision of about  $\pm 0.1$  kcal mol<sup>-1</sup>. For example, they found  $\Delta_{\text{hyd}}H_{298}$  for *cis*- and *trans*-2-butene to be  $-28.33 \pm 0.10$  and  $-27.38 \pm 0.10$  kcal mol<sup>-1</sup> respectively, leading to the isomerization enthalpy  $\Delta_{\text{isom}}H_{298} = -0.95 \pm 0.14$  kcal mol<sup>-1</sup> and showing that the *trans* isomer is the more stable of the two. This was confirmed in 1951 by accurate combustion thermochemistry. Prosen, Maron *et al.* found  $\Delta_{\text{c}}H = -647.65 \pm 0.29$  kcal mol<sup>-1</sup> and  $\Delta_{\text{c}}H = -646.90 \pm 0.23$  kcal mol<sup>-1</sup> respectively, for the two isomers leading to  $\Delta_{\text{isom}}H_{298}^{\circ} = -0.75 \pm 0.37$  kcal mol<sup>-1</sup>, the difference between them. Even in this simple case, the combustion results must be 28 times as precise as the hydrogenation results to achieve the same precision in the enthalpy difference. A similar

calculation for C<sub>8</sub> monoalkenes would require a precision ratio of 56:1, C<sub>12</sub> requires a ratio of 84:1 and so on.

The series of papers written by Kistiakowsky in the late 1930s is arguably the most influential group of research papers ever published on the relationship between experimental thermochemistry and molecular structure, for it contains the first quantitative assessment of the energetic influence conferred upon molecules by the structural features conjugation, hyperconjugation, aromatic resonance, and molecular strain. Later, antiaromaticity and homoaromaticity were added to this list. These structure-energy relationships are referred to directly or indirectly in most elementary organic chemistry textbooks to this day.

Kistiakowsky's work was cut short by World War II, to be taken up briefly by Williams (1942), who carried out the first accurate  $\Delta_{\text{hyd}}H_{298}$  measurements made *in solution*. Though the rationale of hydrogen thermochemistry was investigation of relatively large molecules, the gas-phase method used by Kistiakowsky had pretty nearly reached its limit in size because larger molecules are not volatile enough to be hydrogenated under the conditions he used. The change-over from gas-phase thermochemistry to solution thermochemistry was inevitable if hydrogen thermochemistry was to move in the natural direction, that is, toward the study of larger molecules and molecules less volatile than hydrocarbons. Solution hydrogenation does not suffer restrictions due to volatility and can be carried out, in principle, at any temperature. As an added complication, however, solvent interactions with both reactant and product may influence the measured  $\Delta_{\text{hyd}}H_{298}$ . These influences were treated in detail by Williams (1942).

Following Williams' work, Skinner's group published 3 papers in the late 1950's (Skinner, 1957). Skinner's work is noteworthy for its exploration of intramolecular energetic interactions of alkynes.

Starting contemporaneously with Skinner, Turner's group (Turner *et al.*, 1957) published a much larger body of work ending in 1973. Turner's work produced a substantial amount of data on the relative stability of isomers, for example, *exo-endo* isomers like methylcyclopentene and methylenecyclopentane.

More recent work in hydrogen thermochemistry has been by the groups of Roth (1983) and of Rogers (Bretschneider and Rogers, 1970). Typically, work of the Roth group is characterized by numerous

measurements on structurally interesting molecules, high accuracy (typically  $\pm 0.5$  kJ =  $\pm 0.1$  kcal mol<sup>-1</sup>), and careful correction for small residual solvent effects.

The method we presently use (Caldwell *et al.*, 1997, Rogers *et al.*, 1998) is not as accurate as the best results obtained by the methods above, but it is very sensitive. Within accuracy limits that are never better than  $\pm 0.8$  kJ mol<sup>-1</sup> =  $\pm 0.2$  kcal mol<sup>-1</sup> (Rogers and Crooks, 1983) and may be as high as  $\pm 4$  kJ mol<sup>-1</sup>, we can, in favorable cases, carry out a complete series of  $\Delta_{\text{hyd}}H_{298}$  determinations on a drop of liquid hydrocarbon. Because the molecules one is most interested in are often unstable, difficult to prepare, and difficult to purify (e.g., Rogers *et al.*, 1978), this can be a significant advantage.

### 1.3 Theory and Methodology

Kistiakowsky's apparatus was a flow calorimeter. A mixture of gaseous alkene or alkyne and hydrogen flowed into a reaction chamber filled with finely divided copper catalyst. The reaction product plus heat flowed out of the chamber through a helical glass tube connected to a suitable collection device. The purpose of the helical tube was to convey the heat of reaction to the calorimeter fluid in which the entire reaction system was immersed. Upon reaching a steady state, the amount of heat produced per unit time was measured by the rise in temperature of the calorimeter fluid. The amount of product alkane transferred to the collection device per unit time was also measured. This gave the heat of reaction per mol of reaction product collected. Calibration was by means of a low-voltage electrical heating coil.

Aside from its originality, Kistiakowsky's work is especially impressive in his anticipation of error sources and experimental problems and in the ingenious methods he used to circumvent them or to demonstrate that they had a negligible effect on the final result. In their first paper, the Kistiakowsky group reported results for over 30 full hydrogenation experiments on ethylene. Their final average was  $\Delta_{\text{hyd}}H_{355}^{\text{g}} = -32.824 \pm 0.050$  kcal mol<sup>-1</sup>, where the notation designates reactants and products in the gaseous state at 355 K, reported by Kistiakowsky as 82°C. Kistiakowsky also calculated  $\Delta_{\text{hyd}}H_0^{\text{g}} =$

$$-31.000 \pm 0.150, \quad \Delta_{\text{hyd}} H_{273}^{\text{g}} = -32.460 \pm 0.050, \quad \text{and} \quad \Delta_{\text{hyd}} H_{298}^{\text{g}} = -32.575 \pm 0.050 \pm 0.050.$$

Almost all of Kistiakowsky's further studies were carried out at 355 K and some concern has been expressed in the literature that the difference between  $\Delta_{\text{hyd}} H_{355}$  and  $\Delta_{\text{hyd}} H_{298}$  might invalidate or at least diminish the usefulness of his results. This difference appears to be quite small, however. The change in constant pressure heat capacity,  $\Delta C_p$ , for a reacting system



consists of the difference in  $C_p$  for the alkane and that of the alkene plus  $C_p(\text{H}_2)$ . The  $C_p$  difference between two hydrocarbons is generally quite small, that of the alkene being slightly less than that of the alkane. The difference is partly made up by  $C_p(\text{H}_2)$ , so the change in heat capacity brought about by going from the reactant *system* to the product is small and the change in enthalpy of reaction with temperature is correspondingly small. The  $\Delta C_p \Delta T$  contribution to  $\Delta_{\text{hyd}} H_{298}$  over the temperature range specified is probably not larger than 0.25 kcal mol<sup>-1</sup> (1.0 kJ mol<sup>-1</sup>) per mole of hydrogen consumed in reaction 1.7. This upper limit is calculable from the ethylene data above, because the difference in  $C_p$  is larger for the ethylene-ethane pair than it is for the other hydrocarbon pairs studied by the Kistiakowsky group.

Williams (1942) gave details of the design of the first hydrogen calorimeter constructed specifically for measurements of  $\Delta_{\text{hyd}} H_{302}$  in solution. It was a fairly conventional reaction calorimeter in which the reaction took place in a Dewar flask, but it was made more complicated by the necessity of maintaining the entire system under hydrogen-tight conditions. The sample was contained in a glass ampoule broken by an externally controlled mechanical device to initiate the reaction. The temperature was 302 K, negligibly different as far as this work is concerned from 298 K. Difficulties with different choices of solvent and catalyst were discussed and eventually glacial acetic acid and Pd were selected. We shall discuss solvent effects in Sec. 1.3.1.

The design used by Skinner's group entailed a reaction vessel agitated by vertical oscillation within a conventional Dewar flask. Reaction times were 10-20 minutes as contrasted to several hours

reaction time in the Williams calorimeter. The solvent was glacial acetic acid and the catalyst was reduced PtO. Oscillatory calorimeters have not found favor since this work.

Turner's calorimeter was a modification of the Williams design using rotary stirring and catalyst introduction into the reaction mixture by breaking an ampoule. Turner notes a discrepancy between his results and those of Kistiakowsky for the test compound 1-heptene but does not mention the solvent effect. Turner also points out that the discrepancy is larger for polyenes than it is for monoenes, becoming quite substantial, *viz* 2.3 kcal mol<sup>-1</sup> in the case of cycloheptatriene. Turner's group produced a large amount of excellent thermochemistry but it is regrettable that the solvent corrections necessary to convert their results to the gas phase (see below) were not quantitatively accessed. Careful measurements of solvent effects are a salient feature of Roth's hydrogenation studies described below.

We noticed early in our study of hydrogenation thermochemistry (Rogers and McLafferty, 1971) that glacial acetic acid, the solvent of choice at that time, is not necessary to achieve a useful reaction rate for small samples in the presence of large amounts of activated catalyst. We carried out our work using hydrocarbon solvents as the calorimeter fluid. Hydrocarbon solvents show much reduced solvent effects and have the added advantage of lower heat capacity than acetic acid, thus amplifying the thermal signal  $\Delta T$ . The sample, in the form of a dilute solution in the same hydrocarbon as that chosen as the calorimeter fluid, was injected by means of a microsyringe. Very small samples and large amounts of activated catalyst in the reaction slurry reduced reaction times by 100 fold from the previous minimum to about 10–20 s. With such short reaction times, we chose to operate our microcalorimeter in isoperibol mode, that is, we made no attempt to maintain strictly constant temperature except that conditions were manipulated such that the temperature drift before and after reaction was not steep. Injection of a sample caused a typical sigmoidal temperature *vs.* time curve from which the temperature rise for the reaction was interpolated in the usual way (Rogers and Sasiela, 1973). In later versions of the calorimeter, these curves were stored in microcomputer memory and interpolated digitally (Fang and Rogers, 1992). Calibration of the thermal rise and

conversion to conventional enthalpy units was by comparison to the thermal rise of a “known” such as 1-hexene or cyclohexene.

In this method, corrections are not made for the transfer enthalpy from solution to the gaseous state on the ground that solute molecules in very dilute solution with a noninteracting solvent are essentially independent of one another and mimic the ideal gas state. This assumption has been questioned but the results are confirmed by meticulous combustion experiments where they exist (Steele *et al.*, 2002) and by high level computational values (Rogers, *et al.*, 2004).

Roth (1980) developed a hydrogenation method which also uses alkane solvents, thus minimizing solvent interaction. His calorimeter is a very accurate commercial isothermal titration calorimeter (Christensen *et al.*, 1973) and in his initial paper, he compared results with literature values for five olefins. The reaction vessel was maintained at constant temperature before, during, and after addition of a titer of dilute olefin solution by means of a motor-driven precision microburet. Constant temperature was maintained by means of a constant rate Peltier cooler operating in opposition to a variable heater. The heater delivered a number of fixed energy pulses to the reaction vessel controlled by a circuit with a thermistor inside the vessel. During the titration, heat generated or absorbed within the vessel disturbed the balance between the heating and cooling devices and the number of pulses delivered to the heater changed in response to the control circuit. At the beginning of the titration, a sharp change in the number of pulses was recorded and at the end, a change in the opposite direction was recorded. The size of the step function was proportional to the enthalpy change within the reaction chamber. This was converted to conventional enthalpy units by calibration against the heat output from a “reference” resistance heater. An advantage of this ingenious arrangement is that optimum precision could be obtained by adjusting either the voltage to the reference heater or the speed of the microburet so that the size of the hydrogenation or solution plateau (or depression) was equal to that of the reference plateau.

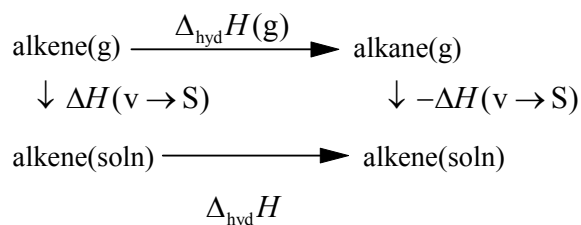
In his initial paper, Roth used acetic acid, methanol, and cyclohexane as solvents and Pd over carbon support, Pt/C, Pt, Pd/BaSO<sub>4</sub>, and PtO<sub>2</sub>. He settled on Pd/C and cyclohexane as optimal. Precision and agreement with Kistiakowsky’s results were in the region of 0.1–0.2 kcal mol<sup>-1</sup>.

### 1.3.1 Correction to the gaseous state

Most contemporary molecular mechanical or quantum mechanical calculations give the properties of a single molecule isolated from all others, that is, a molecule in the ideal gaseous state. Over the years, enthalpies of hydrogenation have been measured by several experimental strategies using a variety of solvents. Only Kistiakowsky's early work on relatively small molecules involved hydrogenation in the gaseous phase. For reasons of limited vapor pressure of substances of current interest, his methods are unlikely to be used again.

Given that some sort of solution thermochemistry is necessary, one must either make the corrections outlined by Williams (1942) and Fuchs and Peacock (1979) or make use of uncorrected or partially corrected data with an awareness of the enthalpic corrections that have been ignored.

Fuchs and Peacock (1979) give the thermodynamic cycle



where (g) denotes the gas phase,  $\Delta_{\text{hyd}}H$  is the uncorrected enthalpy of hydrogenation measured in solution, and  $\Delta H(\text{v} \rightarrow \text{S})$  is the enthalpy of transfer from vapor to solvent

$$\Delta H(\text{v} \rightarrow \text{S}) = \Delta_{\text{soln}}H - \Delta_{\text{vap}}H . \quad (1.8)$$

The influence of experimental strategy on the solvent correction is seen by contrasting the experiments of Williams with those of Turner's group. Williams gives the equation

$$\Delta H_{\text{g}} = \Delta H - ({}_X L_{\text{v}} - {}_Y L_{\text{v}}) - L_{\text{s}} \quad (1.9)$$

where  $L$  designates the molar “latent heats” of vaporization and solution respectively, subscripted X denotes the reactant and Y denotes the product. In the notation we use here,  $L_v = \Delta_{\text{vap}}H$ ,  $L_s = \Delta_{\text{soln}}H$ , and

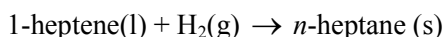
$$\Delta_{\text{hyd}}H_{298}(\text{g}) = \Delta_{\text{hyd}}H - \Delta_{\text{vap}}H_{298}(\text{alkene}) + \Delta_{\text{vap}}H_{298}(\text{alkane}) - \Delta_{\text{soln}}H_{298}(\text{alkane}) \quad (1.10)$$

for the reaction of a liquid alkene to the corresponding liquid alkane where the temperature is taken to be 298 K. If the reactant and product are both solids, Williams’s Eq. 2 is, in our notation,

$$\Delta_{\text{hyd}}H_{298}(\text{g}) = \Delta_{\text{hyd}}H - \Delta_{\text{fus}}H_{298}(\text{alkene}) + \Delta_{\text{fus}}H_{298}(\text{alkane}) - \Delta_{\text{vap}}H_{298}(\text{alkene}) + \Delta_{\text{vap}}H_{298}(\text{alkane}) - \Delta_{\text{soln}}H_{298}(\text{alkane}) \quad (1.11)$$

where  $\Delta_{\text{fus}}H_{298}$  denotes the enthalpy of fusion of the solid at 298 K.

As a trial case, Williams chose hydrogenation of 1-heptene. He equilibrated Pt or Pd catalyst in glacial acetic acid under dry  $\text{H}_2$  at a pressure just over ambient. Upon breaking an ampoule containing 1 to 1.5 g (accurately weighed) of 1-heptene,  $\Delta_{\text{hyd}}H$  was measured for the reaction



where (l) denotes the liquid state and (s) denotes *n*-heptane in solution. The temperature was 302.1 K. Results using Pt catalyst took up more than one equivalent of  $\text{H}_2$  and were deemed unsuitable. The result obtained for 3 runs using Pd catalyst was

$$\Delta_{\text{hyd}}H = -28.280 \pm 0.127 \text{ kcal mol}^{-1}.$$

The enthalpy of solution of *n*-heptane in glacial acetic acid was found in a separate experiment to be  $1.436 \pm 0.006 \text{ kcal mol}^{-1}$ . Williams took enthalpies of vaporization from the literature, obtained by standard classical thermodynamic means, and corrected them to a temperature of 302.1 K to coincide with his  $\Delta_{\text{hyd}}H$  measurements. This led to a difference

$$-\Delta_{\text{vap}}H_{302.1}(\text{1-heptene}) + \Delta_{\text{vap}}H_{302.1}(\text{n-heptane}) = -0.257 \pm 0.152 \text{ kcal mol}^{-1}.$$

The corrected  $\Delta_{\text{hyd}}H_{298}(\text{g})$  is

$$\Delta_{\text{hyd}}H_{298}(\text{g}) = -28.280 \pm 0.127 - 0.257 \pm 0.152 - 1.436 \pm 0.006 \text{ kcal mol}^{-1}$$

which leads to  $\Delta_{\text{hyd}}H_{302.1}(\text{g}) = -29.973 \pm 0.255 \text{ kcal mol}^{-1}$ . This value was further corrected from 302.1 K to 355.1 K in order to coincide with Kistiakowsky's measurements. The result was

$$\Delta_{\text{hyd}}H_{355.1}(\text{g}) = -30.195 \pm 0.285 \text{ kcal mol}^{-1}.$$

This is to be compared to Kistiakowsky's measurement of

$$\Delta_{\text{hyd}}H_{355.1}(\text{g}) = -30.137 \pm 0.037 \text{ kcal mol}^{-1}.$$

Agreement is well within experimental uncertainty. The uncertainty in the difference between the two enthalpies of vaporization is largest and the enthalpies of vaporization contribute least to the result. It is to be anticipated that these enthalpies will not be known for most compounds of future interest, and the temperature at which these experiments were carried out, 302.1 K is closer to the temperature of interest, 298.1 K, so Williams simply dropped the vaporization and temperature corrections to obtain  $\Delta_{\text{hyd}}H_{302.1}(\text{g}) = -29.716 \pm 0.133 \text{ kcal mol}^{-1}$ . The precision of this measurement is about 0.5% or 0.15 kcal mol<sup>-1</sup>. He estimates the over-all uncertainty as  $\pm 1.0\% = 0.3 \text{ kcal mol}^{-1}$ .

Turner's experimental strategy leads to a slightly different correction pattern. In a slight variation in procedure, Turner's group broke the sample ampoule before a similar catalyst ampoule. They re-equilibrated the system before breaking the catalyst ampoule and measured the temperature change. The heat of activation of the catalyst, measured in a separate experiment, was subtracted from the total measured heat. In this way, the liquid  $\rightarrow$  solution reaction of Williams was replaced by a solution  $\rightarrow$  solution reaction, partly escaping the thermal effects of

dissolution of the liquid or solid sample, hence partly escaping the necessity for their correction. The escape was not complete however, because, during hydrogenation in glacial acetic acid, a fairly strong solvent-alkene complex is broken up with formation of a solvent-alkane complex which is weak if it exists at all. Breaking up the complex is endothermic to the extent of about  $0.7 \text{ kcal mol}^{-1}$  per mole of  $\text{H}_2$ , causing the measured  $\Delta_{\text{hyd}}H_{298}$  to be  $0.5 \text{ kcal mol}^{-1}$  less exothermic than it would be in the absence of a solvent effect.

#### 1.4 Accuracy

Literature values of  $\Delta_{\text{hyd}}H_{298}$  are numerous and accurate. There are about 500 known enthalpies of hydrogenation, but there has been no compilation of results since that of Jensen more than a quarter-century ago (Jensen, 1976).

Many of the  $\Delta_{\text{hyd}}H_{298}$  values in the literature have an experimental uncertainty of  $1 \text{ kJ mol}^{-1}$  or less. For example, measurements of  $\Delta_{\text{hyd}}H_{298}$  (1,3,5-cycloheptatriene) using three different techniques in experiments separated by 44 years (Conn *et al.*, 1939, Turner *et al.*, 1973, Roth *et al.*, 1983), have an arithmetic mean experimental uncertainty and a range, when corrected for solvent effects and temperature differences to 298 K, of  $1.1 \text{ kJ mol}^{-1}$ . This level of accuracy is important now that advances in computational methods are such that we may have to decide, between two computational methods that differ by  $2 \text{ kJ mol}^{-1}$ , as to which is in better agreement with experiment (Martin, 1998, Raghavachari *et al.*, 1997). In matters of this kind, the old standard “thermochemical accuracy” of  $1 \text{ kcal mol}^{-1}$  ( $4.2 \text{ kJ mol}^{-1}$ ) no longer suffices.  $\Delta_{\text{hyd}}H$  values are often accurate and precise enough to meet current stringent accuracy standards for use in evaluation and comparison of computational procedures, and for parameterization of empirical or semi-empirical computational methods (e.g., Rogers *et al.*, 1979).

#### 1.5 Applications

A simple determination of resonance stabilization in benzene is shown in Fig. 2. Suppose we take three moles of cyclohexene and one mole of benzene as two different thermodynamic systems, each having three

moles of double bonds. Upon hydrogenation, the heat output is very different for the two systems. The cyclohexene system suffers a decrease of  $\Delta_{\text{hyd}}H_{298} = 3(-28.6) = -85.8 \text{ kcal mol}^{-1} = -359 \text{ kJ mol}^{-1}$ , while the benzene system has  $\Delta_{\text{hyd}}H_{298}$  of only  $-49.8 \text{ kcal mol}^{-1} = -208 \text{ kJ mol}^{-1}$ . Benzene has a lower enthalpy than we might expect it to have and is said to be more stable by  $36 \text{ kcal mol}^{-1} = 151 \text{ kJ mol}^{-1}$  relative to 3 moles of cyclohexene. Stability in benzene is conventionally ascribed to “resonance”, a quantum mechanical property related to the release of spatial constraints on the electrons in benzene relative to those in cyclohexene, i.e., electron delocalization.

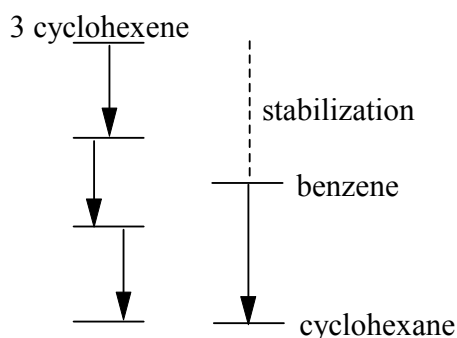


Fig. 1.2 A simple measurement of resonance stabilization.  $\Delta_{\text{hyd}}H(\text{benzene})$  is about  $150 \text{ kJ mol}^{-1}$  less exothermic than  $3 \times \Delta_{\text{hyd}}H(\text{cyclohexene})$ .

Relative methods of calculating resonance stabilization or indeed any relative stabilization, destabilization or strain enthalpies are open to criticism, largely on the choice of a reference state (Fishtik and Datta, 2003). A different reference state, for example three ethene molecules in place of three cyclohexene molecules, gives a different “resonance stabilization” ( $48.6 \text{ kcal mol}^{-1} = 203 \text{ kJ mol}^{-1}$ ). Thermochemical criteria have, however, the virtues of simplicity and of basing theoretical constructs on enthalpies one can, at least in principle, measure directly, as distinct from things (ring currents, *etc.*) that we suppose are correlated with enthalpy. Theoretical artifacts (“hyperconjugation”, “virtual states”, *etc.*) have the disadvantage that they can be molded to fit an author’s preconceived notions (e.g., Jarowski *et al.*, 2004). Thermodynamic

numbers are what they are, impervious to argument. Stability is, in the final analysis, a thermodynamic property.

The thrust of much modern preparative chemistry is toward synthesis and purification of milligram amounts of product. This has great advantage in making micro-purification methods feasible, often providing the experimental thermochemist with 99+ % samples of rare, often unstable compounds, albeit in very small amounts. Synthetic virtuosity feeds the interest of theoretical chemists, but it places correspondingly great demands on the sensitivity of the thermochemical methods to be employed in finding  $\Delta_{\text{hyd}}H$  (or  $\Delta_c H$ ), and ultimately the desired enthalpy of formation  $\Delta_f H_{298}$ .

### 1.6 Details of Calorimeter Construction

Given the availability of modern instrumentation, the contemporary chemist is spared the meticulous and laborious procedures followed in early hydrogen thermochemistry (see, for example, Kistiakowsky, *et al.*, 1935, 1936). Only two more recent hydrogen calorimeter implementations are recommended to the scientist who wishes to pursue this line of research, one a commercial instrument (Tronac Inc. Orem, UT, USA) and one that can be constructed from standard laboratory equipment with a few modifications.

Roth's group has achieved excellent results using a commercial, electrically calibrated, titration calorimeter (Roth, *et al.*, 1980 and following papers). Some of the instrumental details of the calorimeter have been reviewed (Christensen, *et al.*, 1973) along with details of its testing on standard substances (Roth and Lennartz, 1980). In this work, the measured enthalpy of *solution* of, for example, isooctane in cyclohexane becomes smaller during a titration run owing to the change in the nature of the cyclohexane-isooctane mixture as isooctane is added. This nearly linear change was extrapolated to the "first" solution enthalpy, that is,  $\Delta_{\text{soln}}H$  at infinite dilution. A comparable trend in  $\Delta_{\text{hyd}}H$  during the sample addition was not observed.

Because the commercial instrument used by Roth has been fully documented (Christensen *et al.*, 1973), the "home made" device will be more completely described here. We have constructed calorimeters from a design that has evolved with use over a number of years (Rogers, *et al.*,

1971 and following papers), Throughout the evolution of the design, principles of simplicity, economy, miniaturization, and, above all, safety have been followed. Simplicity, economy, and safety need no recommendation. The categories given are not mutually exclusive. For example, the smaller the calorimeter and its attendant hydrogen carrying apparatus, the less hydrogen there is to be controlled, the less hydrogen that will escape in the event of an accident, and the safer the entire procedure is. In 30 years of hydrogenation research, we have suffered no injuries.

Miniaturization is especially advantageous in an era when compounds with extraordinarily interesting structural and thermochemical properties are being synthesized but only in very small amounts. Because the first principle of all calorimetry is that the sample must be well defined and pure (or at least have a small amount of known impurity), microcalorimetry permits use of a wider range of contemporary purification techniques, especially preparative gas chromatography, than traditional calorimetry. There is, of course, no reason to suppose that the evolutionary process of hydrogen calorimeter design cannot be continued to produce smaller, safer, and possibly more accurate instruments.

The calorimeter used in our laboratory was a 25 ml Erlenmeyer flask sealed by means of a serum stopper (Z 10,076-5, Aldrich Chem. Co., P. O. Box 2060, Milwaukee, Wisconsin 53201, USA) containing about 10 ml of a stirred slurry of catalyst and a noninteracting, nonpolar solvent, typically *n*-hexane, but possibly one of many other choices, as the occasion demanded.

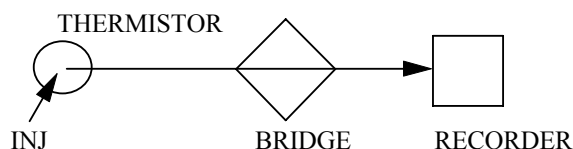


Fig. 1.3 Schematic diagram of the calorimeter.

The temperature monitoring circuit consisted of a thermistor (YSI.com) protruding through the serum stopper into the slurry and connected as one arm of a conventional Wheatstone bridge powered by

an ordinary dry cell, the output of which was fed into a millivolt recorder (Rogers, 1980). Injection of sample or standard causes a rapid reaction in the flask at the left of the schematic diagram in Fig. 1.3, which brings about a change in the resistance of the thermistor and a change in the voltage output of the bridge.

The catalyst charge was 200–300 mg of 5% or 10% Pd or Pt on charcoal (Aldrich). Stirring rates of approximately 400–600 rpm were used (Multistirrer 6 or equivalent, [www.velp.com](http://www.velp.com)). The exact stirring rate is flexible but it must be held constant during a run to achieve a moderate, steady temperature drift before and after the temperature rise due to hydrogenation. The reaction flask, wrapped in an insulating blanket, was firmly held in place by a styrofoam box or plain 600 mL beaker glued to the upper surface of the stirrer so that only the inlet septum protruded slightly from the insulation. In constructing the box, the walls should be thick but the bottom should be thin or there should be no bottom at all in order not to interfere with stirring. This, of course, requires a stirrer that produces very little heat during constant operation over the entire experiment.

Hydrogen was admitted to the reaction flask by means of a hypodermic needle thrust through the septum of the serum stopper. Upon admission of hydrogen, a sharp temperature rise of several mK occurs due to activation of the catalyst. After a few minutes, the temperature begins to drift slowly down. The calorimeter is ready for the first injections of sample and standard when the temperature drift as seen on the recorder or microcomputer monitor (see below) approximates the drift lines in Fig. 1.5. Over a time span of 10–30 s, the drift should be well approximated by a linear function.

The Tygon tube connecting the needle to the hydrogen source should be of as small bore as possible and should be as short as possible. Although we did not use it, if we were to build another hydrogen calorimeter, capillary tubing would be used throughout in order to keep the volume of hydrogen small. Lecture bottles of hydrogen are available ([sigmaaldrich.com](http://sigmaaldrich.com) CAS#295396-56L). Under an internal operating pressure of ~1 atm over ambient pressure, the stopper sometimes pops out. This can be prevented by a drop of “Krazy Glue ®” (Elmer’s Products Inc. Columbus OH 63215-3799). **Safety precaution:** The

stopper must be forced very firmly into the mouth of the flask. Always wrap the flask in a towel or wear protective gloves to prevent cuts in case the flask breaks.

Samples consisting of 20–40  $\mu\text{L}$  of an approximately 10% solution (depending on the degree of unsaturation) were injected through the septum using a 25 or 50  $\mu\text{L}$  microsyringe fitted with a Kelf adaptor (Hamilton Co. P. O. Box 10030, Reno, Nevada 89510, USA).

Determination of  $\Delta_{\text{hyd}}H_{298}$  of an unknown alkene or alkyne was by comparison with that of a standard, usually  $\Delta_{\text{hyd}}H_{298}$  (1-hexene) =  $-30.25 \text{ kcal mol}^{-1}$  (Skinner and Snelson, 1959, Rogers, 1979). Injections of sample were made in alternation with injections of the standard in order to measure the ratio of output heats  $q(\text{sample})/q(\text{standard})$ . Waiting a few moments between injections was sufficient to reestablish a baseline as in Fig. 1.5. Statistical analysis shows that 9 ratios (18 injections in all) are optimum in order to take enough samples for statistical validity of the 95% confidence limit calculation but to avoid needless and redundant measurements.

The heat output of the standard,  $q(\text{standard})$  was adjusted to within a few % of the heat output of the unknown sample  $q(\text{sample})$  by selecting the concentration of the standard solution. Most of the time,  $q(\text{sample})$  could be guessed fairly closely from that of analogous cases, enabling us to select the right concentration of the standard solution at the outset. If the first guess was wrong, results from the first few injections enabled us to calculate the right concentration for the standard. A new standard solution was made up to take the 9 ratio measurements necessary to complete the experiment.

Once  $q(\text{sample}) \cong q(\text{standard})$ , one already knows  $\Delta_{\text{hyd}}H_{298}$  of the sample to within a few percent. The rest of the experiment is devoted to reducing this uncertainty as much as possible through the simple ratio

$$\frac{\Delta_{\text{hyd}}H_{298}(\text{sample})}{30.25} = \frac{q(\text{sample})}{q(\text{standard})}. \quad (1.12)$$

Given the calorimeter dimensions and standard and sample concentrations above, the voltage output of the bridge was 1–2 mv. Rise time of the voltage from a steady drift before reaction to a steady drift

after reaction was 10–12 s. Temperature changes were not calculated; only the ratio of the heats in Eq. (1.12) was needed. Voltage output from the bridge can be input to a potentiometric recorder so as to obtain pairs of standard-sample reactions which give response curves like those in Fig. 1.5. Fitting a pair of verticals to the extrapolated linear drifts before and after reaction for a series of 18 alternating injections of standard and sample leads to a series of 9 ratios of verticals which is the series of  $q(\text{sample})/q(\text{standard})$  ratios we seek for 9 replicate solutions of Eq. (1.12). Calculation of the mean, standard error, and standard deviation follow routinely.

### 1.7 Design Modifications

We used either a commercial Wheatstone bridge or one of several that were easily assembled on a circuit board from commonly available parts.

Working from recorder output is inconvenient, and in some case subjective (as in where, exactly, to draw the vertical when you know the result you want). For this reason we substituted the A-D converter and microcomputer in Fig. 1.4 for the recorder.

The topic of computer interfacing is a large and changing one. An early and very readable introduction to the field was given in the *Bugbooks* by Larsen (1975) and Rony (1976), who were active at the very beginning of the microcomputer revolution. More recently, An (1998) has reviewed the subject.

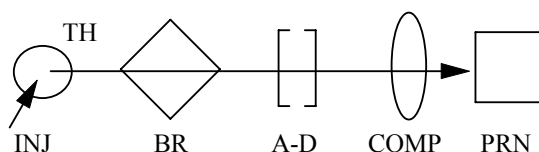


Fig. 1.4 Schematic diagram of the calorimeter with an interfaced computer.

Typically, the bridge output was conveyed through an A-D converter to the computer COMP, where several hundred points on the curve were stored digitally and the curve was displayed on the computer monitor. Operational amplifiers were also used between the bridge and A-D

converter with satisfactory results. Depending on the converter properties, the amplifier may or may not be necessary.

The computer was programmed to perform a linear least squares fit to the temperature drift before and after reaction to give the equation of the upper and lower straight lines in Fig. 1.5. The difference between the two linear least squares functions at the vertical passing through the point 2/3 up the reaction thermogram (Rogers and Dejeroongruang, 1988) is proportional to the heat of reaction.

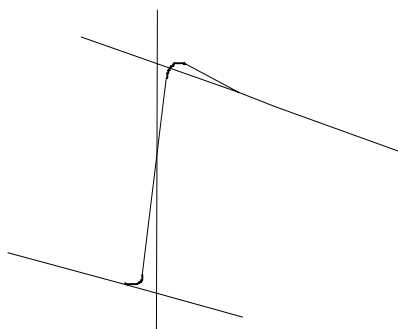


Fig. 1.5 Thermogram with least squares extrapolations.

Alternating sample and standard injections, having previously input the  $\Delta_{\text{hyd}}H_{298}$  of the standard to the computer, the computer carried out a simple arithmetic program to calculate  $q(\text{sample})/q(\text{standard})$  and hence  $\Delta_{\text{hyd}}H_{298}$  by Eq. (1.12). The result was stored digitally, and printed out to PRN to obtain a hard copy record.