

LECTURE NOTES IN PHYSICAL CHEMISTRY CHAPTER FOUR**THERMOCHEMISTRY****1 INTRODUCTION.**

Chemical thermodynamics relies heavily upon the availability of a substantial data - base. One of the most extensive portions of the existing data - base is made up of measured values for enthalpy changes.

We concentrate on enthalpy, rather than internal energy, changes because they are more readily accessible. We recall that::

$$\Delta U = q_v \quad (1)$$

and

$$\Delta H = q_p \quad (2)$$

We repeat the observation that the condition of constant volume is only attainable for gaseous samples. For condensed phase systems, it is only practical to make the heat transfer measurements at constant pressure.

It is instructive to look at the range of the types of enthalpy changes that are important to us.

1.1 Pure Substances.

If there is no change in the phase of a pure substance, we only have to concern ourselves with the effects of changing the conditions.

Changing the pressure at constant temperature has relatively little effect upon the enthalpy and we can almost, but not quite, dismiss it as a curiosity.

$$(\delta H/\delta p)_T = V - T(\delta V/\delta T)_p \quad (3)$$

which is zero for an ideal gas and otherwise quite small.

Experimental estimates of $(\delta H_m/\delta p)_T$ can be obtained from the determination of densities at several different temperatures.

It is worth noting that:

$$\begin{aligned} (\delta H/\delta V)_T &= -(\delta H/\delta p)_T / K_T & (4) \\ &= V/K_T + T(\delta V/\delta T)_p(\delta p/\delta V)_T \\ &= V/K_T - T(\delta p/\delta T)_V \end{aligned}$$

Changing the temperature at constant pressure can have a substantial effect upon the enthalpy. The temperature derivative of the enthalpy at constant pressure is the isobaric heat capacity.

$$(\delta H/\delta T)_p = C_p \quad (5)$$

If the temperature change is over a small enough range, so that the heat capacity, C_p , can be treated as remaining constant, then:

$$\Delta H = C_p \Delta T \quad (6)$$

If there is a larger temperature range and it is necessary to take into account the temperature dependence of the heat capacity then:

$$\Delta H = \int C_p Dt \quad (7)$$

1.2 Phase Changes

Phase changes involve significant changes in enthalpy. The process of converting a solid into a liquid (fusion or melting) requires heat. The **enthalpy of fusion**; $\Delta_{\text{fus}}H$, is always positive. This is the energy that is required to break down the crystal lattice without loss of contact between the component molecules, atoms or ions.

The process of converting a liquid into a gas (vaporization or boiling) also requires heat. The **enthalpy of vaporization**, $\Delta_{\text{vap}}H$ is also always positive and is substantially higher than $\Delta_{\text{fus}}H$. This is the energy required to overcome all of the forces of attraction that exist between the component particles.

When a phase change occurs the two phases are in equilibrium. Thus, at the melting temperature, $\Delta_{\text{fus}}G = 0$, which implies that:

$$\Delta_{\text{fus}}H = T_f \Delta_{\text{fus}}S \quad (8)$$

Similarly

$$\Delta_{\text{vap}}H = T_b \Delta_{\text{vap}}S \quad (9)$$

$$\Delta_{vap}S = S_{gas} - S_{liq}. \quad (10)$$

The entropy of a gas is much higher than that of the corresponding liquid. It has been found that the molar entropies of vaporization differ very little from one substance to another. A typical value is $88 \text{ J K}^{-1} \text{ mol}^{-1}$ so that, to a fair approximation, we can write:

$$\Delta_{vap}H = 88 T_b \text{ J mol}^{-1} \quad (11)$$

This equation is known as Trouton's rule. It underestimates the enthalpy of vaporization for a few highly structured liquids, of which water is a prime example. Otherwise, it can be very useful.

The heat that is required for the direct transition from solid to gas is the **enthalpy of sublimation**, ΔH_{sub} . A fairly good estimate of the molar enthalpy of sublimation can be obtained from adding together the enthalpies of fusion and vaporization. The reason why it is not a perfect estimate is that the two components are normally measured at different temperatures and both vary, to some extent, with temperature.

There is another type of phase change that is encountered from time - to - time and that involves going from one solid allotrope to another. The transition from graphite to diamond is one example of that and that from white to red phosphorus is another. Mention may also be made of the transition between the different liquid phases of helium.

1.3 Enthalpies of Solution.

Enthalpies of solution, ΔH_{soln} , are generally expressed in terms of the isobaric heat absorbed, when one mole of solute, is transferred from its pure state to the solvent. The enthalpies of solution tend to be quite strongly concentration dependent. The values that are most frequently quoted are for the extreme dilution (**infinite dilution** – zero concentration) limit. That corresponds to the situation in which the solute molecules (or ions) are totally dispersed in the solvent medium. These values obviously have to be obtained by extrapolation of experimental data.

We shall limit our discussions to cases where the solvent is a liquid. It will be helpful to differentiate between several different types of solute.

Enthalpies of solution of gaseous solutes are generally negative. That is the case whether the solvent is polar or non - polar. One possible way of looking at the situation is in terms of two steps. First the solute gas is condensed, which is inevitably significantly exothermic; thereafter there is a mixing process which may be either endo- or exo - thermic but of limited magnitude.

Enthalpies of solution of liquid solutes may be either positive or negative as may those of solid solutes.

Much of the interest in enthalpies of solution involves water as the solvent. In that case it is necessary to draw a distinction between non – (or

weak) and strong electrolyte solutes. In either case, it is instructive to break down the dissolution process into a number of distinct steps.

1.3.1 Non Electrolyte Solutes:

We look first at the case of a non-electrolyte solute. We can visualize the dissolution process as involving several stages

Stage 1: The first stage is the **vaporization** of the solute. If the solute is a liquid, we are looking at an enthalpy contribution equal to ΔH_{vap} . If the solute is a solid then the contribution is ΔH_{sub} .

Stage 2: Room needs to be made in the bulk of the solvent to accommodate the individual solute molecules. We may refer to the heat absorbed for this process as the enthalpy of **cavity formation**, ΔH_{cav} . We might expect this contribution to be roughly proportional to the size of the cavity. We might also expect there to be a relationship between the enthalpy of cavity formation and the enthalpy of vaporization of the solvent. In the case of water hydrogen bonds need to be broken to form the cavities.

Stage 3: The solute molecules are placed in the solvent cavities. There will be an enthalpy contribution due to the interaction between the solute species and its solvent co - sphere. In the case of water, there will also be an important contribution due to the structural reorganization of the solvent.

1.3.2 Ionic Solutes.

There are even more stages to be contemplated in the dissolution of an ionic solid in water. The simplest cases are those involving the combination of monatomic cations and monatomic anions. Sodium Chloride is an obvious example.

Stage 1: In this instance, the first stage is to dissociate sodium chloride into its elements.



Here $\Delta H_1 = -\Delta_f H(\text{NaCl})$, where $\Delta_f H(\text{NaCl})$ is the **enthalpy of formation** of sodium chloride.

Stage 2a: Stages 2a and 2b involve converting the two elements into their respective monatomic gaseous forms.



Here $\Delta H_{2a} = \Delta H_{\text{atom}}(\text{Na})$, the enthalpy of atomization of sodium, with appropriate adjustments to correct the temperature to 25° C. This involves **sublimation** of the solid sodium to give the gas phase species $\text{Na}_2(\text{g})$ and then **dissociation** of the diatomic gaseous sodium molecules.



Here $\Delta H_{2b} = \frac{1}{2} \Delta H_{\text{B.E.}}(\text{Cl-Cl})$, which is one half of the Cl -Cl **bond enthalpy**.

Stage 3a: Stage 3a involves the conversion of the monatomic sodium and chlorine species to the corresponding cation and anion.



Here we are looking at the **ionization energy of sodium**.



Here we are dealing with the **electron affinity of monatomic chlorine** (actually minus the electron affinity by most conventions).

$$\Delta H_{3a} + \Delta H_{3b} = \text{I.P. (Na(g))} - \text{E.A. (Cl(g))}$$

Stages 1 - 3b collectively describe a process in which the ions of the sodium chloride lattice are completely separated, one from the other. The enthalpy, which is the reverse of that of the process of lattice formation, is called the **lattice enthalpy** of the system.

$$-\Delta H_{\text{lat}}(\text{NaCl}) =$$

$$-\Delta_f H(\text{NaCl}) + \Delta H_{\text{atom}}(\text{Na}) + \frac{1}{2}\Delta H_{\text{B.E.}}(\text{Cl-Cl}) + \text{I.P. (Na(g))} - \text{E.A. (Cl(g))}$$

All of the quantities on the right hand side should be available from standard tabular sources.

Stage 4:



Stage 4 involves the immersion of both the sodium and chloride ions in water. The enthalpy is the sum of the hydration enthalpies of the two ions.

$$\Delta H_4 = \Delta H_{\text{hyd}}(\text{Na}^+) + \Delta H_{\text{hyd}}(\text{Cl}^-)$$

The total enthalpy of solution, which is a measurable quantity, is thus given by:

$$\Delta H_{\text{soln}} = -\Delta H_{\text{lat}}(\text{NaCl}) + \Delta H_{\text{hyd}}(\text{Na}^+) + \Delta H_{\text{hyd}}(\text{Cl}^-)$$

From the measurement of the isobaric heat of solution, and the calculated value of the lattice enthalpy, we can determine the sum of the two enthalpies of hydration.

$$\Delta H_{\text{hyd}}(\text{Na}^+) + \Delta H_{\text{hyd}}(\text{Cl}^-) = \Delta H_{\text{soln}} - \Delta H_{\text{lat}}(\text{NaCl})$$

Further, we see that if we add together stages 2, 3 and 4, we are looking at the process:



which represents the sum of the formation of the two hydrated ionic species from the elements in their respective standard states. That allows us to write:

$$\Delta_f H(\text{Na}^+_{\text{aq}}) + \Delta_f H(\text{Cl}^-_{\text{aq}}) = \Delta H_{\text{soln}} - \Delta_f H(\text{NaCl})$$

We can determine, with relative ease, both the combined enthalpies of hydration and of formation. What we cannot do, experimentally, is separate those combined enthalpies into their respective two components.

It turns out that this is not really a major problem. All that is necessary is for us to select a value for the enthalpy of hydration, or formation, for just one ion and all the other values can be assigned relative to that benchmark.

The standard benchmark is the assignment of zero to the standard enthalpy of formation of the hydrated proton:



If we split this process into three steps, we can obtain a value for the enthalpy of hydration:



$$\Delta H_{\text{hyd}}(\text{H}^+) = -\frac{1}{2} \Delta H_{\text{BE}}(\text{H-H}) - \text{I.P.}(\text{H})$$

Strictly speaking the ionization potential is an internal energy and not an enthalpy and one might wish to make allowances for the formation of one mole of electrons as a gas at one atmosphere pressure.

1.4 Enthalpies of Mixing.

Some pairs of liquids can be mixed in all proportions. The enthalpies of mixing, ΔH_{mix} , are generally reported per mole of mixture.

1.5 Enthalpies of Reaction.

The most widely used source of enthalpy of reaction data is Bomb Calorimetry. The bomb calorimeters are used to determine the enthalpies of combustion of individual substances.

It is instructive to look at a specific combustion reaction, to see how its enthalpy data fits in with other reaction enthalpies.

One of the simplest of combustion reactions is that of methane:



Since enthalpy is a state property, the enthalpy change in going from reactants to products is the same whether the reaction takes place in one or several steps. That is a statement of **Hess' Law**.

It is convenient to think of the combustion reaction as a two - step process.



We are depicting the reaction as going by way of the component elements. We may write the overall enthalpy as the sum of two parts:

$$\Delta H_{\text{reac}} = \Delta H_1 + \Delta H_2$$

We can further separate each of those two parts into two:

$$\Delta H_1 = \Delta H_{1a} + \Delta H_{1b}$$

Where sub-step **1a** corresponds to $\text{CH}_4(\text{g}) \rightarrow \text{C}(\text{s}) + 2 \text{H}_2(\text{g})$

and sub-step **1b** corresponds to the non-event $\text{O}_2(\text{g}) \rightarrow \text{O}_2(\text{g})$.

$$\Delta H_2 = \Delta H_{2a} + \Delta H_{2b}$$

Sub-step **2a** is $\text{C}(\text{s}) + \text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g})$

and sub-step **2b** is $2 \text{H}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2 \text{H}_2\text{O}(\text{l})$.

The enthalpy change for sub-step 2a is the **enthalpy of formation of $\text{CO}_2(\text{g})$** , while that of sub-step 2b is twice the enthalpy of formation of liquid water. Thus:

$$\Delta H_2 = \Delta_f H (\text{CO}_2(\text{g})) + 2 \Delta_f H (\text{H}_2\text{O}(\text{l}))$$

The enthalpy change for sub-step 1a is that for the dissociation of methane into its elements, which is minus the enthalpy of formation of methane. There is no enthalpy change for sub-step 1b, since the reactant is itself an element and no conversion is required. Thus:

$$\Delta H_1 = - \Delta_f H (\text{CH}_4)$$

It follows that the enthalpy of combustion of methane is given by:

$$\Delta H_{\text{comb}}(\text{CH}_4) = \Delta_f H (\text{CO}_2(\text{g})) + 2 \Delta_f H (\text{H}_2\text{O}(\text{l})) - \Delta_f H (\text{CH}_4)$$

The tabulated values of the standard enthalpies of formation are:

$$\Delta_f H^\circ [\text{CH}_4(\text{g})] = - 74.81 \text{ kJ mol}^{-1}$$

$$\Delta_f H^\circ [\text{CO}_2(\text{g})] = - 393.51$$

$$\Delta_f H^\circ [\text{H}_2\text{O}(\text{l})] = - 285.83$$

That gives:

$$\Delta_{\text{rxn}} H^\circ = - 393.51 - 571.66 - (-74.81) = - 890.36 \text{ kJ}$$

Given that enthalpies of combustion are fairly readily accessible from experiment and that the enthalpies of formation of CO_2 and water are well known, we see that it is readily easy to determine enthalpies of formation of combustible substances.

$$\Delta_f H (\text{CH}_4) = \Delta_f H (\text{CO}_2(\text{g})) + 2 \Delta_f H (\text{H}_2\text{O}(\text{l})) - \Delta H_{\text{comb}}(\text{CH}_4)$$

In general, we can write:

$$\Delta H_{\text{reac}} = \sum_{\text{Prod}} n_P \Delta_f H_P - \sum_{\text{Reac}} n_R \Delta_f H_R$$

Given tabulated values of all of the necessary enthalpies of formation, it is possible to determine the enthalpies of any reaction.

The tabulated information is in the form of **'standard' enthalpies** of formation. This requires that both the compound and its component elements, under the standard conditions of 25°C and 1 atm. pressure, be in their standard states. The standard states are the most stable forms. Thus graphite is the unromantic standard state of carbon and it is the white form of phosphorous that is found to be its standard. The original

standard temperature was 0° C because, in the 19th century, it was one temperature that could easily be maintained, using an ice bath. The development of thermostatic control for electrical heaters led to a switch, first to 20° C and then to 25° C..

There is a strong possibility that the atmosphere will eventually be replaced, by the bar as the standard unit of pressure. The standard atmosphere was originally defined to be the average atmospheric pressure at sea level. Since that is clearly somewhat vague, it was replaced by the pressure exerted by a column of mercury 760 mm. high. It transpires that 1 atm. = 1.0135 x 10⁵ Pa. With the desire to do as many calculations as possible, in the context of the SI, it seems to be appropriate to use the bar which is exactly equal to 10⁵ Pascal.

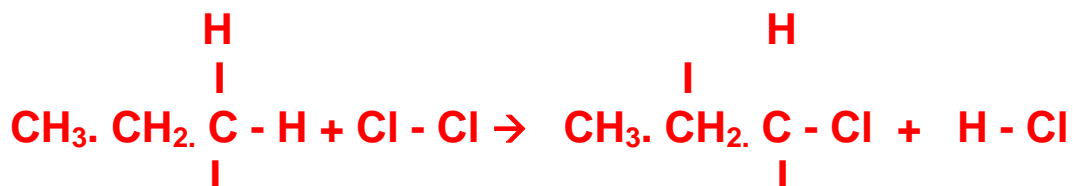
In the event that we do not have access to all of the enthalpies of formation for the reactants and products of a reaction of interest to us, we have an alternative method for predicting reaction enthalpies from tabulated information.

1.6 Bond Enthalpies.

We may look at the reaction in which propane reacts with chlorine to produce 1-chloropropane and hydrogen chloride.



We need to write out the structural formulas for reactants and products:



H**H**

The reaction process involves breaking bonds in the reactant molecules and then rearranging the fragments by forming new bonds to create the product species.

The enthalpy change that is associated with breaking a bond is called the bond enthalpy, $\Delta H_{B.E.}$.

In destroying the reactants, a C-H bond and the Cl-Cl bond need to be broken. To form the products requires the creation of a C-Cl bond and a H-Cl bond. Thus:

$$\Delta H_{\text{reac}} = \Delta H_{B.E.}(\text{C-H}) + \Delta H_{B.E.}(\text{Cl-Cl}) - \Delta H_{B.E.}(\text{C-Cl}) - \Delta H_{B.E.}(\text{H-Cl})$$

Values for the bond enthalpies are tabulated. For a variety of common bond types, the value cited is an average that may have been derived from a substantial number of observations. For example CH bonds are likely to differ in energy when we go from ethyne to benzene to ethene to ethane. There is certainly a substantial difference in those bond lengths.

TABLE 9.5 Some Average Single- and Multiple-Bond Energies*

Single Bonds											
	H	C	N	O	F	Si	P	S	Cl	Br	I
H	436	414	389	464	569	293	318	339	431	368	297
C		347	293	351	439	289	264	259	330	276	238
N			159	201	272		209		201	243?	
O				138	184	368	351		205		201
F					159	540	490	285	255	197?	
Si						176	213	226	360	289	
P							213	230	331	272	213
S								213	251	213	
Cl									243	218	209
Br										192	180
I											151
Multiple Bonds											
			N=N	418		C=C		611			
			N≡N	946		C≡C		837			
			C=N	615		C=O (in O=C=O)		803			
			C≡N	891		C=O (as in H ₂ C=O)		745			
			O=O (in O ₂)	498		C≡O		1075			

*In kilojoules per mole.

2 ENTROPY CHANGES.

2.1 Pure Substances.

If there are no phase changes, we can use the following formulas for the isobaric and isothermal entropy changes.

Since $(\delta S/\delta T)_p = C_p/T$, we may write:

$$\Delta S_p = C_p \ln(T_2/T_1)$$

This requires that C_p can be treated as being constant over the temperature range of interest.

Or:

$$\Delta S_p = \int C_p / T dT$$

if the temperature dependence of C_p needs to be taken into consideration.

Since $(\delta S/\delta p)_T = -(\delta V/\delta T)_p$, we may write:

$$\Delta S_T = -E_p \Delta p$$

for condensed phase materials, assuming that E_p remains constant over the pressure range.

For ideal gases, we can write:

$$\Delta S_T = -R \ln(p_2/p_1)$$

For phase changes, the entropy change is easily calculated from the measured value of the corresponding enthalpy change.

$$\Delta S_{fus} = \Delta H_{fus}/T_f$$

$$\Delta S_{vap} = \Delta H_{vap}/T_b$$

$$\Delta S_{sub} = \Delta H_{sub}/T_{sub}$$

2.2 Entropies of Solution and Mixing.

We can predict the entropy of mixing for an ideal gas fairly easily.

$$\Delta S_{mix}^{ideal} = -R (n_A \ln X_A + n_B \ln X_B)$$

where n_A and X_A are respectively the number of moles and the mole fraction of component A in an ideal gas mixture of A and B.

For the formation of non-ideal mixtures, the entropy changes are derived from a combination of experimental values for the enthalpy and the Gibbs free energy of mixing. We shall worry about how that all fits together at a later juncture.

2.3 Entropies of Reaction.

Entropies of reaction, like the corresponding enthalpies can be obtained from tabulated information. While it is only possible to determine the enthalpies of pure substances relative to a suitable standard, like the

combined enthalpies of the component elements, it is possible to determine absolute values for the molar entropies.

These absolute entropies are generally referred to as the **'third law' entropies**. They are based upon the assumption that the entropy of a substance is zero at absolute zero temperature.

At some temperature T , the absolute entropy is the sum of terms of the type $\Delta S_p = \int C_p / T \, dT$ plus the entropies of fusion and vaporization if and when appropriate.

For gaseous substances, it is possible to determine the absolute entropies from spectroscopic information.

The entropy of a reaction is given by the equation:

$$\Delta S_{\text{reac}} = \sum_{\text{Prod}} n_P S_P - \sum_{\text{Reac}} n_R S_R$$

3 GIBBS FREE ENERGIES.

3.1 Pure substances.

Isobaric Changes:

$$\begin{aligned} \Delta G_p &= \Delta H_p - \Delta(TS)_p \\ &= C_p (T_2 - T_1) + T_2 S_2 - T_1 S_1 \end{aligned}$$

But:

$$S_2 = S_1 + C_p \ln (T_2/T_1)$$

Thus:

$$\Delta G_p = (C_p + S_1) (T_2 - T_1) - T_2 C_p \ln (T_2/T_1)$$

Isothermal changes in free energy will only usually be significant for gases. In the ideal gas case:

$$\Delta G_T = RT \ln (p_2/p_1)$$

3.2 Phase Changes.

For a phase change that is both isothermal and isobaric there is no change in the Gibbs free energy.

$$\Delta G(\alpha \rightarrow \beta) = 0$$

Both solids and liquids are in equilibrium with their respective vapors. That means that we can keep track of the changes in the free energies of the condensed phases by monitoring the changes in the vapor pressure. This is a topic that we will pick up on again when we discuss phase changes in general

3.2 Free Energies of Mixing and Solution.

One of the topics that we shall want to explore in some depth is the thermodynamics of the formation of mixtures and solutions. We already have the ability to give an equation for the free energy of mixing of a pair of ideal gases. That is because each exists as if the other were not present.

$$\Delta G_{mix}^{ideal} = RT (n_A \ln X_A + n_B \ln X_B)$$

3.3 Free Energies of Reaction.

While the concept of the heat (enthalpy) of a reaction is relatively simple as are the principles of its measurement, free energy changes of reactions are less easily visualized and much needs to be learned to grasp the principles of the various experiments that are used to evaluate them.

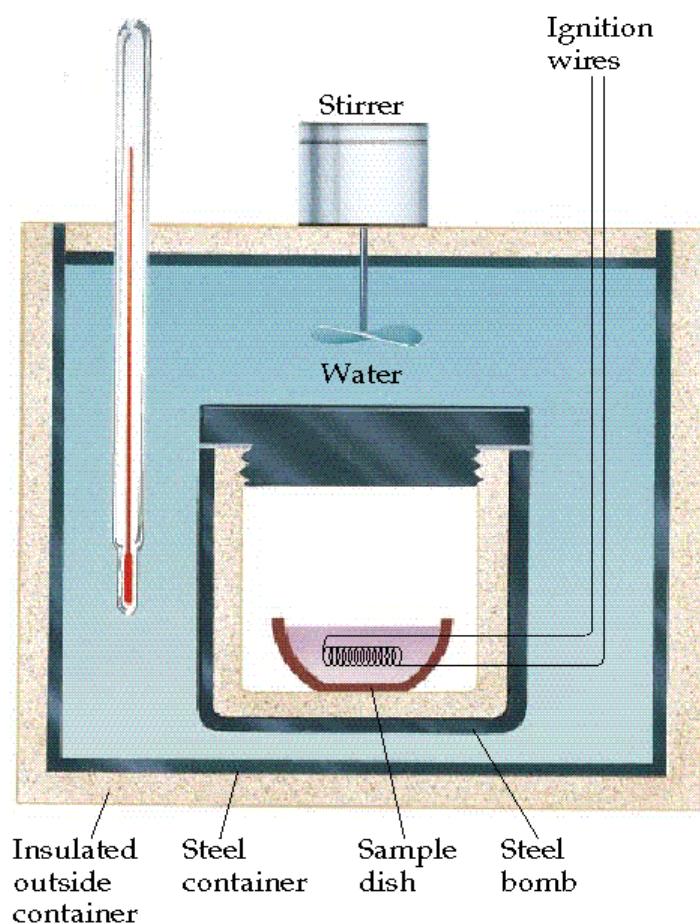
For the moment, we shall simply accept the fact that there exist tables of Gibbs free energies of formation from which we can calculate the Gibbs free energy changes for chemical reactions:

$$\Delta G_{\text{reac}} = \sum_{\text{Prod}} n_{\text{P}} \Delta_f G_{\text{P}} - \sum_{\text{Reac}} n_{\text{R}} \Delta_f G_{\text{R}}$$

4 Calorimetry.

We should take a little time to learn something of the nature of the experimental methods for measuring heats of chemical reactions. The measurement of heat production or absorption is called calorimetry. There are many different designs for calorimeters but they have several features in common. The most widely used calorimeters are probably those designed for the measurement of heats of combustion.

4.1 Bomb Calorimeters



The figure shows a typical configuration for a “bomb” calorimeter

We start by noting that the entire apparatus is enclosed in an insulated container. The importance of that is that any heat that is generated by the combustion reaction is used to raise the temperature of the calorimeter and its contents and is not allowed to “escape” into the room.

The central item is a steel reaction chamber. This will generally have a screw-top lid. The thick steel walls give it both rigidity and good thermal conductivity. Inside the reaction chamber are the reactant materials, one of

which will be oxygen, if the process is combustion. The oxygen is introduced, through the lid, from a gas cylinder before the calorimeter as a whole is assembled.

Most combustion reactions do not take place instantaneously but need to be triggered by something like the spark plug in an automobile engine. In this case an electric current passing through a fine strand of fuse - wire will create a momentary hot spot and initiate the reaction.

Combustion reactions typically generate large amounts of heat. In order to avoid such a large increase in temperature inside the calorimeter that it is virtually impossible to maintain adiabatic conditions (complete insulation), a substantial weighed amount of water surrounds the reaction chamber.

A thermometer is shown. Monitoring the temperature rise is a critical part of the experiment. The picture shows a mercury (or alcohol) - in - glass thermometer but most modern calorimeters use thermistors or thermocouples for temperature measurement.

Whatever heat is generated by the reaction needs to be dissipated rapidly and uniformly throughout the inside of the calorimeter. That requires an efficient stirring mechanism.

The combustion energy is determined by the following procedure.

We consider the nature of the "calorimetric equation".

The heat generated by the reaction equals the heat absorbed by the calorimeter and its contents.

What we monitor is the heat that is absorbed by the calorimeter and its contents q_{cal} .

q_{cal} has two components. The major portion is the heat absorbed by the water. That portion is equal to the product of the mass of water (in grams), the gram specific heat of water ($4.184 \text{ J K}^{-1} \text{ g}^{-1}$) and the temperature increase ΔT . The other portion is the heat needed to raise the temperature, of all of the bits of hardware plus the reaction products, by the same temperature difference.

Thus, we write the calorimetric equation in the form:

$$q_{\text{cal}} = \{ w_{\text{water}} (\text{spec. ht.})_{\text{water}} + C_{\text{cal}} \} \Delta T$$

w_{water} , the mass of water, is easily determined. The specific heat of water is tabulated information and thus the temperature increase, ΔT , is the only thing that needs to be measured during the course of the experiment. The one additional item that is required is the heat capacity of the hardware C_{cal} . That has to be derived from a calibration experiment. The calibration experiment furnishes a known amount of heat and is either the combustion of a reliable calibrant (like benzoic acid) or the output of a calibrated electrical heater.

Having determined the value of q_{cal} , we wish to translate its value into a thermodynamic quantity. For this, we will need to know how much of the combustible material we have used. If that is n_{comb} , we can write:

$$\Delta U_{comb} = - q_{cal} / n_{comb}$$

The heat generated represents a decrease in the internal energy, since the combustion process takes place at constant volume.

To convert this to combustion enthalpies, we write:

$$\Delta H = \Delta U + \Delta(pV)$$

In reactions involving gases, the $\Delta(pV)$ term is dominated by the gases and can be equated to $[\Delta n_{gas}] RT$.

Thus:

$$\Delta H_{comb} = \Delta U_{comb} + [\Delta n_{gas}] RT$$

For the combustion of methane:



$\Delta n_{gas} = -2$. Thus at 25° C:

$$\Delta H_{comb} = \Delta U_{comb} - 4.96 \text{ kJ}$$

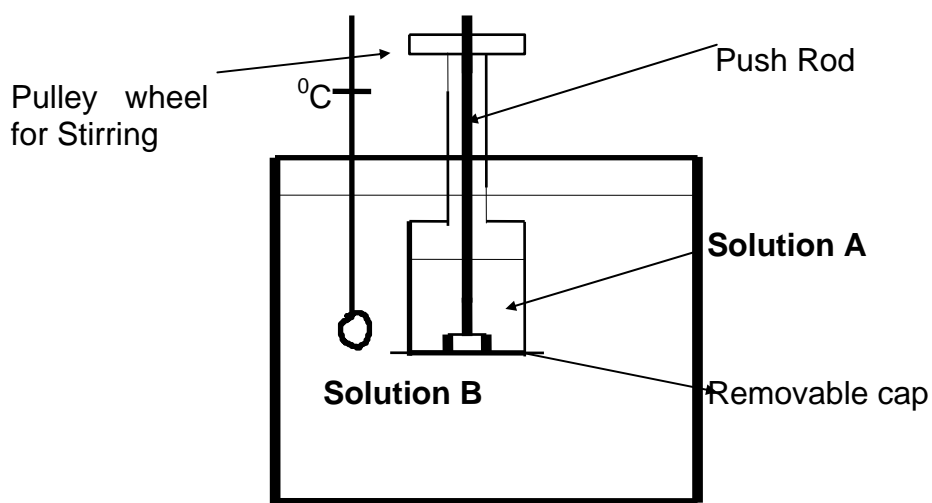
$[\Delta n_{gas}] RT$ is less than 1% of the enthalpy of combustion.

We should mention that, knowing the enthalpies of formation of carbon dioxide and water, it is relatively easy to convert the enthalpies of combustion of pure compounds into their enthalpies of formation.

4.2 Solution Calorimeters.

A second major type of chemical calorimetry involves the measurement of the heats that are absorbed or generated by chemical reactions and mixing processes in solution.

The following figure shows the design of a commercial solution calorimeter.



The reactant species A and B are initially kept apart. The species B is seen to be in solution in the main part of the reaction vessel. The species A is seen to be in a separate solution in the smaller sample vessel in the middle. If we wanted to measure heats of solution or mixing, we could have a pure liquid component B in the reaction vessel and the other solid or liquid component A in the sample vessel.

Typically, the reaction vessel will hold about 100 mL of solution B or solvent, while the sample vessel will accommodate up to 25 mL. At the outset, the two solutions are separated by a teflon cap that fits snugly over the bottom of the sample vessel. When it has been determined that a thermal equilibrium exists between the two solutions and there is a minimal temperature drift in the reaction vessel, the cap is removed by means of a glass push rod.

The temperature change that is brought about by the reaction is usually monitored by means of a thermistor (not a mercury – in –glass thermometer). Stirring is done by rapidly rotating the sample vessel. The entire apparatus is enclosed in an insulated jacket.

The calorimetric equation for this set up is similar to that for a bomb calorimeter. Instead of the contribution for the water in that case, we now need to worry about the heat capacity of the final solution. The process is isobaric (constant pressure) and thus we are measuring an enthalpy change.

5 Entropy Changes.

It is important to try to get a feeling for the nature of the entropy that is more tangible than the defining equation:

$$dq_{rev} = T dS$$

One of the more revealing exercises, in basic thermodynamics, is to consider the entropy change when an ideal gas undergoes isothermal (constant temperature) expansion.

A very important characteristic of an ideal gas is that there is no change in its internal energy so long as its temperature remains constant. We may thus start off by writing:

$$dU = 0 = dq + dw$$

From our earlier considerations we can write the general equation:

$$dw = - p dV$$

and since this is an ideal gas, we can replace p by:

$$p = nRT/V$$

giving:

$$dw = -nRT V^{-1} dV$$

Integration of V^{-1} gives $\ln(V)$, so that if there is a volume change from V_1 to V_2 , we have:

$$w = -nRT \ln[V_2/V_1]$$

We note that if $V_2 > V_1$ (in other words an expansion), then $w < 0$ meaning that the system is doing work on its surroundings.

From:
$$dS = dq / T$$

integration at constant temperature gives:

$$\Delta S = q / T = -w / T$$

or:
$$\Delta S = nR \ln[V_2/V_1]$$

This indicates that there is a substantial increase in entropy when a gas expands. We may recall the old adage about gases expanding to fill the available space. That is, at the same time, a spontaneous and an increasing entropy process.

It is argued that confining the molecules to a small volume is less random and certainly less probable than letting them roam free over all of the available space. In that context, we might describe Border Collies as being agents for decreasing entropy. We can rewrite the equation making use of Boyle's law:

$$\Delta S = nR \ln[p_1/p_2]$$



Since: $p = [n/V] RT = M RT$

where M is the molarity, we can change this to:

$$\Delta S = n R \ln[M_1/M_2]$$

This equation is not only appropriate for ideal gases but also for ideal solutions.

We can apply the equation:

$$\Delta S = q / T$$

to phase changes that take place at constant temperature and pressure.

For fusion (melting), $q = \Delta_{\text{fus}}H$, so that:

$$\Delta_{\text{fus}}S = \Delta_{\text{fus}}H / T_{\text{fus}}$$

$\Delta_{\text{fus}}H$ is always positive, representing the energy required to break down the tidy ordered pattern of the crystalline solid, without completely separating the molecules (or ions).

That implies an association between the break down of order and an increase in entropy.

The situation becomes more acute when we deal with vaporization.

Here:

$$\Delta_{\text{vap}}S = \Delta_{\text{vap}}H / T_b$$

The enthalpy of vaporization is substantially higher than that of fusion. That means that there is a very substantial increase in the entropy when a substance is converted from a liquid into a gas. For water, $\Delta_{\text{vap}}S$ is higher than $110 \text{ J K}^{-1} \text{ mol}^{-1}$. That is a lot larger than the $88 \text{ J K}^{-1} \text{ mol}^{-1}$ that is predicted by ***Trouton's rule***.

It would clearly be desirable for us to be in a position to predict the entropy changes for chemical reactions. While it is impossible to determine absolute enthalpies of pure compounds, and one settles for table of enthalpies of formation, it is possible to determine absolute entropies.

These absolute entropies are customarily called ***Third Law Entropies***. That is because they are based upon the acceptance of a statement that is known as the third law of thermodynamics.

The third law states "***at absolute zero temperature all pure substances have zero entropy***". Actually, it is a theory and not a law, since laws require direct observation. The theory is based upon the idea of perfect order in the arrangement of the molecules. Strictly speaking the word "molecule" does not exist in thermodynamics. For all that, the statement is nearly always correct; although there are a few interesting exceptions that became evident after it became possible to use the methods of quantum mechanics to check the results.

It is interesting to consider the means by which absolute entropies are determined. We shall describe the case of a substance that is a gas at the standard temperature of 25° C. For solids and liquids, the methodology is the same but requires less work.

The central equation is:

$$T(\delta S/\delta T)_p = C_p$$

The molar isobaric heat capacity, C_p , is a quantity that can be measured quite precisely. The partial differential equation can be rewritten in the form:

$$dS_p = [C_p / T] dT$$

That gives us:

$$\Delta S_p = \int [C_p / T] dT$$

Given adequate heat capacity data, it is a simple matter to carry out the integration between any pair of temperatures T_1 and T_2 . It then follows that we can put together each of the contributions to S° , the standard absolute molar entropy:

$$S^\circ = \int_0^{T(fus)} [C_p / T] dT + \Delta_{fus} S^\circ + \int_{T(fus)}^{T(b)} [C_p / T] dT \\ + \Delta_{vap} S^\circ + \int_{T(b)}^{298 K} [C_p / T] dT$$

The field of Statistical Thermodynamics, using spectroscopic data and energy equations derived from quantum mechanics, provides an

accurate means of checking the calorimetric values of absolute molar entropies.

The agreement, between calorimetric and spectroscopic entropies, is very good with some notable exceptions. Two of the exceptions are similar; carbon monoxide CO and nitrous oxide N₂O. Despite the electronegativity differences between the pairs of atoms, things conspire to give both molecules very tiny dipole moments. It is argued that the molecules have no real sense of direction and are thus randomly ordered in the crystalline state. That means that the entropy value obtained by extrapolating back to absolute zero is non-zero. Water is a third example, the explanation that has been given is in terms of the hydrogen atoms being able to migrate along hydrogen bonds from one oxygen atom to the next.

We can write an equation that gives the standard entropy change for a chemical reaction in terms of the standard entropies of its reactants and products.

$$\Delta_{rxn}S^{\circ} = \sum_{Prod} n_{Prod} S^{\circ} [Prod] - \sum_{Reac} n_{Reac} S^{\circ} [Reac]$$

For the combustion of methane, we have then:



$$\begin{aligned} \Delta_{rxn}S^{\circ} &= S^{\circ} [CO_2(g)] + 2 S^{\circ} [H_2O(l)] - S^{\circ} [CH_4(g)] - S^{\circ} [O_2(g)] \\ &= 213.74 + 139.82 - 186.26 - 410.28 \\ &= 353.56 - 596.54 = -242.98 \text{ J K}^{-1} \end{aligned}$$

This represents the substantial decrease in entropy that one learns to expect for a reaction in which there is a decrease in the number of moles of gas.

We should not leave the topic of entropy without mentioning the work of **Boltzmann**. He was responsible for developing a statistical concept of entropy. His celebrated equation is of the form:

$$S = k \ln(W)$$

where the **Boltzmann constant** $k (=R / N_A)$ is equal to the ideal gas constant divided by Avogadro's number. **W** is a measure of the probability that the system we are dealing with can be found in a specific microscopic state. Different possible states of a system have different probabilities. What we observe is the system in its most probable state.

6 Gibbs Free Energy Changes.

In the combustion of methane, we have seen two competing aspects. The enthalpic picture is one that involves the liberation of a substantial amount of heat. That, on its own, favors the conversion of methane and oxygen into CO_2 and water. The entropic aspect of the reaction is, however, one that represents a decrease in "randomness" which is unfavorable.

We combine the enthalpy and entropy in a single function; the Gibbs free energy.

$$G = H - TS$$

Gibbs free energy changes are given by:

$$\Delta G = \Delta H - \Delta(TS)$$

At constant temperature:

$$\Delta G = \Delta H - T\Delta S$$

and, at constant pressure, the enthalpy changes are equal to the measured heats.

For any chemical or physical change that takes place under the constraints of constant temperature and pressure, the condition that $\Delta G < 0$ is indicative of spontaneity. This is a restatement of the second law of thermodynamics. It is perhaps more easily interpreted than the requirement of increasing the entropy for an isolated system.

We should look at some general scenarios.

If ΔH is **positive** and ΔS is **negative**, ΔG is **inevitably going to be positive**, and the process will be **non-spontaneous**, regardless of the temperature. If ΔH is **negative** and ΔS is **positive**, ΔG will be **negative** and the process will be **spontaneous** regardless of the temperature.

If both ΔH and ΔS are **positive**, the sign of ΔG will depend on the temperature. At relatively **low temperatures** the enthalpy term will be dominant and the process **non-spontaneous**. Fusion, vaporization and many decomposition reactions fall into this category. At **higher**

temperatures the entropy becomes dominant and the process becomes **spontaneous**.

If both the **enthalpy and entropy changes are negative**, ΔG will be negative at low temperature and positive at high temperatures.

It is obviously of interest to know, ahead of time, whether a particular reaction will turn out to be spontaneous or not. We can use tables to determine values for $\Delta_{rxn}G^\circ$.

We could use the earlier information and the equation:

$$\Delta_{rxn}G^\circ = \Delta_{rxn}H^\circ - T \Delta_{rxn}S^\circ$$

Thus for the combustion of methane, we would find:

$$\begin{aligned} \Delta_{rxn}G^\circ &= - 890.36 - 298 \times (- 0.243) \text{ kJ} \\ &= - 890.36 + 72.41 = - 817.95 \text{ kJ} \end{aligned}$$

Obviously the reaction is highly spontaneous despite the entropic disadvantage.

Being in a position to calculate the standard enthalpy and the standard entropy of the reaction enables us to calculate $\Delta_{rxn}G^\circ$ at other temperatures than 25° C. This implies that the approximation, that both $\Delta_{rxn}H^\circ$ and $\Delta_{rxn}S^\circ$ can be treated as being independent of temperature, is

valid. It is not too bad an approximation but one needs to be sure that the phases are the same at the new temperature as they are at 25° C.

Most of the tabulations of the enthalpies of formation and the absolute entropies also include values for the standard Gibbs free energies of formation.

That enables us to calculate Standard Gibbs free energies of reaction using:

$$\Delta_{rxn}G^\circ = \sum_{Prod} n_{Prod} \Delta_f G^\circ [Prod] - \sum_{Reac} n_{Reac} \Delta_f G^\circ [Reac]$$

For the combustion of methane, we can write:

$$\Delta_{rxn}G^\circ = \Delta_f G^\circ [CO_2(g)] + 2 \Delta_f G^\circ [H_2O(l)] - \Delta_f G^\circ [CH_4(g)]$$

The tabulated values of the standard Gibbs free energies of formation are:

$$\Delta_f G^\circ [CH_4(g)] = - 50.72 \text{ kJ mol}^{-1}$$

$$\Delta_f G^\circ [CO_2(g)] = - 394.36$$

$$\Delta_f G^\circ [H_2O(l)] = - 237.18$$

That gives:

$$\Delta_{rxn}G^\circ = - 394.36 - 474.36 - (- 50.72) = - 818.00 \text{ kJ}$$

The two values agree, as indeed they should.

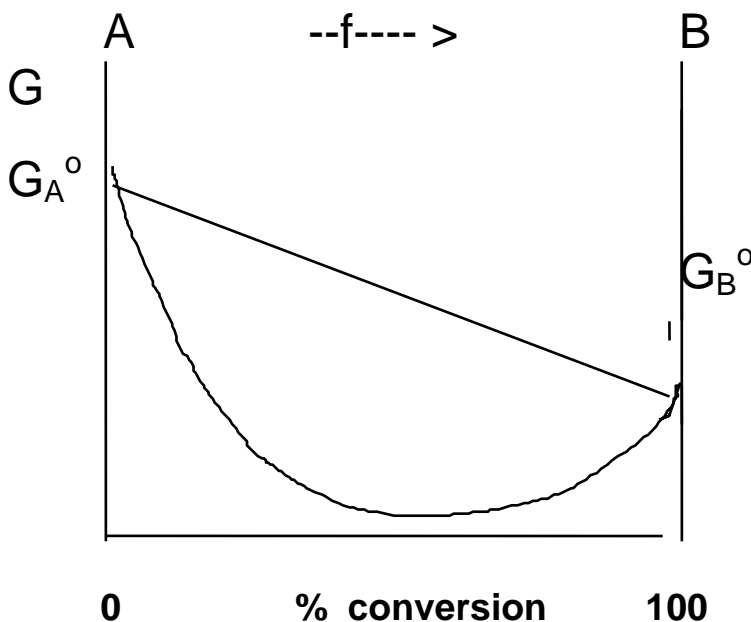
7 Gibbs Free Energy and Chemical Equilibrium.

We have introduced the idea that, at constant temperature and pressure, spontaneous changes take place in the direction of decreasing Gibbs free energy. Chemical reactions will proceed until the condition of chemical equilibrium is reached. We shall try to provide a conceptual link between Gibbs free energies and equilibrium constants.

We start out by examining how the Gibbs free energy of a reaction mixture changes along the path of conversion of reactants to products. We consider the simple gas phase reaction:



We may look at the following diagram:



Instead of the Gibbs free energy decreasing linearly, as reactant changes to product, it goes through a minimum. If the change were linear then the reactants would be flowing downhill all the way to products. Instead, the reaction proceeds to the minimum Gibbs free energy mixture and there it stays, in a state of dynamic chemical equilibrium.

The reactant A starts out at its standard partial pressure of 1 atm. As the reaction proceeds, the partial pressure of A falls while that of B increases.

For the two components, we can write:

$$G_A = G_A^\circ + RT \ln(p_A)$$

and

$$G_B = G_B^\circ + RT \ln(p_B)$$

The difference between the Gibbs free energies of the reactants and products, which is the driving force for chemical change is given by:

$$\Delta G = G_B - G_A = \Delta G^\circ + RT \ln(p_B / p_A)$$

We note that: $(p_B / p_A) = Q$

where Q is the reaction quotient.

We can write, in general that:

$$\Delta G = \Delta G^\circ + RT \ln(Q)$$

The condition for equilibrium is that the combined Gibbs free energies of reactants and products are identical or that $\Delta G = 0$.

At equilibrium, the reaction quotient Q adopts the special value of K, the equilibrium constant. Thus we arrive at the following important relationship.

$$\Delta G^\circ = - RT \ln(K)$$

This is equivalent to :

$$K = \exp(-\Delta G^\circ / RT)$$

Given the value of $R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$ and $T = 298.15 \text{ K}$, $RT = 2.479 \text{ kJ mol}^{-1}$.

For the combustion of methane:

$$K = \exp(818.00 / 2.479) = \exp(330)$$

It is clear that the equilibrium for this reaction is so far over to the right hand side that it is, to all intents and purposes, complete.

7.1 Activities.

In this and the preceding chapters, we have written equilibrium constant expressions that imply ideal behavior. We have, from time to time, acknowledged that the systems that we are dealing with do not always conform to that description. WE might say that there are occasions when these simplified equilibrium constants are non constant.

We can start by looking at the simple gas reaction in which reactant A is changed into product B.

The equation:

$$\Delta G = \Delta G^\circ + RT \ln(p_B / p_A)$$

is only exact as long as the gaseous species A and B and their mixture are behaving in an ideal manner.

When the gases deviate from ideal behavior, we obviously need to modify the equations. We start by writing:

$$G_A = G_A^\circ + RT \ln(f_A)$$

where the **fugacity** f_A has replaced the partial pressure p_A . The fugacity is an effective pressure that differs from p_A for whatever reasons the gaseous species A ceases to behave ideally.

It is possible to determine values for f_A by experimental means. The fugacity is related to the partial pressure by the equation:

$$f_A = \gamma_A p_A$$

The dimensionless quantity γ_A is called the fugacity coefficient (or activity coefficient). Its value is equal to 1 under ideal conditions. Since gases become more ideal as their pressures are decreased, we can write:

$$\text{as } p_A \rightarrow 0 \text{ so } f_A \rightarrow p_A \text{ and } \gamma_A \rightarrow 1$$

For a general chemical reaction:



The equilibrium constant expression is:

$$K = \frac{a_C^c a_D^d}{a_A^a a_B^b}$$

where the quantities of the type a_C are called the **activities**. The nature of the activities is determined by the physical state of the species.

If substance C is a gas, then its activity is its normalized partial pressure:

$$a_C = p_C / p^\circ$$

where p° is the standard pressure. If there is a deviation from ideality then we should replace the partial pressure by the fugacity.

If substance C is a pure solid or liquid, its activity is equal to 1.0 and is therefore excluded from the equilibrium constant expression.

If C is a solute species, we will wish to work with concentration units. The most common situation is that in which the concentration is expressed in moles per liter. In the ideal case, we write:

$$a_c = M_c / M^\circ$$

where M_c is the molarity (concentration) of substance C and M° is the standard molarity of 1 mol / L.

Note that in each case, we have chosen to make the activity a dimensionless (unitless) quantity. That is necessary if we are going to be using their logarithms

If the solute is not behaving ideally, we introduce an activity coefficient γ_c and write:

$$a_c = (M_c \gamma_c) / M^\circ$$

Solutions tend to become more nearly ideal at very low concentrations so that we can write:

$$a_c \rightarrow M_c / M^\circ \text{ and } \gamma_c \rightarrow 1 \text{ as } M_c \rightarrow 0$$

The use of activity coefficients is particularly important when dealing with solutions of electrolytes that deviate very strongly from ideality at all but extremely low concentrations.

There is a marked tendency among physical chemists to use molalities, instead of molarities, as the concentration unit of choice.

8.2 The Temperature Dependence of Equilibrium Constants.

From the equation:

$$\ln K = -\Delta G^\circ / RT$$

and:

$$\Delta G^\circ = \Delta H^\circ - T \Delta S^\circ$$

$$\Delta G^\circ / T = \Delta H^\circ / T - \Delta S^\circ$$

$$(\delta(\Delta G^\circ / T) / \delta T)_p = \Delta H^\circ (\delta(1/T) / \delta T)_p + T^1 (\delta(\Delta H^\circ / \delta T)_p -$$

$$(\delta(\Delta S^\circ / \delta T)_p$$

$$(\delta(\Delta G^\circ / T) / \delta T)_p = \Delta H^\circ (\delta(1/T) / \delta T)_p + C_p / T - C_p / T$$

$$(\delta(\Delta G^\circ / T) / \delta T)_p = -\Delta H^\circ / T^2$$

Since $\ln K = -(\Delta G^\circ / RT)$

$$(\delta \ln K / \delta T)_p = \Delta H^\circ / RT^2$$

The implication is that, if the reaction is endothermic ($\Delta H^\circ > 0$), then $(\delta \ln K / \delta T)_p > 0$ and the equilibrium constant increases with increasing temperature.

Obviously the opposite is true for exothermic reactions.