

## 6.1: Gibbs Energy Determines the Direction of Spontaneity at Constant Pressure and Temperature

The Helmholtz energy  $A$  is developed for isochoric changes and as we have often said before it is much easier to deal with isobaric ones where  $P = \text{constant}$ . We can therefore repeat the above treatment for the enthalpy and introduce another state function the Gibbs energy

$$\begin{aligned} G &\equiv H - TS \\ &= U + PV - TS \\ &= A + PV \end{aligned}$$

If we take both  $T$  and  $P$  constant we get

$$\begin{aligned} dU - TdS + PdV &\leq 0 \\ dG &\leq 0 \end{aligned}$$

$G$  either decreases (spontaneously) or is constant (at equilibrium). Calculating the state function between two end points we get:

$$\Delta G = \Delta H - T\Delta S \leq 0 (T, P \text{ constant})$$

This quantity is key to the question of spontaneity under the conditions we usually work under. If for a process  $\Delta G$  is positive it does not occur spontaneous and can only be made to occur if it is 'pumped', i.e. coupled with a process that has a negative  $\Delta G$ . The latter is spontaneous.

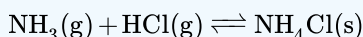
If  $\Delta G = 0$  then the system is as **equilibrium**.

### 6.1.1: Direction of the spontaneous change

Because the  $\Delta S$  term contains the temperature  $T$  as coefficient the spontaneous direction of a process, e.g. a chemical reaction can **change** with temperature depending on the values of the enthalpy and the entropy change  $\Delta H$  and  $\Delta S$ . This is true for the melting process, e.g. for water below  $0^\circ\text{C}$  we get water  $\Rightarrow$  ice, above this temperature ice melts to water, but it also goes for chemical reactions.

#### ✓ Example

Consider



$\Delta_r H$  at 298K / 1 bar is -176.2 kJ. The change in entropy is -0.285 kJ/K so that at 298K  $\Delta G$  is -91.21 kJ. Clearly this is a reaction that will proceed to the depletion of whatever is the limiting reagent on the left.

However at 618 K this is a different story. Above this temperature  $\Delta G$  is positive! (assuming enthalpy and entropy have remained the same, which is almost but not completely true) The reaction will not proceed. Instead the *reverse* reaction would proceed spontaneously. The salt on the right would decompose in the two gases -base and acid- on the left.

### 6.1.2: Meaning of the $\Delta G$ term

As we have seen,  $\Delta A$  can be related to the maximal amount of work that a system can perform at constant  $V$  and  $T$ . We can hold an analogous argument for  $\Delta G$  except that  $V$  is not constant so that we have to consider volume work (zero at constant volume).

$$dG = d(U + PV - TS) = dU - TdS - SdT - PdV + VdP$$

As  $dU = TdS + \delta w_{rev}$

$$dG = \delta w_{rev} - SdT + VdP + PdV$$

As the later term is  $-\delta w_{volume}$

$$dG = \delta w_{rev} - SdT + VdP - \delta w_{volume}$$

At constant  $T$  and  $P$  the two middle terms drop out

$$dG = \delta w_{rev} - \delta w_{volume} = \delta w_{otherusefulwork}$$

#### Note

$\Delta G$  stands for the (maximal) reversible, isobaric isothermal non- $PV$  work that a certain spontaneous change can perform. The volume work may not be zero, but is corrected for.

### 6.1.3: Natural variables of $G$

Because  $G \equiv H - TS$ , we can write

$$\begin{aligned} dG &= dH - TdS - SdT \\ &= TdS + VdP - TdS - SdT = VdP - SdT \end{aligned}$$

The natural variables of  $G$  are pressure  $P$  and temperature  $T$ . This is what makes this function the most useful of the four  $U$ ,  $H$ ,  $A$ , and  $G$ : these are the natural variables of most of your laboratory experiments!

### 6.1.4: Summary

We now have developed the basic set of concepts and functions that together form the framework of thermodynamics. Let's summarize four very basic state functions:

state function	natural variables
$dU = -PdV + TdS$	$U(V, S)$
$dH = +VdP + TdS$	$H(P, S)$
$dA = -PdV - SdT$	$A(V, T)$
$dG = +VdP - SdT$	$G(P, T)$

Note:

1. The replacement of  $\delta q$  by  $TdS$  was based on *reversible* heat. This means that in the irreversible case the expressions for  $dU$  and  $dH$  become inequalities
2. We only include *volume* work in the above expressions. If other work (elastic, electrical e.g.) is involved extra terms need to be added:  $dU = TdS - PdV + xdx$  etc.

We are now ready to begin applying thermodynamics to a number of very diverse situations, but we will first develop some useful partial differential machinery.

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