

## GIBBS ENERGY IN BATTERIES

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Reference: Daniel V. Schroeder, *An Introduction to Thermal Physics*, (Addison-Wesley, 2000) - Problems 5.3 - 5.4.

The Gibbs free energy is defined as

$$(1) \quad G \equiv U - TS + PV = H - TS$$

The enthalpy  $H$  is the total energy required to create the system from nothing, in which the environment at constant pressure  $P$  must be pushed back to create the volume  $V$  in which the new system is to be stored. If the system is created in a constant temperature environment as well, then its entropy  $S$  can be found from the amount of heat  $Q$  absorbed from the surroundings as  $S = Q/T$ . This heat forms part of the enthalpy that is required to create the system, so by subtracting it out to get  $G$ , we're left with the amount of energy that must be supplied as work.

If we reverse the process, then the system's entropy must be transferred back to the surroundings. Since everything is happening at a constant temperature  $T$ , the entropy can be restored to the environment by transferring the same amount  $Q = TS$  of heat from the system being dismantled to the environment. The remaining energy (which is still  $G$ ) is therefore the amount of energy that can, in principle, be recovered as work.

All of this assumes that no new entropy is created; we are merely transferring the entropy  $S = Q/T$  back and forth between the system and its surroundings. If the process generates new entropy (that is, the process is irreversible), then  $S > Q/T$  so the amount of work recoverable decreases. We can see this from 1 if we consider the change  $\Delta G$  in a process that occurs at constant  $T$  and  $P$ :

$$(2) \quad \Delta G = \Delta U - T\Delta S + P\Delta V$$

The change in energy  $\Delta U$  is due to heat  $Q$  flowing into the system and work  $W$  done on the system:

$$(3) \quad \Delta U = Q + W$$

The work can be due to the system's volume changing at constant pressure, plus 'other' work  $W_{other}$  (such as electrical work). If the system's

volume changes by  $\Delta V$ , the work done *on* the system is  $-P\Delta V$  (negative, because if the system expands,  $\Delta V > 0$  and the system is doing work *on* the surroundings, which is equivalent to negative work being done *on* the system; keeping these signs straight can be confusing!). That is

$$(4) \quad W = -P\Delta V + W_{other}$$

The work done by expansion thus cancels out of  $\Delta G$  and we're left with

$$(5) \quad \Delta G = Q - T\Delta S + W_{other}$$

In a reversible isothermal process,  $\Delta S = Q/T$  so in that case

$$(6) \quad \Delta G = W_{other}$$

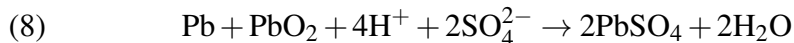
so that  $\Delta G$  gives a direct measure of how much 'other' work must be provided to construct the system (or, in the reverse process, can be extracted from the system). In an irreversible process,  $\Delta S > Q/T$  so, more generally,

$$(7) \quad \Delta G \leq W_{other}$$

Another way of looking at it is as follows. Suppose we construct a system via an irreversible process by providing an amount of heat  $Q$  and work  $W$ , giving it an energy of  $\Delta U = Q_{in} + W_{in}$ . Since the process is irreversible, the amount of entropy transferred into the system is  $S_{in} > Q_{in}/T$ . Since the second law requires entropy never to decrease, if we dismantle the system, at least this amount of entropy must be dumped into the environment. If this is done by means of a transfer of amount  $Q_{out}$  of heat, so that  $S_{out} = S_{in} = Q_{out}/T$ , then the amount of heat transferred out is  $Q_{out} = TS_{in} > Q_{in}$ . Therefore, the amount of energy left that is available for work  $W_{out}$  must be less than  $W_{in}$  (by conservation of energy):  $W_{out} < W_{in} = -P\Delta V + W_{other}$ . Since the  $P\Delta V$  terms are equal and opposite in the creation and destruction of the system, the amount of work that can be extracted from the system must be less than  $W_{other}$ . This amount of available work is what  $\Delta G$  represents.

In other words,  $\Delta G$  gives the maximum amount of energy that can be extracted as non-expansion work from a system. The 'non-expansion' condition is important, because  $W_{other}$  specifically excludes the  $P\Delta V$  term as we've seen above.

**Example 1.** As an example, consider the lead-acid battery used in most cars. The battery works by means of the chemical reaction



Looking up the  $\Delta G$  and  $\Delta H$  values in Schroeder's book, we have (all values for 1 mole at 298 K and 1 bar):

	$\Delta G$ (kJ)	$\Delta H$ (kJ)
Pb	0	0
PbO <sub>2</sub>	-217.33	-277.4
H <sup>+</sup>	0	0
SO <sub>4</sub> <sup>2-</sup>	-744.53	-909.27
PbSO <sub>4</sub>	-813.0	-920.0
H <sub>2</sub> O	-237.13	-285.83

The  $\Delta G$  for the reaction is the sum of the values for the products minus the sum for the reactants:

$$(9) \quad \Delta G = (-2 \times 813.0 - 2 \times 237.13) - (0 - 217.33 + 4 \times 0 - 2 \times 744.53) = -393.87 \text{ kJ mol}^{-1}$$

The value is per mole of lead atoms.

A negative  $\Delta G$  means that the energy of the products is lower than that of the reactants, so the tendency is for the reaction to 'run downhill', that is, it will occur spontaneously in the direction shown.

The corresponding  $\Delta H$  is found the same way:

$$(10) \quad \Delta H = (-2 \times 920.0 - 2 \times 285.83) - (0 - 277.4 + 4 \times 0 - 2 \times 909.27) = -315.72 \text{ kJ mol}^{-1}$$

From 1 at constant temperature

$$(11) \quad \Delta G = \Delta H - T\Delta S$$

and since  $\Delta H > \Delta G$  here,  $\Delta S > 0$  so there is an increase in entropy as the reaction proceeds. In this case,  $\Delta V = 0$  (car batteries don't expand) so  $\Delta U = \Delta H$ . Thus the energy extracted as work ( $-\Delta G = 393.87 \text{ kJ mol}^{-1}$ ) is actually greater than the enthalpy change (and hence the energy change of the chemicals) due to the reaction on its own. The extra energy is absorbed from the environment (which serves as a thermal reservoir), and it's this imported heat that is responsible for the increase in entropy, since  $\Delta S = Q/T = (\Delta H - \Delta G)/T = 78.15 \times 10^3/298 = 262 \text{ J K}^{-1}$ .

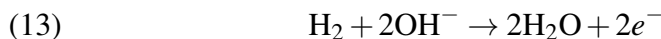
**Example 2.** As another example, consider the electrolysis of water into its constituent gases, H<sub>2</sub> and O<sub>2</sub>. The overall reaction is



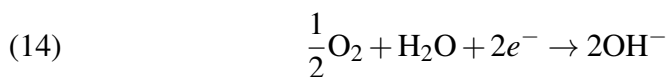
As Schroeder shows in the textbook by calculating  $\Delta G$  from tabulated values of  $\Delta H$  and  $S$ , the  $\Delta G$  for this reaction is positive:  $\Delta G = +237$  kJ. Because  $\Delta G > 0$ , the reaction does not occur spontaneously (we'd be in trouble if it did, since water would spontaneously disintegrate into hydrogen and oxygen), and  $\Delta G$  here gives the amount of work that must be input (in the form of electric current) to force the reaction to proceed.

The reverse reaction in which hydrogen and oxygen combine to make water is, of course, highly spontaneous (in fact, it's explosive, as the makers of early hydrogen-filled airships discovered to their cost). However, if the reaction is controlled, it can act as the basis for a hydrogen fuel cell, in which we can extract 237 kJ of electrical work (at least in principle). The actual energy output of the reaction is given by the enthalpy difference  $\Delta H$  which can be seen from the above table to be 285.83 kJ. The difference  $\Delta G - \Delta H = T\Delta S$  so the heat lost is 48.7 kJ and the entropy that is transferred to the environment is  $\Delta S = 163.4 \text{ J K}^{-1}$ .

If the fuel cell is used as a battery, we can work out the voltage by finding the electrical work per electron. To do this, we need to know how many electrons are involved in each instance of the reaction. The overall reaction occurs in two phases, one at each electrode. At the negative electrode we have



At the positive electrode, we have



Thus for each hydrogen molecule in the reaction, two electrons are produced at the negative electrode and consumed at the positive electrode. Thus the energy imparted to each electron is

$$(15) \quad E = \frac{2.37 \times 10^5}{2 \times 6.02 \times 10^{23}} = 1.97 \times 10^{-19} \text{ J} = \frac{1.97}{1.6} \text{ eV} = 1.23 \text{ eV}$$

As 1 eV is the energy obtained by an electron that drops through a potential difference of 1 volt, the fuel cell has a voltage of 1.23 volts. This is also the voltage required to separate water by electrolysis, since electrolysis is simply the inverse reaction to that in the fuel cell.

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