

CHAPTER OVERVIEW

5: Helmholtz and Gibbs Energy

Entropy ultimately explains why things occur. By “occur”, we mean that a process is spontaneous and has a $\Delta S_{tot} > 0 \text{ J/K}$, where the total is the sum of system’s and surrounding’s entropy changes. Recall from the previous chapter that we can associate a negative change in energy with an increase in total entropy, so long as the natural variables of energy are held constant. Thus, spontaneous means $\Delta U < 0 \text{ J}$ if system entropy *and volume* do not change. However, *if instead pressure* and system entropy are held constant then a spontaneous process has a negative ΔH . In both cases we see that there cannot be a change in system entropy, which is only true for the adiabatic and reversible condition that describes systems at equilibrium. But what about all the other types of transitions? After all most things aren’t at equilibrium!

Before we consider what makes a non-equilibrium process spontaneous, first consider the following question: is the world adiabatic or isothermal? While you may be thinking about how the outside temperature changes during the seasons (hence the Earth is adiabatic), it is also true that our planet is not encapsulated in insulated glass wool like the flask in Figure 2.1. For the most part, we live in an isothermal system. Next: is the world at constant volume or constant pressure? As Earth is not enclosed in a metal box, we live in a constant pressure environment. Clearly we need to know what type of energy dictates whether a process is spontaneous under isothermal, constant pressure conditions, because internal energy and enthalpy aren’t it!

[5.1: Helmholtz Energy \(and The Clausius Inequality Pt. II\)](#)

[5.2: Gibbs Energy](#)

[5.3: Calculations- Numerical and Derivations](#)

[5.4: Advanced Derivations - Maxwell Relationships II](#)

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