Statistical Molecular Thermodynamics

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Video 8.2

Gibbs Free Energy

Spontaneity Re-redux

$$dA \leq 0$$ is the condition for spontaneity at constant T and V

To maintain constant volume, we need a very stiff and well sealed container, which is not always convenient.

Consider a system at constant T and P. The system can expand or contract in volume subject to a constant external pressure (e.g., atmospheric pressure) and heat can be exchanged with the surroundings.

Now, what is the criterion for a spontaneous process at constant T and P?

SPONTANEITY AT CONSTANT *T* AND *P*
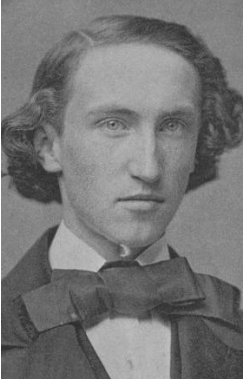
First and Second Laws provide a useful starting point, as always

$$dU = \delta q + \delta w \qquad \delta q \leq TdS \qquad \delta w = -PdV$$

Josiah Willard Gibbs

$$dU \leq TdS - PdV \longrightarrow dU - TdS + PdV \leq 0$$

At constant P and T: $\quad d\left(U - TS + PV\right) \leq 0$

Define a new state function, **the Gibbs Free Energy**, G: $\quad G = U - TS + PV$

(constant T and P) $\quad dG \leq 0 \quad$ defines spontaneity

Gibbs
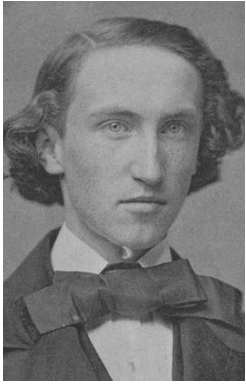
Josiah Willard Gibbs

In 1863, awarded the 1st U.S. Ph.D. in engineering (5th U.S. Ph.D. in any field) by Yale College.

Did fundamental work on gears, brakes, steam engines, vector calculus, optics, and statistical mechanics, but virtually unknown in his home, the United States, during his lifetime.

JOSIAH WILLARD GIBBS
THERMODYNAMICIST
usa 37
2005
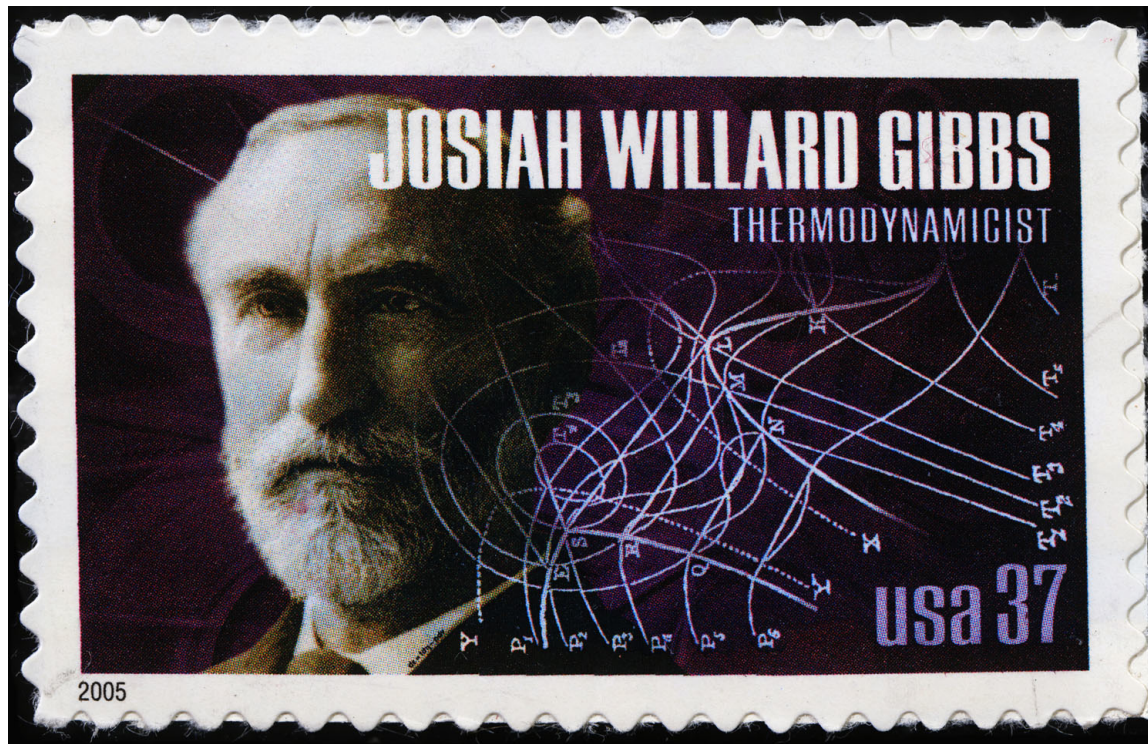
"[Gibbs] among the most renowned theoretical physicists of all times." *Max Planck*

"[Gibbs] the greatest mind in American history." *Albert Einstein*

THE GIBBS FREE ENERGY

$$G = U - TS + PV$$

$$H = U + PV \quad\longrightarrow\quad G = H - TS$$

$$A = U - TS \quad\longrightarrow\quad G = A + PV$$

Relating A and G in the same way as U and H.

spontaneous

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

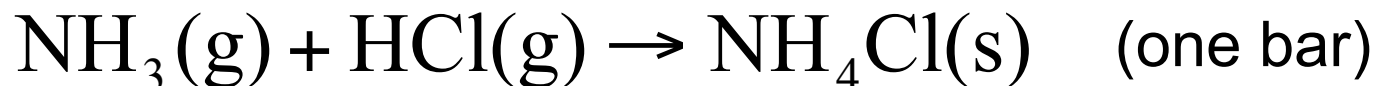**at equilibrium**

If both ΔH and ΔS have the same sign then there is a compromise between minimizing H and maximizing S. Entropy becomes more important at higher temperatures.

GIBBS FREE ENERGY EXAMPLE

$$\Delta G = \Delta H - T\Delta S \quad \text{(constant } P \text{ and } T\text{)}$$

Consider:

$$NH_3(g) + HCl(g) \rightarrow NH_4Cl(s) \quad \text{(one bar)}$$

$$\Delta_r H = -176.2 \text{ kJ} \text{ at } 298.15 \text{ K}$$

$$\Delta_r S = -0.285 \text{ kJ} \cdot \text{K}^{-1} \quad \textit{(gases to solid)}$$

$$\Delta_r G = \Delta_r H - T\Delta_r S = -91.21 \text{ kJ} \text{ at } 298.15 \text{ K}$$

Although ΔS is *negative*, this reaction is spontaneous at 298.15 K and 1 bar because ΔH is more negative than $-T\Delta S$ is positive. Entropy *would* overwhelm enthalpy at 618 K.

Isothermal Work from a Spontaneous Process

$$G = U - TS + PV$$

differentiate $\quad dG = dU - TdS - SdT + PdV + VdP$

use $\quad dU = TdS + \delta w_{rev} \quad \longrightarrow \quad dG = \delta w_{rev} - SdT + PdV + VdP$

use $\quad \delta w_{rev} = \delta w_{PV} + \delta w_{nonPV} = -PdV + \delta w_{nonPV}$

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

$$\boxed{dG = \delta w_{nonPV}} \quad \text{(reversible, constant } T \text{ and } P\text{)}$$

- For $dG < 0$: spontaneous, equals maximum non-PV work process can do

- For $dG > 0$: not spontaneous, equals minimum non-PV work to drive process