

Auxiliary functions, maximum work, and combined first and second law

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Two criteria for equilibrium are $(dU)_{S,v} \leq 0$ and

$$(dS)_{U,V} \geq 0$$

Using the Clausius inequality

$$dS \geq Dq/T$$

in the first law, we get for a system doing only $P-V$ work

$$dU \leq TdS - P_{\text{ext}}dV$$

At constant S and V , this yields

$$dU \leq 0$$

as a criterion for spontaneity. Alternatively,

$$dS \geq \frac{1}{T}(dU + P_{\text{ext}}dV),$$

which yields at constant U and V

$$dS \geq 0$$

Gibbs and Helmholtz energy give more practical conditions for spontaneity

Isolated (const. U) or isentropic (const. S) are rare in chemistry

$$dU - TdS \leq -P_{ext}dV$$

At constant T ,

$$dU - TdS - SdT \leq -P_{ext}dV \Rightarrow d(U - TS) \leq -P_{ext}dV$$

Defining $A = U - TS$, we have at constant T and V

$$dA \leq 0$$

Similarly, at constant P ($P_{ext} = P$) and T

$$dU - TdS + PdV - SdT + VdP \leq 0$$

Defining $G = U + PV - TS$ or $G = H - TS$

$$dG \leq 0$$

Maximum attainable work is equal to $-dA$

We rewrite $dU \leq TdS + Dw$ in terms on work done by the system
 $= -Dw$

$$-Dw \leq -dU + TdS$$

At constant temperature

$$-Dw \leq -dU + TdS + SdT \Rightarrow -Dw \leq -dA$$

All reversible isothermal processes, leading from the same initial to the same final states, perform the same amount of work, $-\Delta A$. In any actual isothermal process the work performed is less, owing friction and other sources of degradation.

Maximum attainable non-PV work is equal to $-dG$

$$Dw = Dw_{PV} + Dw_{non-PV} = -P_{ext}dV + Dw_{non-PV}$$

$$P_{ext}dV - Dw_{non-PV} \leq -dA$$

At constant P , $P_{ext} = P$ and $VdP = 0$

$$-Dw_{non-PV} \leq -d(A + PV)$$

$$-Dw_{non-PV} \leq -dG$$

In any process occurring at constant temperature and pressure, $-\Delta G$ is the maximum of work which can be obtained from a given process and applied to useful purposes. It is for this reason that G is known as the free energy.

A fundamental equation is obtained by combining the first and second law

For a reversible process

$$Dq = TdS \quad \text{and} \quad Dw = -PdV$$

Substituting this in the first law

$$dU = Dq + Dw$$

$$dU = TdS - PdV$$

Right hand side is a function of state and can be used for any reversible or irreversible state change.

Maxwell equation

Comparing $dU = TdS - PdV$ with

$$dU = \left(\frac{\partial U}{\partial V}\right)_S dV + \left(\frac{\partial U}{\partial S}\right)_V dS,$$

gives

$$\left(\frac{\partial U}{\partial V}\right)_S = -P \text{ and } \left(\frac{\partial U}{\partial S}\right)_V = T$$

Because U is a state function

$$\left(\frac{\partial^2 U}{\partial S \partial V}\right) = \left(\frac{\partial^2 U}{\partial V \partial S}\right)$$

$$\frac{\partial}{\partial S} \left(\frac{\partial U}{\partial V}\right)_S = \frac{\partial}{\partial V} \left(\frac{\partial U}{\partial S}\right)_V \text{ or } \left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V$$

Fundamental property relations from H , A , and G

$$dH = TdS + VdP$$

$$\left(\frac{\partial H}{\partial P}\right)_S = V \text{ and } \left(\frac{\partial H}{\partial S}\right)_P = T$$

$$dA = -SdT - PdV$$

$$\left(\frac{\partial A}{\partial T}\right)_V = -S \text{ and } \left(\frac{\partial A}{\partial V}\right)_T = -P$$

$$dG = -SdT + VdP$$

$$\left(\frac{\partial G}{\partial T}\right)_P = -S \text{ and } \left(\frac{\partial G}{\partial P}\right)_T = V$$

Other Maxwell relations

$$\left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P$$

$$\left(\frac{\partial S}{\partial V}\right)_T = -\left(\frac{\partial P}{\partial T}\right)_V$$

$$-\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P$$