

Spontaneous Change

For a system in thermal equilibrium with its surroundings,

Clausius inequality

At constant

$$dq_V = dU$$

no work

$$TdS - dU \geq 0$$

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

isolated system

$$(dU)_{S,V} \leq 0$$

At constant pressure:

$$dq_P = dH$$

PV work only

$$TdS - dH \geq 0$$

$$(dH)_{S,P} \leq 0$$

For convenience, define:

$$A =$$

$$dA = dU - TdS - SdT$$

$$G = H - TS$$

$$dG = dH - TdS - SdT$$

Then the conditions for change become:

$$(dA)_{T,V} \leq 0$$

$$(dG)_{T,P} \leq 0$$

Spontaneous Change

For a system in thermal equilibrium with its surroundings,

$$dS \geq \frac{\delta q}{T} \quad \text{Clausius inequality}$$

At constant volume:

$$dq_V = dU \quad \text{no work}$$

$$TdS - dU \geq 0$$

$$(dS)_{U,V} \geq 0 \quad \text{isolated system}$$

$$(dU)_{S,V} \leq 0$$

At constant pressure:

$$dq_P = dH \quad \text{PV work only}$$

$$TdS - dH \geq 0$$

$$(dH)_{S,P} \leq 0$$

For convenience, define:

$$A = U - TS$$

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Then the conditions for spontaneous change become:

$$(dA)_{T,V} \leq 0 \quad (dG)_{T,P} \leq 0$$

Helmholtz Energy F (or A)

Helmholtz energy; Helmholtz free energy; Helmholtz function;
Maximum work function (F for Function or A for Arbeit)

For spontaneous change at constant

$$dA = dU - TdS \leq 0$$

Note that it is the *total* function A that tends to a minimum;
this is the same as minimizing U and maximizing S .

Maximum Work

Combine $dU = \delta q + \delta w$ and $TdS \geq \delta q$

$$\Rightarrow dU \leq TdS + \delta w$$

equality for
reversible change

Work done by
the system

$$(-\delta w) \leq TdS - dU$$

$$(-\delta w)_{\max} = TdS - \delta q_{\text{rev}} - \delta w_{\text{rev}} = -\delta w_{\text{rev}}$$

A system does maximum work when it is operating

But $(dA)_T = dU - TdS = dU - \delta q_{\text{rev}} = \delta w_{\text{rev}}$

Therefore, for macroscopic changes

$$-w_{\max} = -\Delta A = T\Delta S - \Delta U \quad \text{constant } T$$

$(-w)$ can be or less than ΔU according to the sign of ΔS .

For $\Delta S > 0$, heat flows into the system to fuel the extra work.

Helmholtz Energy F (or A)

Helmholtz energy; Helmholtz free energy; Helmholtz function;
Maximum work function (F for Function or A for Arbeit)

For spontaneous change at constant T and V

$$dA = dU - TdS \leq 0$$

Note that it is the *total* function A that tends to a minimum;
this is *not* the same as minimizing U and maximizing S .

Maximum Work

Combine $dU = \delta q + \delta w$ and $TdS \geq \delta q$

$$\Rightarrow dU \leq TdS + \delta w$$

equality for
reversible change

Work done by
the system

$$(-\delta w) \leq TdS - dU$$

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A system does maximum work when it is operating reversibly.

But $(dA)_T = dU - TdS = dU - \delta q_{\text{rev}} = \delta w_{\text{rev}}$

Therefore, for macroscopic changes

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constant T

$(-w)$ can be more or less than ΔU according to the sign of ΔS .

For $\Delta S > 0$, heat flows into the system to fuel the extra work.

Gibbs Energy G

Gibbs free energy, Gibbs function

❖ Very important in chemistry since it tells whether a particular reaction can at a given T and P .

For spontaneous change,

$$(dG)_{T,P} \leq 0 \qquad \Delta G = G_{\text{products}} - G_{\text{reactants}} \leq 0$$

$\Delta G_{T,P}$ for reactions can be calculated from tabulated data

$$\Delta G^\circ(T) = \Delta H^\circ(T) - T\Delta S^\circ(T)$$

If ΔH is	and ΔS is	then ΔG	the reaction proceeds
-ve	+ve	<u> </u>	at all temperatures
+ve	-ve	<u> </u>	at no temperatures
-ve	-ve	...	if $T < \Delta H / \Delta S$
+ve	+ve	...	if $T > \Delta H / \Delta S$

Maximum Work:

$$(dG)_T = dH - TdS$$

$$(dG)_{T,P} = dU + PdV - TdS$$

$$= \delta q_{\text{rev}} + \delta w_{\text{rev}} + PdV - TdS$$

$$= \delta w_{\text{rev}} + \underline{\hspace{2cm}}$$

$$= \delta w_{\text{max}} (\text{non-PV})$$

$$\Delta w_{\text{max}} (\text{non-PV}) = \Delta G \qquad \text{constant } T, P$$

Gibbs Energy G

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If ΔH is	and ΔS is	then ΔG	the reaction proceeds
-ve	+ve	< 0	at all temperatures
+ve	-ve	> 0	at no temperatures
-ve	-ve	...	if $T < \Delta H / \Delta S$
+ve	+ve	...	if $T > \Delta H / \Delta S$

Maximum Work:

$$(dG)_T = dH - TdS$$

$$(dG)_{T,P} = dU + PdV - TdS$$

$$= \delta q_{\text{rev}} + \delta w_{\text{rev}} + PdV - TdS$$

$$= \delta w_{\text{rev}} + PdV$$

$$= \delta w_{\text{max}} (\text{non-PV})$$

$$\Delta w_{\text{max}} (\text{non-PV}) = \Delta G \quad \text{constant } T, P$$

Basic Thermodynamic Relations 1

$$dU = \delta q - PdV \quad \dots(1)$$

$$dS = \delta q_{\text{rev}} / T \quad \dots(2)$$

$$H = U + PV \quad \dots(3)$$

$$A = U - TS \quad \dots(4)$$

$$G = H - TS \quad \dots(5)$$

$$dU = TdS - PdV \quad \dots(6)$$

$$dH = TdS + VdP \quad \dots(7)$$

$$dA = -SdT - PdV \quad \dots(8)$$

$$dG = -SdT + VdP \quad \dots(9)$$

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

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

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

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

Basic Thermodynamic Relations 1

Laws

$$dU = \delta q - PdV \quad \dots(1)$$

$$dS = \delta q_{\text{rev}} / T \quad \dots(2)$$

Definitions

$$H = U + PV \quad \dots(3)$$

$$A = U - TS \quad \dots(4)$$

$$G = H - TS \quad \dots(5)$$

Fundamental Equations

$$dU = TdS - PdV \quad \dots(6)$$

$$dH = TdS + VdP \quad \dots(7)$$

$$dA = -SdT - PdV \quad \dots(8)$$

$$dG = -SdT + VdP \quad \dots(9)$$

Partial Differentials

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

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

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

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

Basic Thermodynamic Relations 2

From (6) $\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V \dots(10)$

From (7) $\left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P \dots(11)$

From (8) $\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V \dots(12)$

From (9) $-\left(\frac{\partial S}{\partial P}\right)_T = \left(\frac{\partial V}{\partial T}\right)_P \dots(13)$

Thermodynamic

$$dU = TdS - PdV \dots(6)$$

$$\left(\frac{\partial U}{\partial V}\right)_T =$$

Substituting

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

$$\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\alpha}{\kappa}\right) - P$$

Basic Thermodynamic Relations 2

Maxwell Relations

From (6) $\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V \dots(10)$

From (7) $\left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P \dots(11)$

From (8) $\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V \dots(12)$

From (9) $-\left(\frac{\partial S}{\partial P}\right)_T = \left(\frac{\partial V}{\partial T}\right)_P \dots(13)$

Thermodynamic Equation of State

$$dU = TdS - PdV \dots(6)$$

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

Substituting (12) $\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V - P$

$$\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\alpha}{\kappa}\right) - P$$

How Free Energy Depends on P

$$dG = VdP - SdT$$

So: $\left(\frac{\partial G}{\partial P}\right)_T = V$

$$\therefore \Delta G = G_2 - G_1 = \int_1^2 VdP$$

For a perfect gas $V = \frac{nRT}{P}$

$$\Delta G_T = nRT \ln(P_2 / P_1)$$

$$G = G^\circ(T) + nRT \ln(P / P^\circ)$$

where G° is the defined at $P^\circ=1$ bar

At equilibrium and constant P and T :

$$\Delta G = G_{\text{prods}} - G_{\text{rxnts}} = \text{}$$

$$\Delta G^\circ(T) = -nRT \ln(P_{\text{prods}} / P^\circ) + nRT \ln(P_{\text{rxnts}} / P^\circ)$$

The equilibrium constant, K_{eq} , is "".

So:
$$\Delta G^\circ(T) = -nRT \ln K_{eq}$$

How Free Energy Depends on T

$$G = H - TS \quad \dots(1) \quad \text{definition}$$

$$\Delta G = \Delta H - T\Delta S \quad \dots(2) \quad \text{constant } T$$

$$dG = VdP - SdT \quad \dots(3)$$

$$\left(\frac{\partial G}{\partial T}\right)_P = -S = \frac{G - H}{T}$$

from

$$\therefore \left(\frac{\partial G}{\partial T}\right)_P - \frac{G}{T} = -\frac{H}{T} \quad \dots(4)$$

But $\left(\frac{\partial(G/T)}{\partial T}\right)_P = \frac{1}{T}\left(\frac{\partial G}{\partial T}\right)_P - \frac{G}{T^2} \quad \dots(5)$

Gibbs-Helmholtz Equation

$$\left(\frac{\partial(G/T)}{\partial T}\right)_P = -\frac{H}{T^2}$$

substitute (4) in (5)

alternative form:

$$= H$$

By applying the Gibbs-Helmholtz equation to both reactants and products of a chemical reaction,

$$\Rightarrow \left(\frac{\partial(\Delta G/T)}{\partial T}\right)_P = -\frac{\Delta H}{T^2}$$