5. Spontaneity and Equilibrium

5.1 The General Conditions for Equilibrium and Spontaneity

What characteristics distinguish irreversible (real) transformations from reversible (idealized) transformations?

At every stage of a reversible transformation, the system departs from equilibrium only infinitesimally. The system is transformed, yet remains effectively at equilibrium throughout a reversible change in state. The condition for reversibility is therefore a condition of equilibrium.
The condition for reversibility
is that $T\mathrm{d}\boldsymbol{S} = \eth q_{rev}$
therefore the <u>*condition of equilibrium*</u>
is that $T\mathrm{d}\boldsymbol{S} = \eth q_{rev}$

The condition placed on an irreversible change in state is the Clausius inequality,

$\Delta\boldsymbol{S} \geq \int \text{đ}q_{irrev}/T$ *Clausius inequality*

or write it in the form: $T\mathrm{d}\boldsymbol{S} > \text{đ}q_{irrev}$

or include both: $T\mathrm{d}\boldsymbol{S} \geq \text{đ}q$

First Law says $\text{đ}q = \mathrm{d}\boldsymbol{U} - \text{đ}W$

Therefore, $T\mathrm{d}\boldsymbol{S} \geq \mathrm{d}\boldsymbol{U} - \text{đ}W$

or $-\mathrm{d}\boldsymbol{U} + \text{đ}W + T\mathrm{d}\boldsymbol{S} \geq 0$

This work includes all kinds

$\text{đ}W = -p_{op}\mathrm{d}V + \text{đ}W_{other}$

Thus,

$$\boxed{\begin{array}{r} -\mathrm{d}\boldsymbol{U} - p_{op}\mathrm{d}V + \text{đ}W_{other} + T\mathrm{d}\boldsymbol{S} \geq 0 \\ > \text{spontaneous}, = \text{reversible} \end{array}}$$

5.2 Define Helmholtz Free Energy, *A* ; Define Gibbs Free Energy, *G*

Conditions for Equilibrium and Spontaneity <u>under constraints</u>

(1) Transformations in ***isolated system***

$$\mathrm{d}\boldsymbol{U} = 0,\ \eth W = 0,\ \eth q = 0,\ \boxed{T\mathrm{d}\boldsymbol{S} \geq 0}$$

(2) Transformations at ***constant T***

since $\mathrm{d}\boldsymbol{T} = 0$, $\quad -\mathrm{d}\boldsymbol{U} + \eth W + T\mathrm{d}\boldsymbol{S} + \boldsymbol{S}\mathrm{d}T \geq 0$

$-\,\mathrm{d}\,(\boldsymbol{U} - \boldsymbol{TS}\,) \geq -\,\eth W$

Define $\quad \boldsymbol{A} \equiv \boldsymbol{U} - \boldsymbol{TS}$

$$\boxed{\mathrm{d}\,\boldsymbol{A} \geq \ \eth W}$$

(3) Transformations at ***constant T and p***

At constant pressure, $p_{op} = p$, the equilibrium pressure of the system.

since $\mathrm{d}p = 0$, and $\mathrm{d}T = 0$,

$$-\,\mathrm{d}\boldsymbol{U} - \mathrm{d}(pV) + \text{đ}W_{other} + \mathrm{d}(T\boldsymbol{S}) \geq 0$$

$$-\,\mathrm{d}(\boldsymbol{U} + pV) + \mathrm{d}(T\boldsymbol{S}) \geq -\,\text{đ}W_{other}$$

$$-\mathrm{d}(\boldsymbol{U} + pV - T\boldsymbol{S}) \geq -\,\text{đ}W_{other}$$

Define $\boldsymbol{G} \equiv \boldsymbol{H} - T\boldsymbol{S} = \boldsymbol{U} + pV - T\boldsymbol{S} = \boldsymbol{A} + pV$

constant T, p	$-\mathrm{d}\boldsymbol{G} \geq -\text{đ}W_{other}$
	$\mathrm{d}\boldsymbol{G} = \text{đ}W_{other,\ rev}$
	$-\Delta\boldsymbol{G} \geq -W_{other}$
if $\text{đ}W_{other} = 0$:	$-\mathrm{d}\boldsymbol{G} \geq 0$

$\Delta\boldsymbol{G}$ is –	spontaneous change
$\Delta\boldsymbol{G} = 0$	equilibrium
$\Delta\boldsymbol{G}$ is +	natural direction is opposite

For constant T and p, spontaneous changes can continue until $\mathrm{d}\boldsymbol{G} = 0$.

Summary

Constraint	Condition for spontaneity	Equilibrium condition
none	$-(\mathrm{d}\boldsymbol{U}+p\mathrm{d}V-T\mathrm{d}\boldsymbol{S}) + \eth W_{other} = +$	$-(\mathrm{d}\boldsymbol{U}+p\mathrm{d}V-T\mathrm{d}\boldsymbol{S}) + \eth W_{other} = 0$
isolated system	$\mathrm{d}\boldsymbol{S} = +$	$\mathrm{d}\boldsymbol{S} = 0$
T constant	$\mathrm{d}\boldsymbol{A} - \eth W = -$	$\mathrm{d}\boldsymbol{A} - \eth W = 0$
T,p constant	$\mathrm{d}\boldsymbol{G} - \eth W_{other} = -$	$\mathrm{d}\boldsymbol{G} - \eth W_{other} = 0$
$W_{other} = 0$, T, V constant	$\mathrm{d}\boldsymbol{A} = -$	$\mathrm{d}\boldsymbol{A} = 0$
$W_{other} = 0$, T,p constant	$\mathrm{d}\boldsymbol{G} = -$	$\mathrm{d}\boldsymbol{G} = 0$

Maximum work that a system can do:

First Law says $\eth q = \mathrm{d}\boldsymbol{U} - \eth W$

Since $\mathrm{d}\boldsymbol{S} = \eth q_{rev}/T$ or $T\mathrm{d}\boldsymbol{S} = \eth q_{rev}$

but if not reversible $T\mathrm{d}\boldsymbol{S} > \eth q_{irrev}$

Therefore, $T\mathrm{d}\boldsymbol{S} \geq \mathrm{d}\boldsymbol{U} - \eth W$

or $\eth W \geq \mathrm{d}\boldsymbol{U} - T\mathrm{d}\boldsymbol{S}$

Equality holds for reversibility:
the most negative value of $\eth W$ *and therefore the maximum magnitude of* $|\eth W|$ is given by $\mathrm{d}\boldsymbol{U} - T\mathrm{d}\boldsymbol{S}$.

At constant T then,

$$W_{max} = \Delta\boldsymbol{U} - T\Delta\boldsymbol{S}$$

This says that in some cases, depending on the sign of $\mathrm{d}\boldsymbol{S}$, not all the change in internal energy of the system may be available for doing work. If the change occurs with a decrease in $\boldsymbol{S}$ of the system, then the right hand side of the eqn. is not as negative as $\Delta\boldsymbol{U}$ itself and the maximum work is less than $\Delta\boldsymbol{U}$.

$$W_{max} = \Delta \boldsymbol{U} - T\Delta \boldsymbol{S}$$

If the change occurs with a decrease in $\boldsymbol{S}$ of the system, for the change to be *spontaneous*, some of the energy must escape as heat so as to generate enough entropy in the surroundings to overcome the reduction in entropy in the system.
In this case Nature is demanding a tax on the internal energy as it is converted into work that passes across the boundary into the surroundings.

Definition: $\boldsymbol{A} \equiv \boldsymbol{U} - T\boldsymbol{S}$
At constant T, $\Delta \boldsymbol{A}_T = \Delta \boldsymbol{U} - T\Delta \boldsymbol{S}$
What we found above, $W_{max} = \Delta \boldsymbol{U} - T\Delta \boldsymbol{S}$
says: $\Delta \boldsymbol{A}$ is *that part of the change in internal energy that we are free to use to do work.*

Consider a change in state of the system such that

$\Delta \boldsymbol{U} = -10\text{kJ}$ and $T\Delta \boldsymbol{S} = -1\text{ kJ}$

Can we get as much as 10 kJ of work to appear in the surroundings? What are the limitations?

(A) Carry out the change ***reversibly***:

$\int T\mathrm{d}S = \int \eth q_{rev} = q_{rev} = -1$ kJ

W_{rev} from $\Delta U = q_{rev} + W_{rev}$

$-10 \text{ kJ} = -1 + W_{rev}$

$W_{rev} = -9 \text{ kJ} = W_{max} = \Delta U - T\Delta S$

Here, $\mathrm{d}S < 0$, so the change in state can only happen if heat q is passed to the surroundings to make $T\Delta S_{surr} > 0$ so that $\Delta S_{tot} \geq 0$. In this case $\Delta S_{tot} = 0$ (**rev**).

(B) Carry out the change ***irreversibly*** :

$\int T\mathrm{d}S = -1$ kJ still true

Clausius inequality : $T\mathrm{d}S > \eth q_{irrev}$

then $q_{irrev} < -1$ kJ e.g., $q_{irrev} = -1.2$ kJ

$W_{irrev} + q_{irrev} = \Delta U$ is still true, therefore $W_{irrev} = -8.8$ kJ. Less work appears in the surroundings for the irreversible process. $\Delta S_{tot} > 0$.

Consider a change in state of the system such that

$\Delta \boldsymbol{U} = -10\text{kJ}$ and $T\Delta \boldsymbol{S} = +1\text{ kJ}$

(A) Carry out the change ***reversibly***:

$\int T\text{d}\boldsymbol{S} = \int \text{đ}q_{rev} = q_{rev} = +1\text{ kJ}$

W_{rev} from $\Delta \boldsymbol{U} = q_{rev} + W_{rev}$

$$-10\text{ kJ} = +1 + W_{rev}$$

$$W_{rev} = -11\text{ kJ}$$

$$W_{max} = \Delta \boldsymbol{U} - T\Delta \boldsymbol{S}$$

Here, $\text{d}\boldsymbol{S} > 0$ and heat q is taken from the surroundings, $T\Delta \boldsymbol{S}_{surr} = -1\text{ kJ}$ so that $\Delta \boldsymbol{S}_{tot} = 0$ (***rev***)

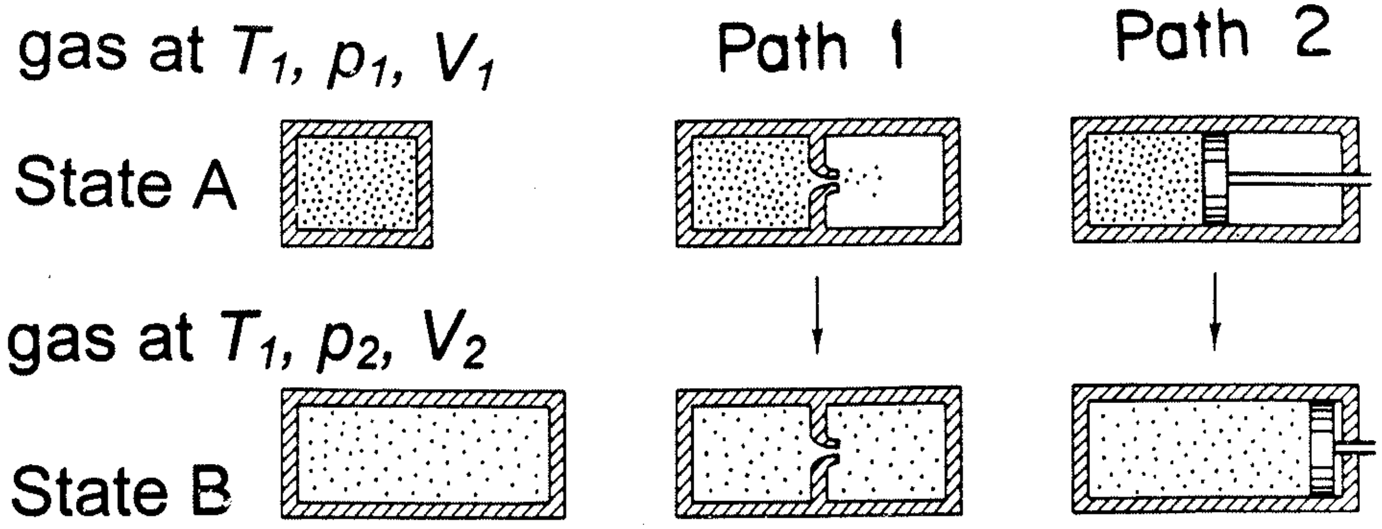
(B) Carry out the change ***irreversibly*** :

$\int T\text{d}\boldsymbol{S} = +1\text{ kJ}$ still true

Clausius inequality : $T\text{d}\boldsymbol{S} > \text{đ}q_{irrev}$

then $q_{irrev} < +1\text{ kJ}$ e.g., $q_{irrev} = +0.8\text{ kJ}$

$W_{irrev} + q_{irrev} = \Delta \boldsymbol{U}$ is still true, therefore $W_{irrev} = -10.8\text{ kJ}$. Less work than maximum work appears in the surroundings for the irreversible process.



Path 1 | Path 2

$$\boxed{\Delta \boldsymbol{E} = 0}$$

$q_{\text{irrev}} = - w_{\text{irrev}}$ | $q_{\text{rev}} = - w_{\text{rev}}$

$w_{\text{irrev}} = 0$ | $w_{\text{rev}} = - RT \ln [V_{\text{final}} / V_{\text{initial}}]$

$q_{\text{irrev}} = 0$ | $q_{\text{rev}} = RT \ln [V_{\text{final}} / V_{\text{initial}}]$

$$\boxed{q_{\text{system}} = - q_{\text{surr}}}$$

$$\boxed{\Delta \boldsymbol{S}_{system} = R \ln [V_{\text{final}} / V_{\text{initial}}]}$$

$q_{\text{surr}} = 0$ | $q_{\text{surr}} = - RT \ln [V_{\text{final}} / V_{\text{initial}}]$

$$\boxed{\Delta \boldsymbol{S}_{surr} = \int \mathrm{d}q_{\text{surr}} / T}$$

$\Delta \boldsymbol{S}_{surr} = 0$ | $\Delta \boldsymbol{S}_{surr} = - R \ln [V_{\text{final}} / V_{\text{initial}}]$

$$\boxed{\Delta \boldsymbol{S}_{universe} = \Delta \boldsymbol{S}_{system} + \Delta \boldsymbol{S}_{surr}}$$

$\Delta \boldsymbol{S}_{universe} = R \ln [V_{\text{final}} / V_{\text{initial}}] > 0$
spontaneous

$\Delta \boldsymbol{S}_{universe} = 0$
at equilibrium

5.3 The Fundamental Equations of Thermodynamics; The Maxwell Relations

Properties of a system:

- mechanical properties: p, V
- fundamental properties defined by the laws of thermodynamics: T, $\boldsymbol{U}$, $\boldsymbol{S}$
- composite properties: $\boldsymbol{H}$, $\boldsymbol{A}$, $\boldsymbol{G}$

The equations that relate these properties to one another:

$\mathrm{d}\boldsymbol{U} = T\mathrm{d}\boldsymbol{S} - p\mathrm{d}V$ general condition of equilibrium, from 1st and 2nd Law

The definitions of the composite properties:

$\boldsymbol{H} = \boldsymbol{U} + pV$; $\boldsymbol{A} = \boldsymbol{U} - T\boldsymbol{S}$; $\boldsymbol{G} = \boldsymbol{H} - T\boldsymbol{S}$

From these, we get by differentiation:

$\mathrm{d}\boldsymbol{H} = \mathrm{d}\boldsymbol{U} + p\mathrm{d}V + V\mathrm{d}p$

$\mathrm{d}\boldsymbol{A} = \mathrm{d}\boldsymbol{U} - T\mathrm{d}\boldsymbol{S} - \boldsymbol{S}\mathrm{d}T$

$\mathrm{d}\boldsymbol{G} = \mathrm{d}\boldsymbol{U} + p\mathrm{d}V + V\mathrm{d}p - T\mathrm{d}\boldsymbol{S} - \boldsymbol{S}\mathrm{d}T$

Now introduce the 1st and 2nd Law:

$\mathrm{d}\boldsymbol{U} = T\mathrm{d}\boldsymbol{S} - p\mathrm{d}V$ into each, to get

$\mathrm{d}\boldsymbol{H} = T\mathrm{d}\boldsymbol{S} - p\mathrm{d}V + p\mathrm{d}V + V\mathrm{d}p = T\mathrm{d}\boldsymbol{S} + V\mathrm{d}p$

$\mathrm{d}\boldsymbol{A} = T\mathrm{d}\boldsymbol{S} - p\mathrm{d}V - T\mathrm{d}\boldsymbol{S} - \boldsymbol{S}\mathrm{d}T = -p\mathrm{d}V - \boldsymbol{S}\mathrm{d}T$

$\mathrm{d}\boldsymbol{G} = T\mathrm{d}\boldsymbol{S} - p\mathrm{d}V + p\mathrm{d}V + V\mathrm{d}p - T\mathrm{d}\boldsymbol{S} - \boldsymbol{S}\mathrm{d}T$

$= V\mathrm{d}p - \boldsymbol{S}\mathrm{d}T$

These equations are sometimes called the four fundamental equations of thermodynamics

$$\mathrm{d}\boldsymbol{U} = T\mathrm{d}\boldsymbol{S} - p\mathrm{d}V$$

$$\mathrm{d}\boldsymbol{H} = T\mathrm{d}\boldsymbol{S} + V\mathrm{d}p$$

$$\mathrm{d}\boldsymbol{A} = -p\mathrm{d}V - \boldsymbol{S}\mathrm{d}T$$

$$\mathrm{d}\boldsymbol{G} = V\mathrm{d}p - \boldsymbol{S}\mathrm{d}T$$

Since each of these equations is an exact differential, the cross derivatives are equal, from which we obtain
the four Maxwell relations:

$$\left(\frac{\partial T}{\partial V}\right)_{\mathbf{s}} = -\left(\frac{\partial p}{\partial \mathbf{S}}\right)_V$$

$$\left(\frac{\partial T}{\partial p}\right)_{\mathbf{s}} = \left(\frac{\partial V}{\partial \mathbf{S}}\right)_p$$

$$\boxed{\begin{aligned} \left(\frac{\partial \mathbf{S}}{\partial V}\right)_T &= \left(\frac{\partial p}{\partial T}\right)_V \\ -\left(\frac{\partial \mathbf{S}}{\partial p}\right)_T &= \left(\frac{\partial V}{\partial T}\right)_p \end{aligned}}$$

5.4 The Properties of *G*, The Gibbs Helmholtz Eqn.

Starting from

$$dG = Vdp - SdT$$

and considering the Gibbs free energy as a function of temperature and pressure

$$dG = (\partial G/\partial T)_p \, dT + (\partial G/\partial p)_T \, dp$$

We find that

$$(\partial G/\partial T)_p = -S$$

$$(\partial G/\partial p)_T = V$$

These are two of the most important pieces of information in thermodynamics. the first one says "*Increase in temperature decreases the Gibbs free energy if pressure is kept constant*"

The second one says *"Increase in pressure increases the Gibbs free energy at constant temperature"*.

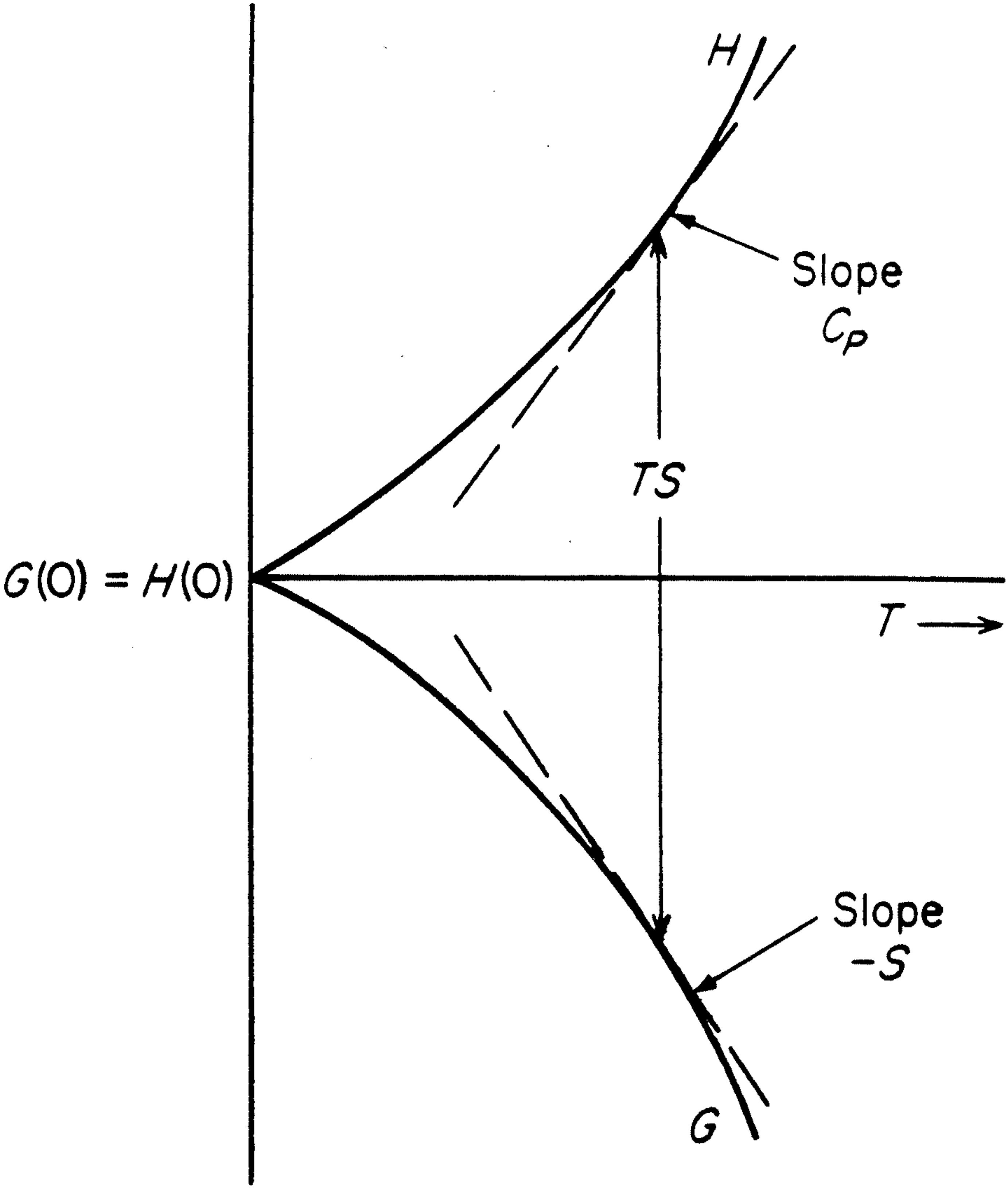
The Gibbs free energy of any pure material at a given temperature is

$\int \mathrm{d}\boldsymbol{G} = \int V\mathrm{d}p$ at temperature T

$$\boldsymbol{G}(T) = \boldsymbol{G}^{\ominus}_{T} + \int_{1}^{p} V\,dp.$$

For an ideal gas

$$\boldsymbol{G}(T) = \boldsymbol{G}^{\ominus}_{T} + \int_{1}^{p} \frac{nRT}{p}\,dp\ .$$



Variation of free energy G and enthalpy *H* of a pure substance with *T* at constant *P*.

Temperature Dependence of the Free Energy

Consider **G/T:**

$(\partial(\mathbf{G}/T)/\partial T)_p = -(\mathbf{G}/T^2) + (1/T)(\partial \mathbf{G}/\partial T)_p$

substitute $\mathbf{G} \equiv \mathbf{H} - T\mathbf{S}$

$(\partial(\mathbf{G}/T)/\partial T)_p = -(\mathbf{H} - T\mathbf{S})/T^2$

$+ (1/T)(\partial \mathbf{G}/\partial T)_p$

Recall that: $(\partial \mathbf{G}/\partial T)_p = -\mathbf{S}$

Thus,

$$\boxed{(\partial(\mathbf{G}/T)/\partial T)_p = -(\mathbf{H}/T^2)}$$

Alternate derivation:

using $\mathbf{G} \equiv \mathbf{H} - T\mathbf{S}$ $\quad \mathbf{G}/\mathbf{T} = \mathbf{H}/T - \mathbf{S}$

$(\partial(\mathbf{G}/T)/\partial T)_p = -(\mathbf{H}/T^2) + (1/T)(\partial \mathbf{H}/\partial T)_p$

$- (\partial \mathbf{S}/\partial T)_p$

But $(\partial \mathbf{H}/\partial T)_p = C_p$ and $(\partial \mathbf{S}/\partial T)_p = C_p/T$

Thus,

$$\boxed{(\partial(\mathbf{G}/T)/\partial T)_p = -(\mathbf{H}/T^2)}$$

This is the Gibbs-Helmholtz equation.

$$\boxed{(\partial(\mathbf{G}/T)/\partial T)_p = -(\mathbf{H}/T^2)}$$

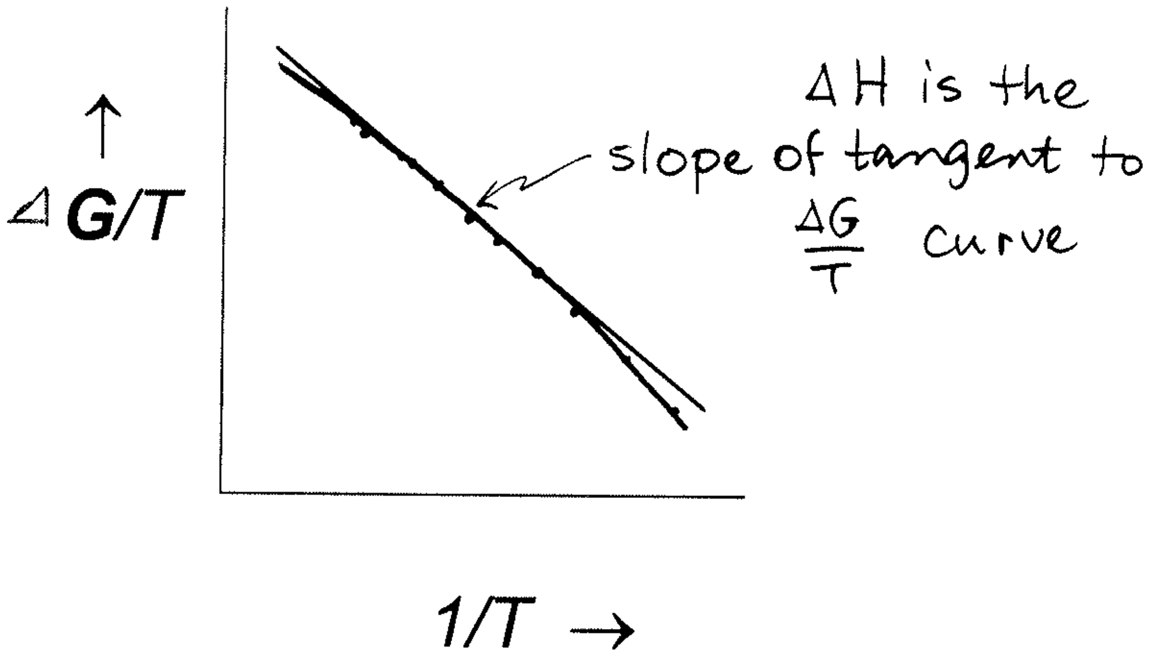
Since these relations apply to both $\mathbf{G}_f$ and $\mathbf{G}_i$, then

$$\boxed{(\partial(\Delta\mathbf{G}/T)/\partial T)_p = -(\Delta\mathbf{H}/T^2)}$$

a very useful relation.

also can be written in the form

$$\boxed{\begin{gathered}(\partial(\mathbf{G}/T)/\partial(1/T))_p = \mathbf{H}\\ (\partial(\Delta\mathbf{G}/T)/\partial(1/T))_p = \Delta\mathbf{H}\end{gathered}}$$



ΔH is the slope of tangent to $\frac{\Delta G}{T}$ curve

5.5 The Chemical Potential, μ of a Pure Substance, fugacity

$$\frac{G(T)}{n} = \frac{G^{\ominus}_{T}}{n} + RT \ln \frac{p}{1} \quad \text{(ideal gas)}$$

Define the free energy per mole (***the chemical potential***):

$$\mu(T) = \mu^{\ominus}_{T} + RT \ln \frac{p}{1} \quad \text{(ideal gas)}$$

Thus, pressure measures the free energy of an ideal gas.

For a real gas, define a function of the state which will express the molar free energy of a real gas in the same form as for an ideal gas: ***the fugacity f***

$$\boxed{\mu(T) = \mu^{\ominus}_{T} + RT \ln \frac{f}{1} \quad \text{(real gas)}}$$

fugacity measures the free energy of a real gas.

Start from

$$dG = Vdp \text{ at temperature } T$$

consider one mole

$d\mu = Vdp$ (real gas) $d\mu_{id} = V_{id}\,dp$ (ideal)

subtract

$$d(\mu - \mu_{id}) = (V - V_{id})\,dp$$

Integrate between limits p^* and p

$$(\mu - \mu_{id}) - (\mu^* - \mu_{id}^*) = \int_{p^*}^{p} (V - V_{id})\,dp.$$

Now let $p^* \to 0$,

In this limit as $p^* \to 0$, $\mu^* \to \mu_{id}^*$

Thus the equation becomes

$$(\mu - \mu_{id}) = \int_{0}^{p} (V - V_{id})\,dp.$$

Into this, insert the following:

$$\mu_{id}(T) = \mu^{\ominus}_{T} + RT \ln \frac{p}{1}$$

$$\mu(T) = \mu^{\ominus}_{T} + RT \ln \frac{f}{1} \qquad \text{(real gas)}$$

$$RT \ln \frac{f}{p} = \int_0^p (V - V_{\mathrm{id}})\, dp$$

$$\ln \frac{f}{p} = \int_0^p \frac{(V - V_{\mathrm{id}})}{RT}\, dp$$

The compressibility factor of a real gas is

$Z = pV/RT$ *or* $V/RT = Z/p$

whereas $V_{\mathrm{id}}/RT = 1/p$

Thus,

$$\boxed{\ln \frac{f}{p} = \int_0^p \frac{(Z - 1)}{p}\, dp}$$

Plot $(Z-1)/p$ and measure the area under the curve. This area is dimensionless and provides $\ln(f/p)$.

Since Z is a function of both temperature and pressure, so is $f(T,p)$.

The ***standard state of a gas*** is a hypothetical state in which the gas is at a pressure 1 bar and behaving perfectly