Maxwell's relation: Born Diagram

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1. Born diagram

(N. Hashitsume, Thermodynamics, Iwanami)

In thermodynamics, we often use the following four thermodynamic potentials, *E*, *F*, *G*, and *H*. The diagram (called the Born's diagram) was introduced by Born (Max). In order to memorize this diagram, we give interpretation for the letters. The sun (*S*; entropy) pours lights on the trees (*T*; temperature). The water falls from the peak (P; pressure) of mountain into the valley (V; volume). We draw a square with four vertices noted by S, T, P, and V. . The light propagates from the point S to the point T. The water flows from the point *P* to the point *V*. These two arrows are denoted by the vectors given by $\overrightarrow{ST}$ (the direction of light flow) and $\overrightarrow{PV}$ (the direction of water flow). These vectors are perpendicular to each other. The four sides of the square are denoted by E, F, G, and H in a clockwise direction. Note that the side *H* (H: heaven) is between two vertices S (sun) and *P* (peak).

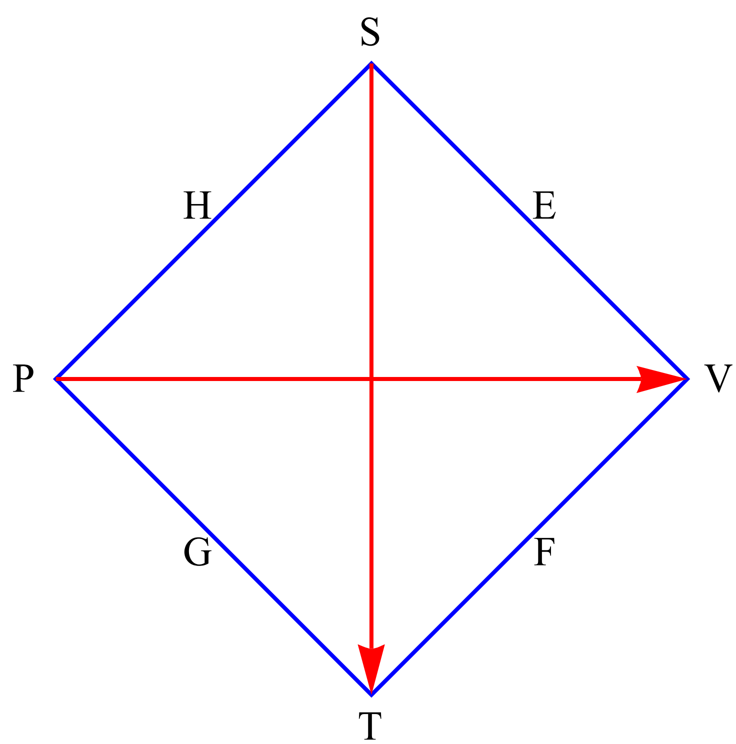


Fig. Born diagram. *S*: entropy. *T*: temperatute. *P*: pressure. *V*: volume. *H*: heaven (between S and P). $E \rightarrow F \rightarrow G \rightarrow H$ (clockwise). The water flow from *P* (peak) to *V* (valley). The sun light from *S* (sun) to *T* (tree). Note that $U = E$. $F = E - ST$. $G = F + PV$. $H = E + PV$.

(i) The natural variables of the internal energy *E* is *S* and *V*.

$$dE = TdS - PdV$$

The sign before *T* is determined as plus from the direction of the vector $\overrightarrow{ST}$ ($\overrightarrow{ST}$: the direction of light). The sign before *P* is determined as minus from the direction of the vector $\overrightarrow{VP} = -\overrightarrow{PV}$ ($\overrightarrow{PV}$; the direction of water flow).

(ii) The natural variables of the Helmholtz energy *F* is *V* and *T*.

$$dF = -SdT - PdV$$

The sign before *S* is determined as minus from the direction of the vector $\overrightarrow{TS} = -\overrightarrow{ST}$ ($\overrightarrow{ST}$: the direction of light). The sign before *P* is determined as minus from the direction of the vector $\overrightarrow{VP} = -\overrightarrow{PV}$ ($\overrightarrow{PV}$; the direction of water flow).

(iii) The natural variables of the Gibbs energy *G* is *P* and *T*.

$$dG = VdP - SdT$$

The sign before *S* is determined as minus from the direction of the vector $\overrightarrow{TS} = -\overrightarrow{ST}$ ($\overrightarrow{ST}$: the direction of light). The sign before *V* is determined as plus from the direction of the vector $\overrightarrow{PV}$ ($\overrightarrow{PV}$; the direction of water flow).

(iv) The natural variables of the enthalpy *H* is *S* and *P*.

$$dH = TdS + VdP.$$

The sign before *T* is determined as minus from the direction of the vector $\overrightarrow{ST}$ ($\overrightarrow{ST}$: the direction of light). The sign before *V* is determined as plus from the direction of the vector $\overrightarrow{PV}$ ($\overrightarrow{PV}$; the direction of water flow).

Maxwell's relation

(i) The internal energy $E = E(S, V)$

For an infinitesimal reversible process

$$dE = TdS - PdV$$

showing that

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

The Maxwell's relation;

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

((**Note**))

$$\begin{aligned}
\left(\frac{\partial T}{\partial V}\right)_S &= \left(\frac{\partial}{\partial V}\right)_S \left(\frac{\partial E}{\partial S}\right)_V \\
&= \frac{\partial^2 E}{\partial V \partial S} \\
&= \frac{\partial^2 E}{\partial S \partial V} \\
&= \left(\frac{\partial}{\partial S}\right)_V \left(\frac{\partial E}{\partial V}\right)_S \\
&= -\left(\frac{\partial P}{\partial S}\right)_V
\end{aligned}$$

(ii) The enthalpy $H = H(S, P)$ is defined as

$$H = E + PV$$

For an infinitesimal reversible process

$$\begin{aligned}
dH &= dE + PdV + VdP \\
&= TdS - PdV + PdV + VdP \\
&= TdS + VdP
\end{aligned}$$

showing that

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

The Maxwell's relation:

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

((**Note**))

$$\begin{aligned}
\left(\frac{\partial T}{\partial P}\right)_S &= \left(\frac{\partial}{\partial P}\right)_S \left(\frac{\partial H}{\partial S}\right)_P \\
&= \frac{\partial^2 H}{\partial P \partial S} \\
&= \frac{\partial^2 H}{\partial S \partial P} \\
&= \left(\frac{\partial}{\partial S}\right)_P \left(\frac{\partial H}{\partial P}\right)_S \\
&= \left(\frac{\partial V}{\partial S}\right)_P
\end{aligned}$$

(iii) The Helmholtz free energy $F = F(T, V)$ is defined as

$$F = E - ST \qquad \text{or} \qquad E = F + ST$$

For an infinitesimal reversible process

$$\begin{aligned}
dF &= dE - SdT - TdS \\
&= TdS - PdV - SdT - TdS \\
&= -PdV - SdT
\end{aligned}$$

showing that

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

The Maxwell's relation:

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

((**Note**))

$$\begin{aligned}
\left(\frac{\partial S}{\partial V}\right)_T &= -\left(\frac{\partial}{\partial V}\right)_T \left(\frac{\partial F}{\partial T}\right)_V \\
&= -\frac{\partial^2 F}{\partial V \partial T} \\
&= -\frac{\partial^2 F}{\partial T \partial V} \\
&= -\left(\frac{\partial}{\partial T}\right)_V \left(\frac{\partial F}{\partial V}\right)_T \\
&= \left(\frac{\partial P}{\partial T}\right)_V
\end{aligned}$$

(iv) The Gibbs free energy $G = G(T, P)$ is defined as

$$G = H - ST = (E + PV) - ST = F + PV$$

Then we have

$$dG = VdP - SdT$$

showing that

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

((**Note**))

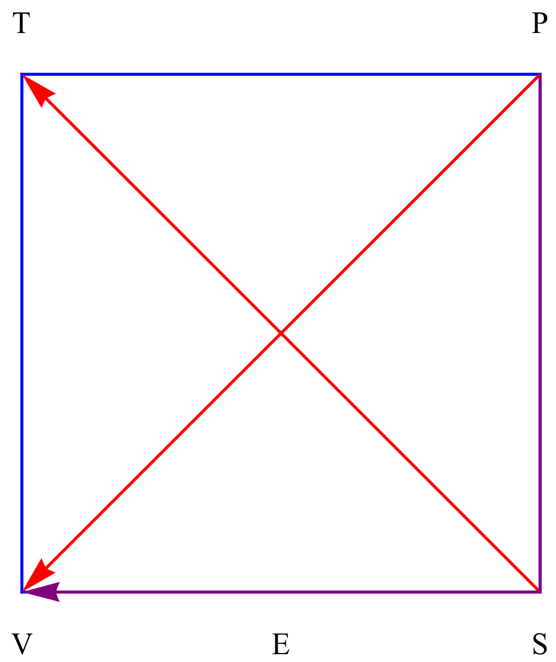
$$
\begin{aligned}
\left(\frac{\partial S}{\partial V}\right)_T &= -\left(\frac{\partial}{\partial V}\right)_T \left(\frac{\partial F}{\partial T}\right)_V \\
&= -\frac{\partial^2 F}{\partial V \partial T} \\
&= -\frac{\partial^2 F}{\partial T \partial V} \\
&= -\left(\frac{\partial}{\partial T}\right)_V \left(\frac{\partial F}{\partial V}\right)_T \\
&= \left(\frac{\partial P}{\partial T}\right)_V
\end{aligned}
$$

(1) The Maxwell's equation:

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

Here we consider the Maxwell's relation $\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V$

For $\left(\frac{\partial P}{\partial S}\right)_V$, in the Born diagram, we draw the lines along the vectors $\overrightarrow{PS}$ and $\overrightarrow{SV}$. The resulting vector is $\overrightarrow{PV} = \overrightarrow{PS} + \overrightarrow{SV}$ (the direction of water flow)



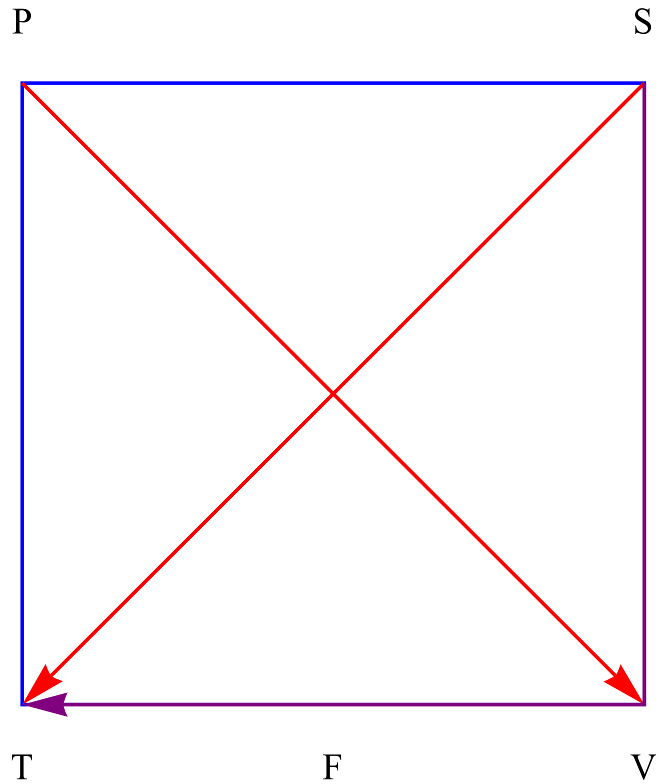
For $\left(\frac{\partial T}{\partial V}\right)_S$, in the Born diagram, we draw the lines along the vectors $\overrightarrow{TV}$ and $\overrightarrow{VS}$. The resulting vector is $\overrightarrow{TS} = \overrightarrow{TV} + \overrightarrow{VS} = -\overrightarrow{ST}$ (anti-parallel to the propagating direction of light). Then we have the negative sign in front of $\left(\frac{\partial P}{\partial S}\right)_V$ such that

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

(ii) Maxwell's relation $\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$

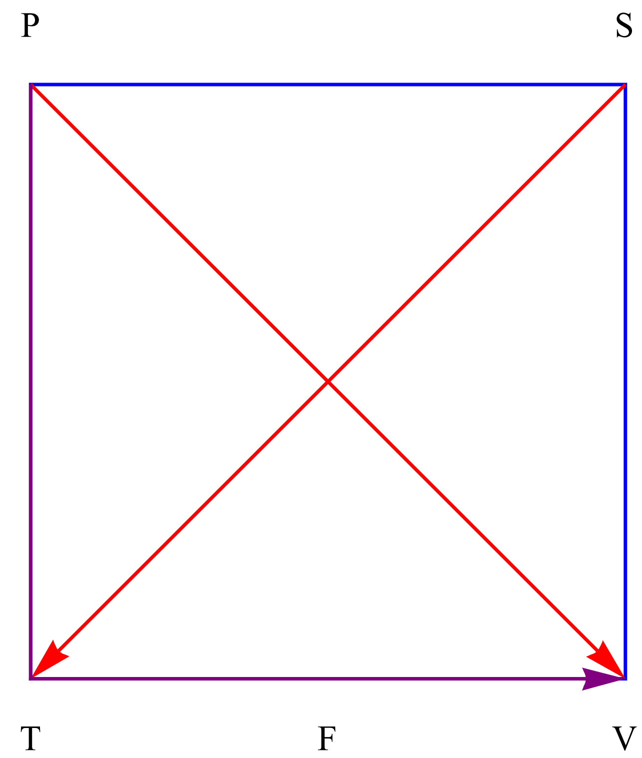
Here we consider the Maxwell's relation $\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$

For $\left(\frac{\partial S}{\partial V}\right)_T$, in the Born diagram, we draw the lines along the vectors $\overrightarrow{SV}$ and $\overrightarrow{VT}$. The resulting vector is $\overrightarrow{ST} = \overrightarrow{SV} + \overrightarrow{VT}$ (the direction of sun light)



For $\left(\frac{\partial P}{\partial T}\right)_V$, in the Born diagram, we draw the lines along the vectors $\overrightarrow{PT}$ and $\overrightarrow{TV}$. The resulting vector is $\overrightarrow{PV} = \overrightarrow{PT} + \overrightarrow{TV}$ (the direction of water flow). Then we have the positive sign in front of $\left(\frac{\partial P}{\partial T}\right)_V$ such that

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



2. Alternative derivation of Maxwell's relations (Blundell and Blundell)

The following derivation is more elegant, but requires a knowledge of Jacobians: Consider a cyclic process which can be described in both the *T*-*S* and *P*-*V* planes. The internal energy U is a state function and therefore does not change in a cycle, so

$$\oint dU = \oint TdS - \oint PdV = 0 \qquad \text{or} \qquad \oint TdS = \oint PdV$$

This is equivalent to

$$\iint dTdS = \iint dPdV$$

So that the work done (the area enclosed by the cycle in the *P*-*V* plane) is equal to the heat absorbed (the area enclosed by the cycle in the *T*-*S* plane). However, one can also write

$$\iint dPdV = \iint \frac{\partial(P,V)}{\partial(T,S)} dTdS = \iint dTdS$$

or

$$\iint dTdS = \iint \frac{\partial(T,S)}{\partial(P,V)} dPdV = \iint dPdV$$

Where $\frac{\partial(T,S)}{\partial(P,V)}$ is the Jacobian of the transformation from the *T*-*S* plane to the P-V plane, and so this implies that

$$\frac{\partial(T,S)}{\partial(P,V)} = 1.$$

Similarly we have

$$\frac{\partial(P,V)}{\partial(T,S)} = \frac{1}{\frac{\partial(T,S)}{\partial(P,V)}} = 1$$

Note that

$$\frac{\partial(T,S)}{\partial(P,V)} = 1$$

is correct, but $\frac{\partial(S,T)}{\partial(P,V)} = -1$. So we need to use the relation $\partial(S,T) = -\partial(P,V)$

This equation is sufficient to generate all four Maxwell relations via

$$\frac{\partial(T,S)}{\partial(x,y)} = \frac{\partial(P,V)}{\partial(x,y)}$$

Where (x,y) are taken as

(i) (T,P),
(ii) (T,V)
(iii) (P,S),
(iv) (S,V)

And using the identities such as

$$\frac{\partial(P,T)}{\partial(V,T)} = \left(\frac{\partial P}{\partial V}\right)_T$$

We use the relation

$$\frac{\partial(T,S)}{\partial(x,y)} = \frac{\partial(P,V)}{\partial(x,y)}$$

(a) $x = P$, $y = T$

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

(b) $x = T$, $y = V$

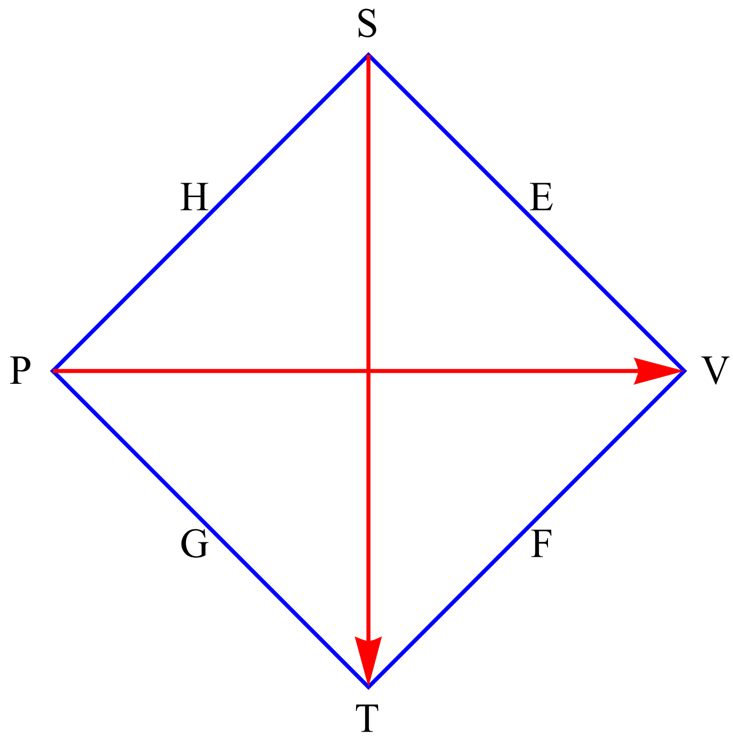
$$\frac{\partial(T,S)}{\partial(T,V)} = \frac{\partial(P,V)}{\partial(T,V)} \quad \text{or} \quad \left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$$

(c) $x = V$, $y = S$

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

(d) $x = S$, $y = P$

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



3. Problem and solution (I)

C. Kittel and H. Kromer, Thermal Physics (W.H. Freeman, 1980).

Problem 9-1 (a part)
Thermal expansion near absolute zero
(a) Prove a Maxwell relation

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

(b) Show that the volume coefficient of thermal expansion

$$\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P$$

approaches zero as $T \rightarrow 0$.

((**Solution**))

Then we have

$$dG = VdP - SdT$$

showing that

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

Maxwell relation

$$\begin{aligned}\left(\frac{\partial V}{\partial T}\right)_P &= \left(\frac{\partial}{\partial T}\right)_P\left(\frac{\partial G}{\partial P}\right)_T \\ &= \frac{\partial^2 G}{\partial T \partial P} \\ &= \frac{\partial^2 G}{\partial P \partial T} \\ &= \left(\frac{\partial}{\partial P}\right)_T\left(\frac{\partial G}{\partial T}\right)_P \\ &= -\left(\frac{\partial S}{\partial P}\right)_T\end{aligned}$$

(b)
The volume coefficient of thermal expansion

$$\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P = -\frac{1}{V}\left(\frac{\partial S}{\partial P}\right)_T$$

$\left(\frac{\partial S}{\partial P}\right)_T$ vanishes for $T = 0$. since $S = 0$ for $T = 0$ K and any pressure. Then we have

$$\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P \to 0$$