第一章　concise review of basic concepts and definitions

1.1　偏微分形式的热力学恒等式

本节为补充内容，相关推导过程参考了知乎用户 Harogenshi 和 mosekyo 的文章，特此致谢。

引理 1.1.1. 偏导数之间的运算规则

- 倒数法则 (INV)

$$\left(\frac{\partial X}{\partial Y}\right)_Z\left(\frac{\partial Y}{\partial X}\right)_Z=1$$

- 三元轮换法则 (TRI)

$$\left(\frac{\partial X}{\partial Y}\right)_Z\left(\frac{\partial Y}{\partial Z}\right)_X\left(\frac{\partial Z}{\partial X}\right)_Y=-1$$

- 复合法则 (CP)

$$\left(\frac{\partial X}{\partial Y}\right)_Z=\left(\frac{\partial X}{\partial A}\right)_B\left(\frac{\partial A}{\partial Y}\right)_Z+\left(\frac{\partial X}{\partial B}\right)_A\left(\frac{\partial B}{\partial Y}\right)_Z$$

  - (CP1 $B=Z$)

$$\left(\frac{\partial X}{\partial Y}\right)_Z=\left(\frac{\partial X}{\partial A}\right)_Z\left(\frac{\partial A}{\partial Y}\right)_Z$$

  - (CP2 $B=Y$)

$$\left(\frac{\partial X}{\partial Y}\right)_Z=\left(\frac{\partial X}{\partial A}\right)_Y\left(\frac{\partial A}{\partial Y}\right)_Z+\left(\frac{\partial X}{\partial Y}\right)_A$$

推论 1.1.2. 用大写字母表示 $EorU$、H、S、$AorF$、G，用小写字母表示 p、V、T。

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$$\left(\frac{\partial b}{\partial a}\right)_Z=-\frac{1}{\left(\frac{\partial a}{\partial Z}\right)_b\left(\frac{\partial Z}{\partial b}\right)_a}=-\frac{\left(\frac{\partial Z}{\partial a}\right)_b}{\left(\frac{\partial Z}{\partial b}\right)_a}$$

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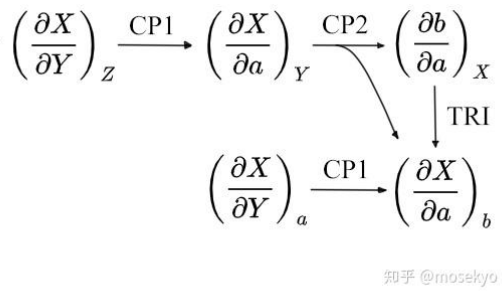
$$\left(\frac{\partial X}{\partial Y}\right)_a=\left(\frac{\partial X}{\partial b}\right)_a\left(\frac{\partial b}{\partial Y}\right)_a=\frac{\left(\frac{\partial X}{\partial b}\right)_a}{\left(\frac{\partial Y}{\partial b}\right)_a}$$

- $$\left(\frac{\partial X}{\partial a}\right)_Y=\left(\frac{\partial X}{\partial a}\right)_b+\left(\frac{\partial X}{\partial b}\right)_a\left(\frac{\partial b}{\partial a}\right)_Y=\left(\frac{\partial X}{\partial a}\right)_b+\left(\frac{\partial X}{\partial b}\right)_a-\frac{\left(\frac{\partial Y}{\partial a}\right)_b}{\left(\frac{\partial Y}{\partial b}\right)_a}$$

- $$\begin{aligned}\left(\frac{\partial X}{\partial Y}\right)_Z&=\left(\frac{\partial X}{\partial a}\right)_Z\left(\frac{\partial a}{\partial Y}\right)_Z\\&=\left(\left(\frac{\partial X}{\partial a}\right)_b+\left(\frac{\partial X}{\partial b}\right)_a-\frac{\left(\frac{\partial Z}{\partial a}\right)_b}{\left(\frac{\partial Z}{\partial b}\right)_a}\right)\left(\frac{1}{\left(\frac{\partial Y}{\partial a}\right)_b+\left(\frac{\partial Y}{\partial b}\right)_a-\frac{\left(\frac{\partial Z}{\partial a}\right)_b}{\left(\frac{\partial Z}{\partial b}\right)_a}}\right)\end{aligned}$$



综合上述公式，我们可以把所有的偏微分关系式化成一阶的关系式 $\left(\frac{\partial X}{\partial a}\right)_b$

例 1.1.1. U 的偏微分关系

1. $$\left(\frac{\partial U}{\partial T}\right)_V=C_V$$

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2. $$\left(\frac{\partial U}{\partial p}\right)_V\overset{CP1}{=}\left(\frac{\partial U}{\partial T}\right)_V\left(\frac{\partial T}{\partial V}\right)_V=C_V\left(\frac{\partial T}{\partial p}\right)_V$$

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3. $$\left(\frac{\partial U}{\partial T}\right)_p=\left(\frac{\partial H}{\partial T}\right)_p-p\left(\frac{\partial H}{\partial T}\right)_p=C_p-p\left(\frac{\partial V}{\partial T}\right)_p$$

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4. $$\left(\frac{\partial U}{\partial V}\right)_p=\left(\frac{\partial U}{\partial T}\right)_p\left(\frac{\partial T}{\partial V}\right)_p\overset{3}{=}C_p\left(\frac{\partial T}{\partial V}\right)_p-p\left(\frac{\partial V}{\partial T}\right)_p\left(\frac{\partial T}{\partial V}\right)_p=C_p\left(\frac{\partial T}{\partial V}\right)_p-p$$

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5. $$\begin{aligned}\left(\frac{\partial U}{\partial V}\right)_T&\overset{CP2}{=}\left(\frac{\partial U}{\partial V}\right)_p+\left(\frac{\partial U}{\partial p}\right)_V\left(\frac{\partial p}{\partial V}\right)_T\\&\overset{2}{\underset{4}{=}}C_p\left(\frac{\partial T}{\partial V}\right)_p-p+C_V\left(\frac{\partial T}{\partial p}\right)_V\left(\frac{\partial p}{\partial V}\right)_T\end{aligned}$$

$$
\begin{aligned}
&\overset{TRI}{=} C_p\left(\frac{\partial T}{\partial V}\right)_p - p - C_V\left(\frac{\partial T}{\partial V}\right)_p \\
&= (C_p - C_V)\left(\frac{\partial T}{\partial V}\right)_p - p
\end{aligned}
$$

6.

$$
\begin{aligned}
\left(\frac{\partial U}{\partial p}\right)_T &\overset{INV}{=} \left(\frac{\partial U}{\partial V}\right)_T\left(\frac{\partial V}{\partial p}\right)_T \\
&\underset{TRI}{\overset{5}{=}} -(C_p - C_V)\left(\frac{\partial T}{\partial p}\right)_V - p\left(\frac{\partial V}{\partial p}\right)_T
\end{aligned}
$$

例 1.1.2. H 的偏微分关系

1.

$$
\left(\frac{\partial H}{\partial T}\right)_p = C_p
$$

2.

$$
\left(\frac{\partial H}{\partial V}\right)_p \overset{CP1}{=} \left(\frac{\partial H}{\partial T}\right)_p\left(\frac{\partial T}{\partial V}\right)_p = C_p\left(\frac{\partial T}{\partial V}\right)_p
$$

3.

$$
\begin{aligned}
\left(\frac{\partial H}{\partial p}\right)_T &= \left(\frac{\partial U}{\partial p}\right)_T + \left(\frac{\partial (pV)}{\partial p}\right)_T = \left(\frac{\partial U}{\partial p}\right)_T + V + p\left(\frac{\partial V}{\partial p}\right)_T \\
&= V - (C_p - C_V)\left(\frac{\partial T}{\partial p}\right)_V
\end{aligned}
$$

4.

$$
\begin{aligned}
\left(\frac{\partial H}{\partial T}\right)_V &\overset{CP2}{=} \left(\frac{\partial H}{\partial T}\right)_p + \left(\frac{\partial H}{\partial p}\right)_T\left(\frac{\partial p}{\partial T}\right)_V \overset{3}{=} C_p + \left[V + p\left(\frac{\partial V}{\partial p}\right)_T\right]\left(\frac{\partial p}{\partial T}\right)_V \\
&= C_V + V\left(\frac{\partial p}{\partial T}\right)_V
\end{aligned}
$$

5.

$$
\begin{aligned}
\left(\frac{\partial H}{\partial V}\right)_T &\overset{CP2}{=} \left(\frac{\partial H}{\partial V}\right)_p + \left(\frac{\partial H}{\partial p}\right)_V\left(\frac{\partial p}{\partial V}\right)_T \\
&\underset{3}{\overset{2}{=}} C_p\left(\frac{\partial T}{\partial V}\right)_p + \left[V + p\left(\frac{\partial V}{\partial p}\right)_T\right]\left(\frac{\partial p}{\partial V}\right)_T \\
&\overset{TRI}{=} V\left(\frac{\partial p}{\partial V}\right)_T + (C_p - C_V)\left(\frac{\partial T}{\partial V}\right)_p
\end{aligned}
$$

6.

$$
\begin{aligned}
\left(\frac{\partial H}{\partial p}\right)_V &\overset{CP1}{=} \left(\frac{\partial H}{\partial T}\right)_V\left(\frac{\partial T}{\partial p}\right)_V \overset{4}{=} \left[C_p + \left(V + p\left(\frac{\partial V}{\partial p}\right)_T\right)\left(\frac{\partial p}{\partial T}\right)_V\right]\left(\frac{\partial T}{\partial p}\right)_V \\
&= C_V + V\left(\frac{\partial p}{\partial T}\right)_V
\end{aligned}
$$

例 1.1.3. S 的偏微分关系

1.
$$\left(\frac{\partial S}{\partial T}\right)_V=\left(\frac{\partial S}{\partial U}\right)_V\left(\frac{\partial U}{\partial T}\right)_V=\frac{C_V}{T}$$

2.
$$\left(\frac{\partial S}{\partial T}\right)_p=\left(\frac{\partial S}{\partial H}\right)_p\left(\frac{\partial H}{\partial T}\right)_p=\frac{C_p}{T}$$

3.
$$\left(\frac{\partial S}{\partial V}\right)_T\overset{\text{Maxwell}}{=}\left(\frac{\partial p}{\partial T}\right)_V\qquad(\text{由}dA=-SdT-pdV)$$

4.
$$\left(\frac{\partial S}{\partial p}\right)_T\overset{\text{Maxwell}}{=}-\left(\frac{\partial V}{\partial T}\right)_p\qquad(\text{由}dG=-SdT+Vdp)$$

5.
$$\left(\frac{\partial S}{\partial V}\right)_p\overset{CP1}{=}\left(\frac{\partial S}{\partial T}\right)_p\left(\frac{\partial T}{\partial V}\right)_p\overset{\frac{2}{3}}{=}\frac{C_p}{T}\left(\frac{\partial T}{\partial V}\right)_p$$

6.
$$\left(\frac{\partial S}{\partial p}\right)_V\overset{CP1}{=}\left(\frac{\partial S}{\partial T}\right)_V\left(\frac{\partial T}{\partial p}\right)_V\overset{\frac{1}{4}}{=}\frac{C_V}{T}\left(\frac{\partial T}{\partial p}\right)_V$$

例 1.1.4. A 的偏微分关系

1.
$$\left(\frac{\partial A}{\partial T}\right)_V=-S\quad(\text{由 }dA=-SdT-pdV)$$

2.
$$\left(\frac{\partial A}{\partial V}\right)_T=-p\quad(\text{由 }dA=-SdT-pdV)$$

3.
$$\left(\frac{\partial A}{\partial p}\right)_V\overset{CP1}{=}\left(\frac{\partial A}{\partial T}\right)_V\left(\frac{\partial T}{\partial p}\right)_V\overset{1}{=}-S\left(\frac{\partial T}{\partial p}\right)_V$$

4.
$$\left(\frac{\partial A}{\partial p}\right)_T\overset{CP1}{=}\left(\frac{\partial A}{\partial V}\right)_T\left(\frac{\partial V}{\partial p}\right)_T\overset{2}{=}-p\left(\frac{\partial V}{\partial p}\right)_T$$

5.

$$\left(\frac{\partial A}{\partial T}\right)_p \overset{CP2}{=} \left(\frac{\partial A}{\partial T}\right)_V + \left(\frac{\partial A}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_p$$
$$\overset{1}{\underset{2}{=}} -S - p\left(\frac{\partial V}{\partial T}\right)_p$$

6.

$$\left(\frac{\partial A}{\partial T}\right)_p \overset{CP2}{=} \left(\frac{\partial A}{\partial T}\right)_V \left(\frac{\partial T}{\partial V}\right)_p + \left(\frac{\partial A}{\partial V}\right)_T$$
$$\overset{1}{\underset{2}{=}} -S\left(\frac{\partial T}{\partial V}\right)_p - p$$

例 1.1.5. G 的偏微分关系

1.

$$\left(\frac{\partial G}{\partial T}\right)_p = -S \quad (\text{由 } dG = -SdT + Vdp)$$

2.

$$\left(\frac{\partial G}{\partial p}\right)_T = V \quad (\text{由 } dG = -SdT + Vdp)$$

3.

$$\left(\frac{\partial G}{\partial V}\right)_P \overset{CP1}{=} \left(\frac{\partial G}{\partial T}\right)_p \left(\frac{\partial T}{\partial V}\right)_p \overset{1}{=} -S\left(\frac{\partial p}{\partial V}\right)_T$$

4.

$$\left(\frac{\partial G}{\partial V}\right)_T \overset{CP1}{=} \left(\frac{\partial G}{\partial p}\right)_T \left(\frac{\partial p}{\partial V}\right)_T \overset{2}{=} V\left(\frac{\partial p}{\partial V}\right)_T$$

5.

$$\left(\frac{\partial G}{\partial T}\right)_V \overset{CP2}{=} \left(\frac{\partial G}{\partial T}\right)_p + \left(\frac{\partial G}{\partial p}\right)_T \left(\frac{\partial p}{\partial T}\right)_V$$
$$\overset{1}{\underset{2}{=}} -S + V\left(\frac{\partial p}{\partial T}\right)_V$$

6.

$$\left(\frac{\partial G}{\partial T}\right)_V \overset{CP2}{=} \left(\frac{\partial G}{\partial T}\right)_p \left(\frac{\partial T}{\partial p}\right)_V + \left(\frac{\partial G}{\partial p}\right)_T$$
$$\overset{1}{\underset{2}{=}} -S\left(\frac{\partial T}{\partial p}\right)_V + V$$