● 一般の場合

$$dS = \frac{d'Q}{T} = \frac{1}{T}\left(\frac{\partial U}{\partial T}\right)_V dT + \frac{1}{T}\left[\left(\frac{\partial U}{\partial V}\right)_T + p\right]dV \quad \leftarrow \quad (80)$$

(83) より
$$\frac{\partial}{\partial V}\left(\frac{1}{T}\frac{\partial U}{\partial T}\right) = \frac{\partial}{\partial T}\left[\frac{1}{T}\left(\frac{\partial U}{\partial V} + p\right)\right]$$

$$\frac{1}{T}\frac{\partial^2 U}{\partial V \partial T} = -\frac{1}{T^2}\left(\frac{\partial U}{\partial V} + p\right) + \frac{1}{T}\left(\frac{\partial^2 U}{\partial T \partial V} + \frac{\partial p}{\partial T}\right)$$

$$\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial p}{\partial T}\right)_V - p \qquad (88)$$

$pV = RT$ の場合

$$\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial}{\partial T}\frac{RT}{V}\right)_V - \frac{RT}{V} = 0$$

理想気体のエネルギーは温度のみの関数で，体積によらない

● **变数变换：** $(T,V)\to(T,p)$

$$d'Q = dU + p dV$$

$$d'Q = \left(\frac{\partial U}{\partial T}\right)_p dT + \left(\frac{\partial U}{\partial p}\right)_T dp + p\left(\frac{\partial V}{\partial T}\right)_p dT + p\left(\frac{\partial V}{\partial p}\right)_T dp$$

$$= \left[\left(\frac{\partial U}{\partial T}\right)_p + p\left(\frac{\partial V}{\partial T}\right)_p\right]dT + \left[\left(\frac{\partial U}{\partial p}\right)_T + p\left(\frac{\partial V}{\partial p}\right)_T\right]dp$$

$$dS = \frac{1}{T}\left[\left(\frac{\partial U}{\partial T}\right)_p + p\left(\frac{\partial V}{\partial T}\right)_p\right]dT + \frac{1}{T}\left[\left(\frac{\partial U}{\partial p}\right)_T + p\left(\frac{\partial V}{\partial p}\right)_T\right]dp$$

$$\frac{1}{T}\frac{\partial}{\partial p}\left[\left(\frac{\partial U}{\partial T}\right)_p + p\left(\frac{\partial V}{\partial T}\right)_p\right] = \frac{\partial}{\partial T}\left[\frac{1}{T}\left(\frac{\partial U}{\partial p}\right)_T + \frac{p}{T}\left(\frac{\partial V}{\partial p}\right)_T\right]$$

$$\frac{1}{T}\frac{\partial^2 U}{\partial p \partial T} + \frac{1}{T}\left(\frac{\partial V}{\partial T}\right)_p + \frac{p}{T}\frac{\partial^2 V}{\partial p \partial T} = \frac{-1}{T^2}\left(\frac{\partial U}{\partial p}\right)_T + \frac{1}{T}\frac{\partial^2 U}{\partial T \partial p} + \left(\frac{\partial}{\partial T}\frac{p}{T}\right)_p\left(\frac{\partial V}{\partial p}\right)_T + \frac{p}{T}\frac{\partial^2 V}{\partial T \partial p}$$

$$\frac{1}{T}\left(\frac{\partial V}{\partial T}\right)_p = -\frac{1}{T^2}\left(\frac{\partial U}{\partial p}\right)_T - \frac{p}{T^2}\left(\frac{\partial V}{\partial p}\right)_T$$

$$\left(\frac{\partial U}{\partial p}\right)_T = -p\left(\frac{\partial V}{\partial p}\right)_T - T\left(\frac{\partial V}{\partial T}\right)_p \qquad \textbf{(89)}$$

- **变数变换：** $(T,V)\to(p,V)$

$$\mathrm{d}'Q=\mathrm{d}U+p\mathrm{d}V$$

$$\mathrm{d}'Q=\left(\frac{\partial U}{\partial p}\right)_V\mathrm{d}p+\left[\left(\frac{\partial U}{\partial V}\right)_p+p\right]\mathrm{d}V$$

$$\mathrm{d}S=\frac{\mathrm{d}'Q}{T}=\frac{1}{T}\left(\frac{\partial U}{\partial p}\right)_V\mathrm{d}p+\frac{1}{T}\left[\left(\frac{\partial U}{\partial V}\right)_p+p\right]\mathrm{d}V$$

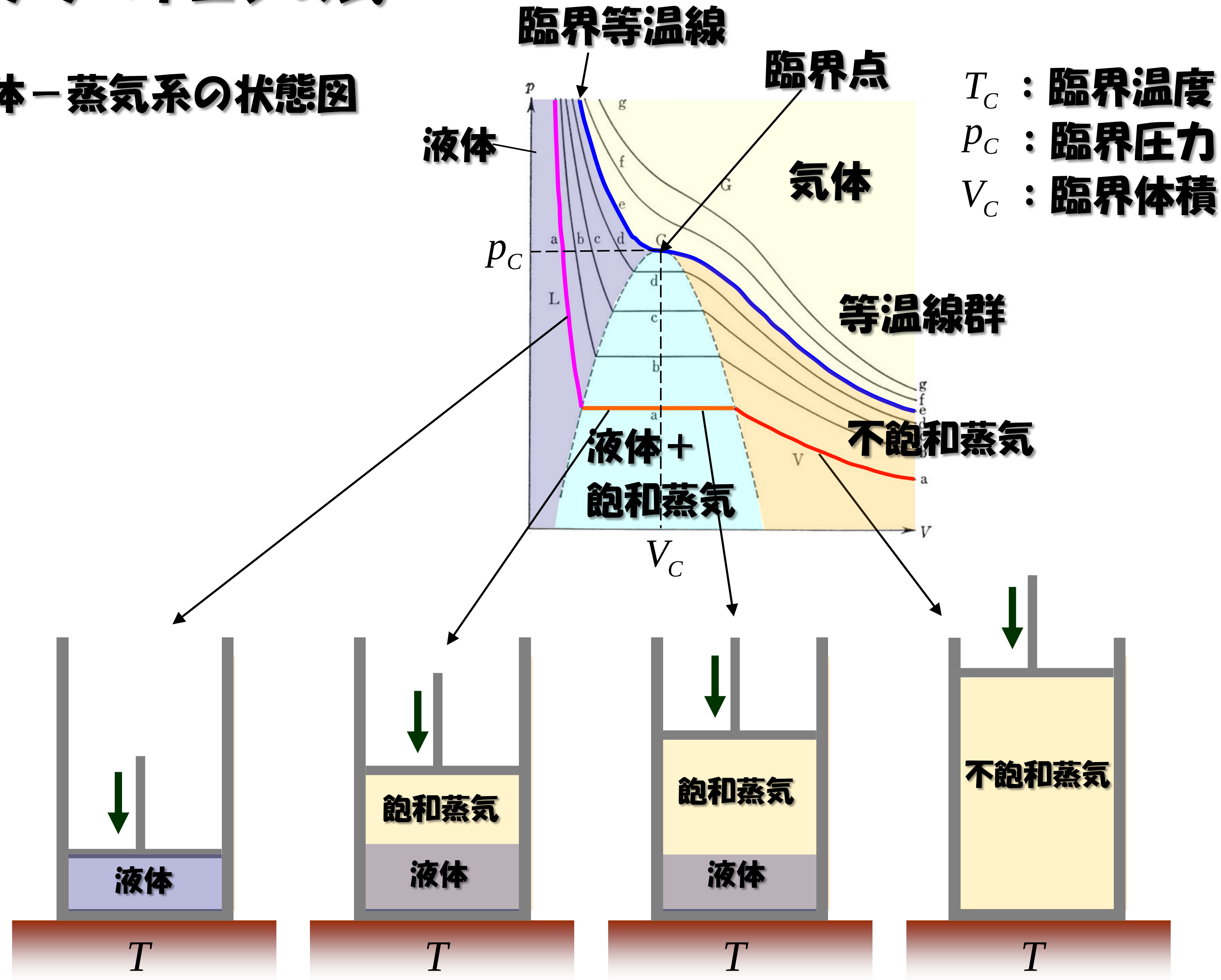
$$\frac{\partial}{\partial V}\left[\frac{1}{T}\left(\frac{\partial U}{\partial p}\right)_V\right]=\frac{\partial}{\partial p}\left[\frac{1}{T}\left[\left(\frac{\partial U}{\partial V}\right)_p+p\right]\right]$$

$$\frac{-1}{T^2}\left(\frac{\partial T}{\partial V}\right)_p\left(\frac{\partial U}{\partial p}\right)_V+\frac{1}{T}\frac{\partial^2 U}{\partial V\partial p}=\frac{-1}{T^2}\left(\frac{\partial T}{\partial p}\right)_V\left(\frac{\partial U}{\partial V}\right)_p+\frac{1}{T}\frac{\partial^2 U}{\partial p\partial V}+\frac{1}{T}-\frac{p}{T^2}\left(\frac{\partial T}{\partial p}\right)_V$$

$$T=\left[\left(\frac{\partial U}{\partial V}\right)_p+p\right]\left(\frac{\partial T}{\partial p}\right)_V-\left(\frac{\partial U}{\partial p}\right)_V\left(\frac{\partial T}{\partial V}\right)_p \qquad (90)$$

15. クラペイロンの式

■　液体－蒸気系の状態図

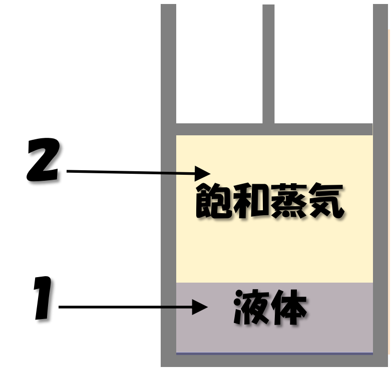


■ クラペイロンの式

m_1, m_2 ：液体と蒸気の質量

u_1, u_2 ：液体と蒸気の単位質量当たりのエネルギー

v_1, v_2 ：液体と蒸気の単位質量当たりの体積



dm を液体状態から蒸気状態へ移す等温過程を考える

－圧力一定－

	前			後		
	質量	体積	エネルギー	質量	体積	エネルギー
液体	m_1	$m_1 v_1$	$m_1 u_1$	$m_1 - \mathrm{d}m$	$(m_1 - \mathrm{d}m)v_1$	$(m_1 - \mathrm{d}m)u_1$
蒸気	m_2	$m_2 v_2$	$m_2 u_2$	$m_2 + \mathrm{d}m$	$(m_2 + \mathrm{d}m)v_2$	$(m_2 + \mathrm{d}m)u_2$
液体 + 蒸気	$m = m_1 + m_2$ $V = m_1 v_1(T) + m_2 v_2(T)$ $U = m_1 u_1(T) + m_2 u_2(T)$			$m = m_1 + m_2$ $V + \mathrm{d}V = (m_1 - \mathrm{d}m)v_1(T) + (m_2 + \mathrm{d}m)v_2(T) = V + \{v_2(T) - v_1(T)\}\mathrm{d}m$ $U + \mathrm{d}U = (m_1 - \mathrm{d}m)u_1(T) + (m_2 + \mathrm{d}m)u_2(T) = U + \{u_2(T) - u_1(T)\}\mathrm{d}m$		

$$dV = \{v_2(T) - v_1(T)\}dm \quad (91)$$

$$dU = \{u_2(T) - u_1(T)\}dm \quad (92)$$

$$d'Q = dU + pdV$$
$$= dm\{u_2 - u_1 + p(v_2 - v_1)\}$$

$$\frac{d'Q}{dm} = u_2 - u_1 + p(v_2 - v_1) = \lambda \quad (93)$$

λ ：単位質量の液体を温度一定で蒸発させるのに必要な熱量

－蒸発の潜熱－

(91)、(92) より $$\left(\frac{\partial U}{\partial V}\right)_T = \frac{u_2(T) - u_1(T)}{v_2(T) - v_1(T)} = \frac{\lambda}{v_2 - v_1} - p$$ ← (93)

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

$$\frac{dp}{dT} = \frac{\lambda}{T(v_2 - v_1)} \quad (94)$$

クラペイロンの式

λ ：蒸発の潜熱

■ クラペイロンの式の応用－沸点での水蒸気の $\frac{\mathrm{d}p}{\mathrm{d}T}$ －

$$\frac{\mathrm{d}p}{\mathrm{d}T} = \frac{\lambda}{T(v_2 - v_1)}$$

$$\lambda = 540\ cal/g = 2260 \times 10^7\ erg/g$$

$$v_2 = 1677\ cc/g,\ v_1 = 1.043\ cc/g$$

$$T = 373.1\ K$$

$$\frac{\mathrm{d}p}{\mathrm{d}T} = \frac{2260 \times 10^7}{373.1(1677 - 1.043)} = 3.61 \times 10^4\ dyne/cm^2 \cdot K = 2.7\ cmHg/K$$

● **近似** $v_2 >> v_1 \rightarrow v_2 - v_1 \approx v_2$

1グラムの蒸気 $pv_2 = \frac{R}{M}T$ **(95)**

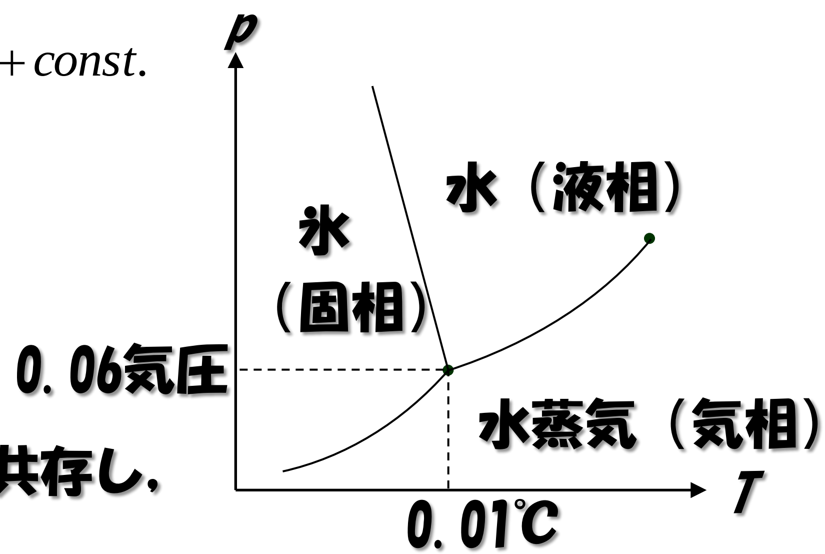
$$\frac{\mathrm{d}p}{\mathrm{d}T} = \frac{\lambda}{T(v_2 - v_1)} \approx \frac{\lambda}{Tv_2} = \frac{\lambda M}{RT^2}p \qquad (96)$$

$$\frac{\mathrm{d}p}{\mathrm{d}T} = \frac{\lambda M}{RT^2}p = \frac{2260 \times 10^7 \times 18}{8.314 \times 10^7 \times 373.1^2} 1.013 \times 10^6 = 3.56 \times 10^4$$

$$\frac{1}{p}\frac{\mathrm{d}p}{\mathrm{d}T} = \frac{\lambda M}{RT^2}$$

$$\frac{\mathrm{d}\log p}{\mathrm{d}T} = \frac{\lambda M}{RT^2} \quad (97) \;\Rightarrow\; \log p = -\frac{\lambda M}{RT} + const.$$

$$p = const.\exp\left(-\frac{\lambda M}{RT}\right) \quad (98)$$



- **固体の融解－固体－液体系－**
  固体が融解するとき，固体と液体が共存し，クラペイロンの式が成り立つ

氷-水の系

$$\lambda = 80\ cal/g = 335\times10^7\ erg/g \qquad T = 273.1\ K$$

$$v_1 = 1.0907\ cc/g,\ v_2 = 1.00013\ cc/g$$

$$\frac{\mathrm{d}p}{\mathrm{d}T} = -1.35\times10^8\ dyne/cm^2\cdot\mathrm{deg} = -134\ atm/\mathrm{deg}$$

圧力が134気圧増すと氷の融点は1℃下がる

圧力が増加すると氷の融点は下がる！

● 氷河