T,P 一定で，モル数nが変化する場合

$$dG = G(T,P,n+dn) - G(T,P,n)$$

$$= \left(\frac{\partial G}{\partial n}\right)_{T,P} dn$$

$$= \mu dn$$

$$\mu \equiv \left(\frac{\partial G}{\partial n}\right)_{T,P}$$

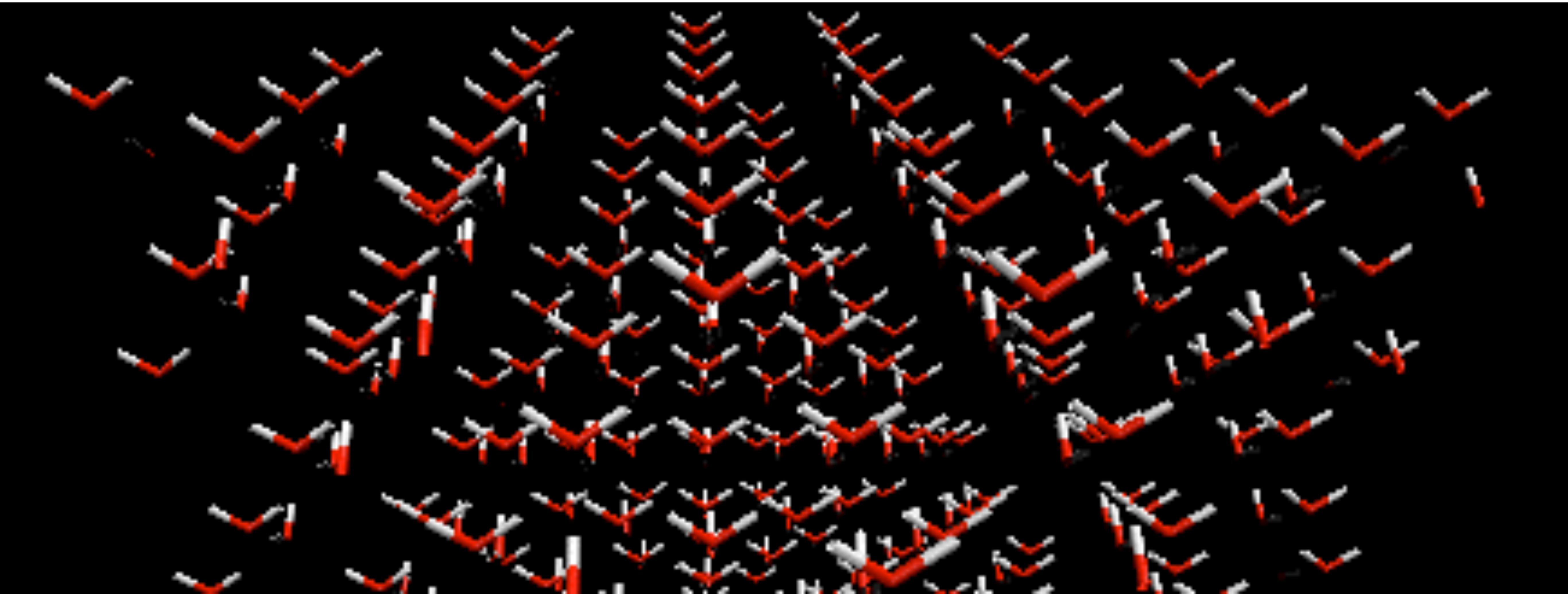
化学ポテンシャル

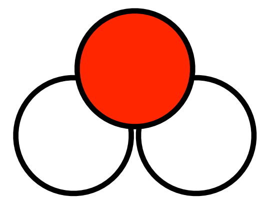
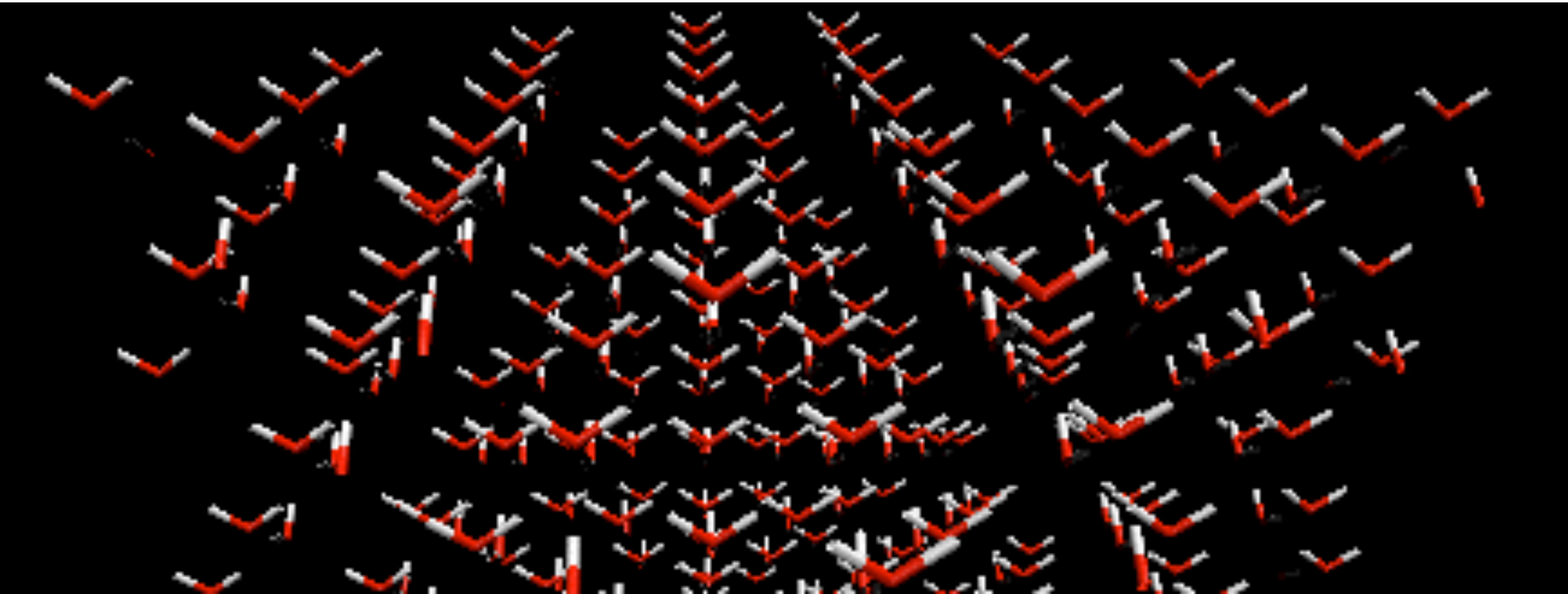
chemical potential

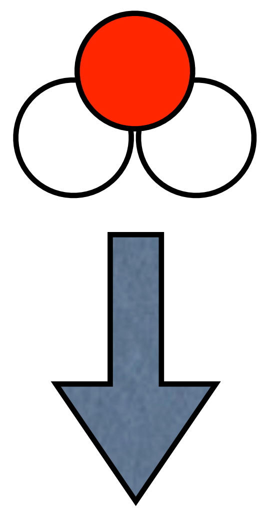
モル数（分子数）が増えると

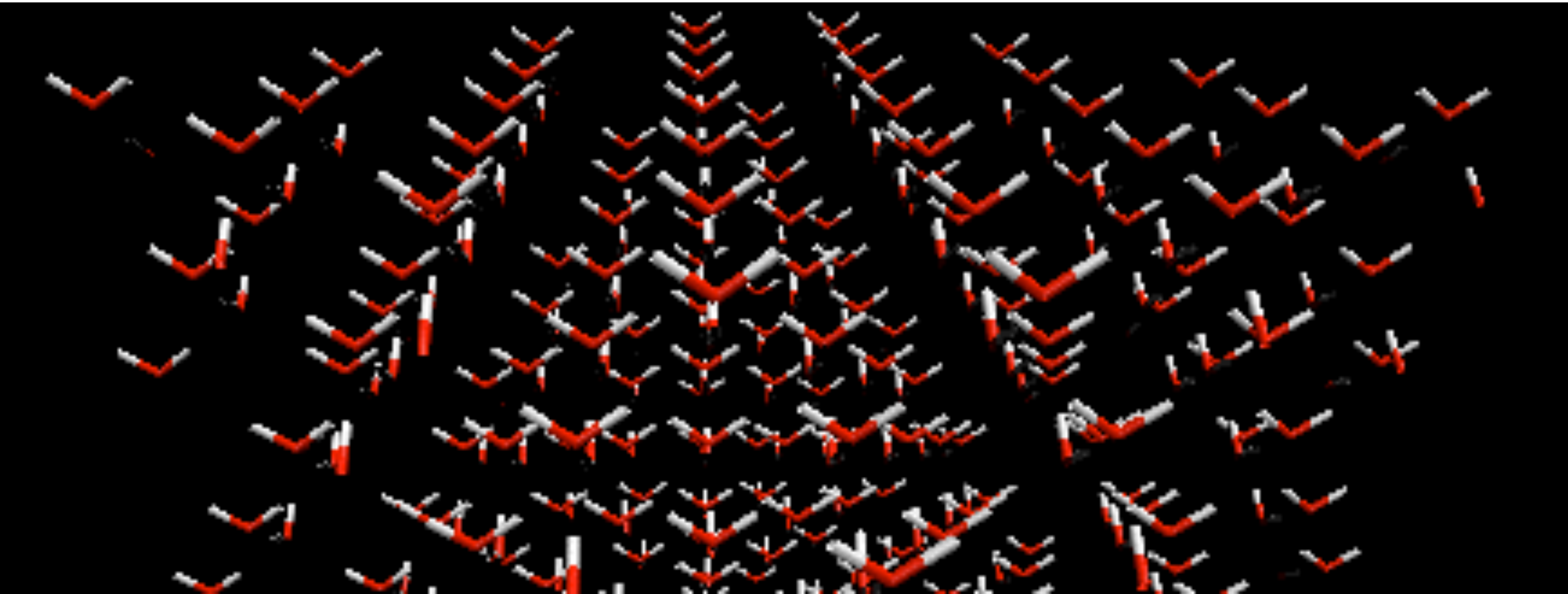
どれだけギブズエネルギーが変化するか

という量

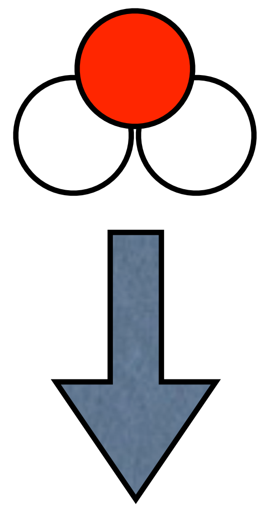


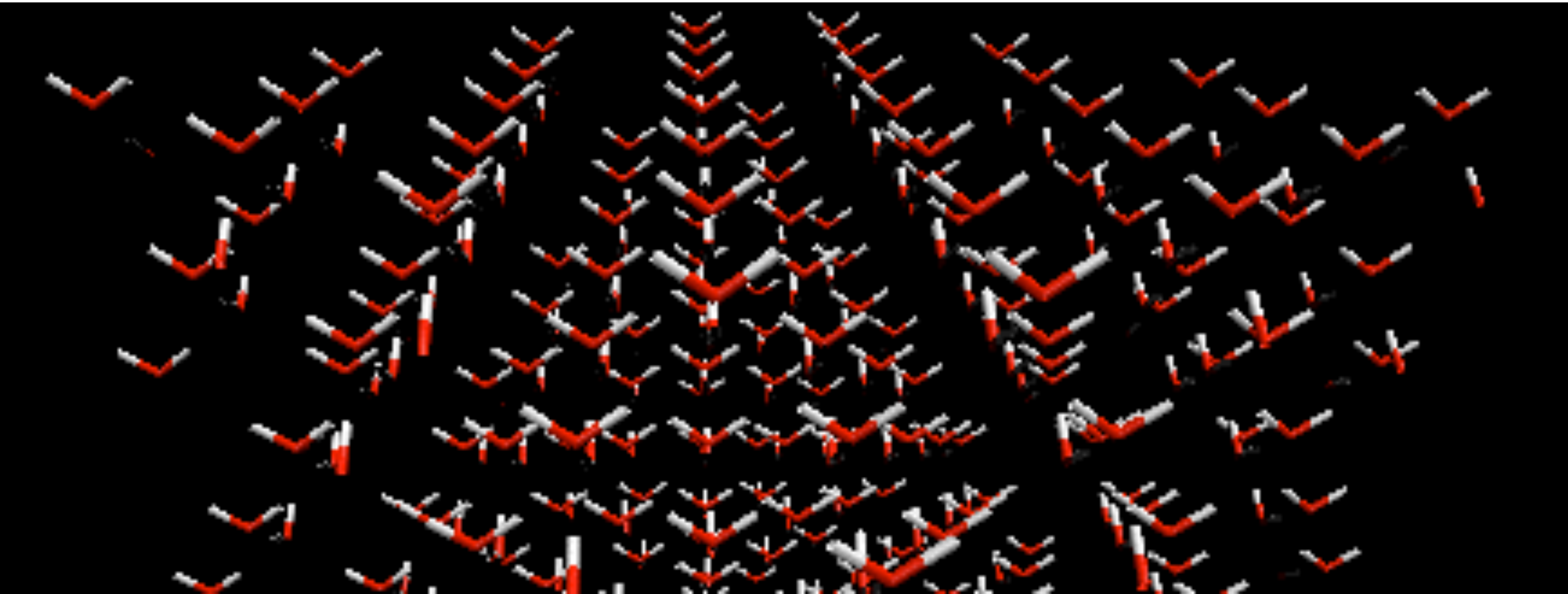




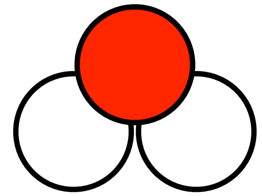
$-\mu_g$



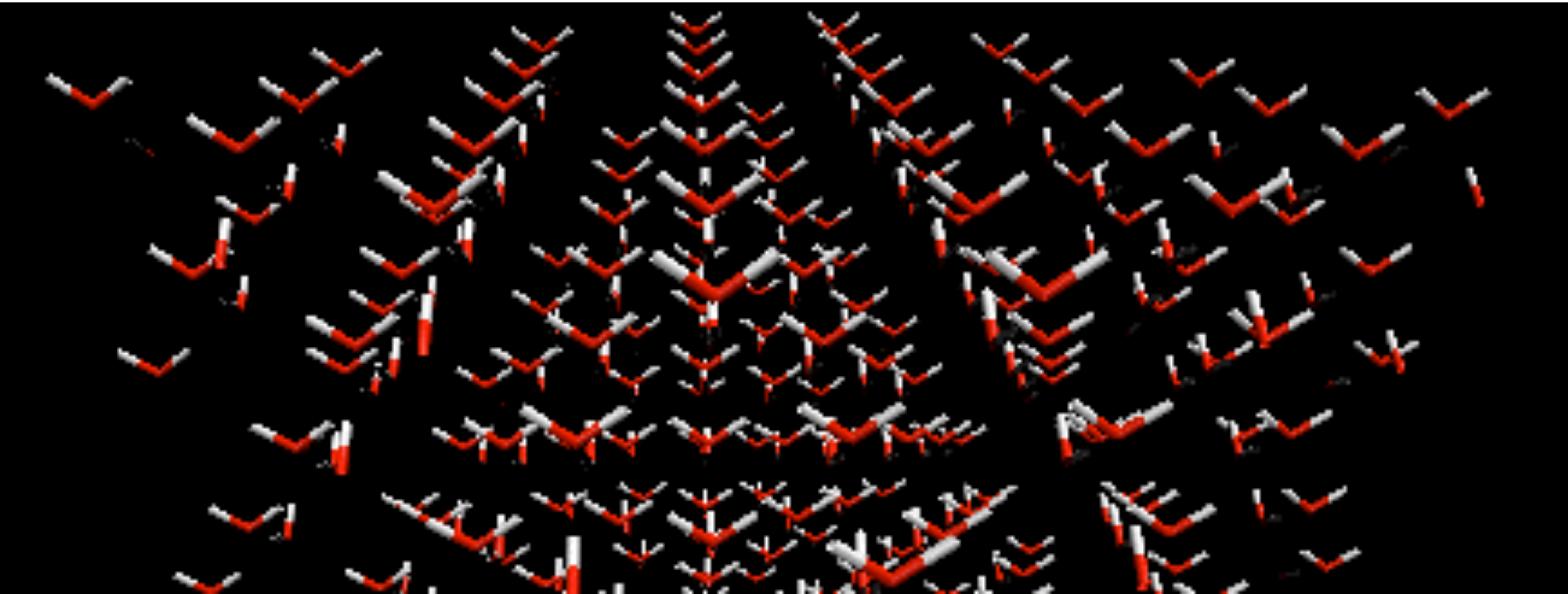
$+\mu_l$



$$-\mu_g$$

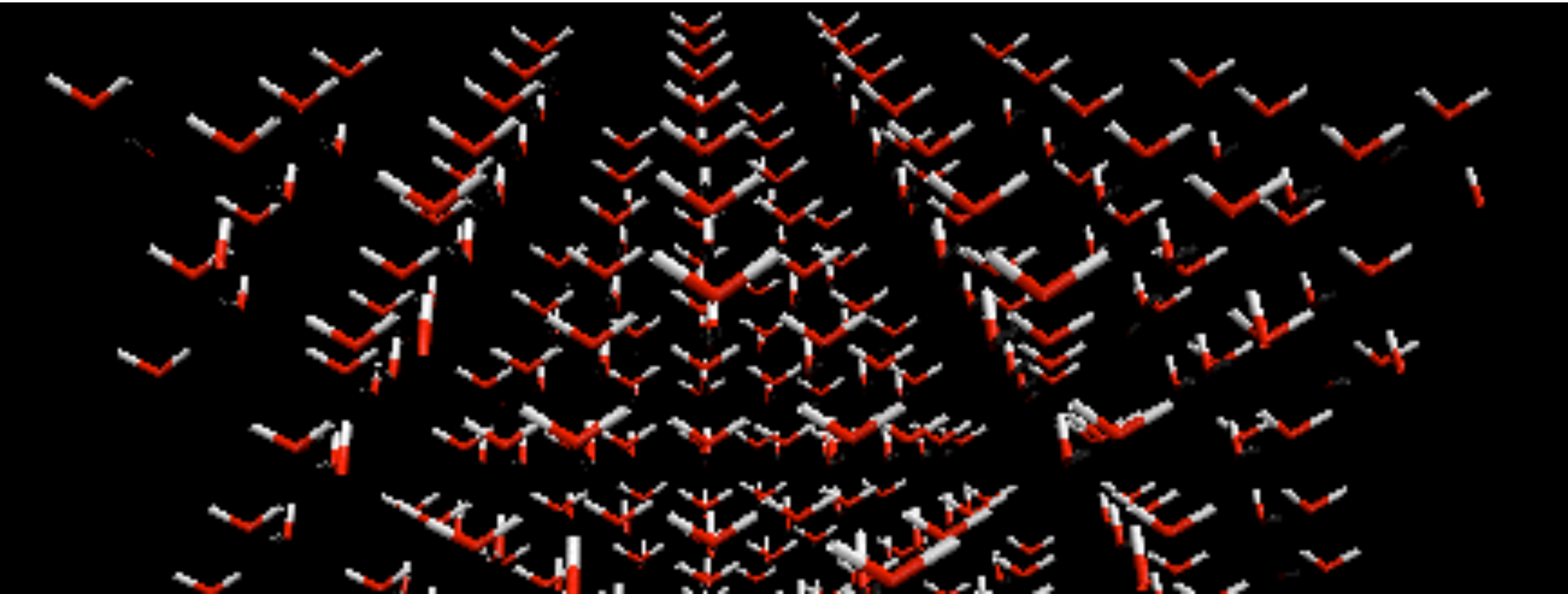


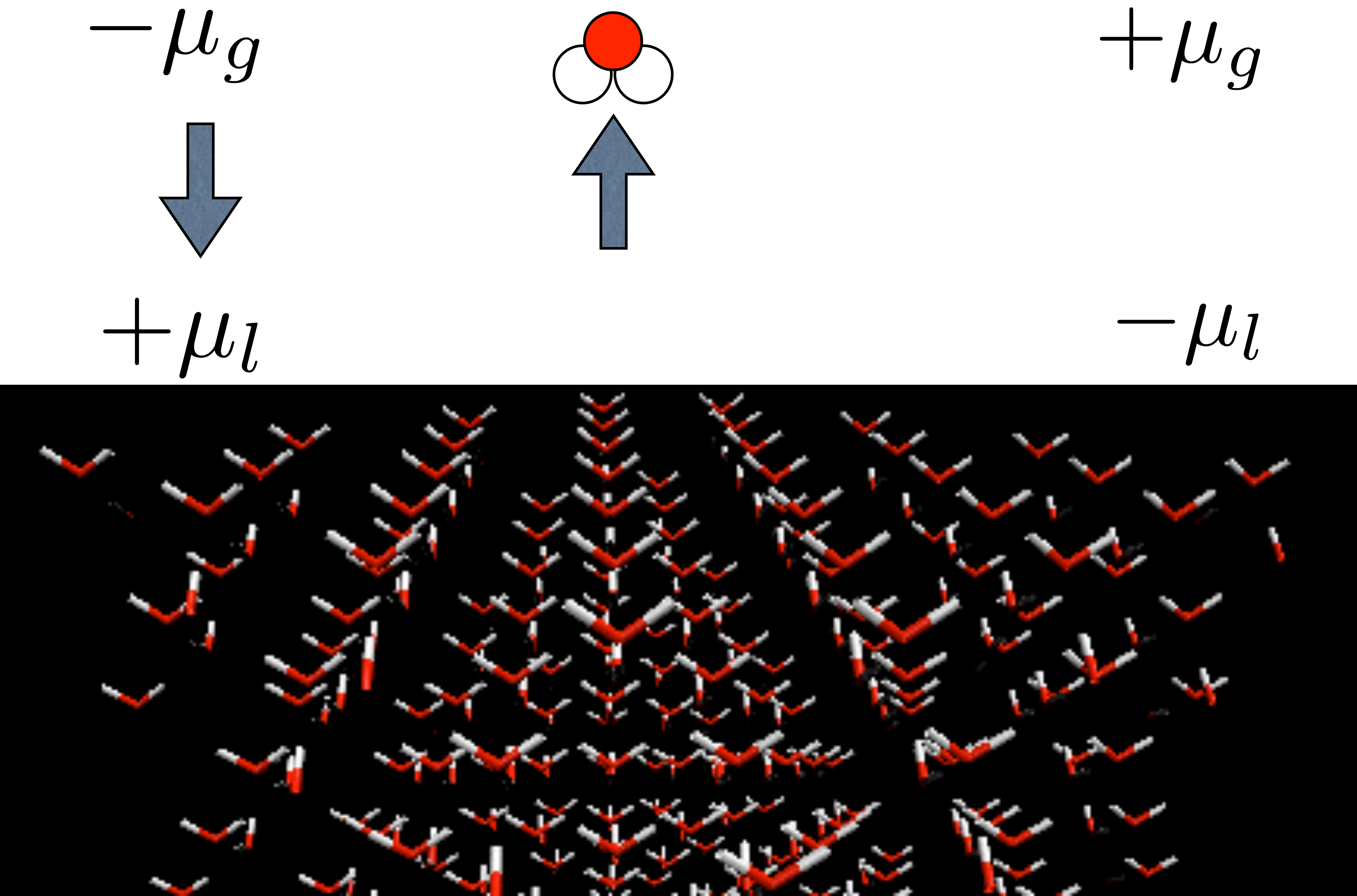
$$+\mu_l$$

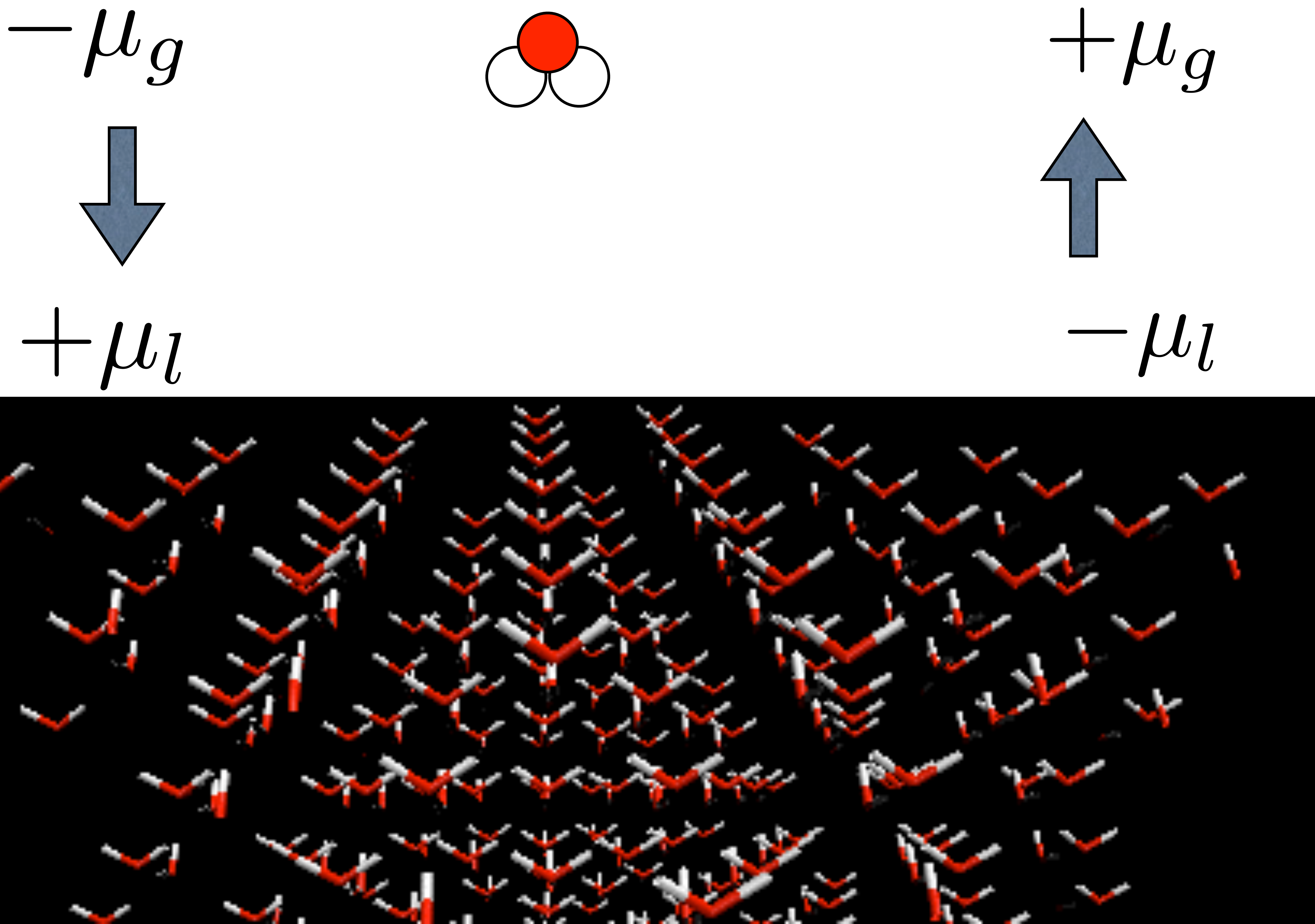


$-\mu_g$

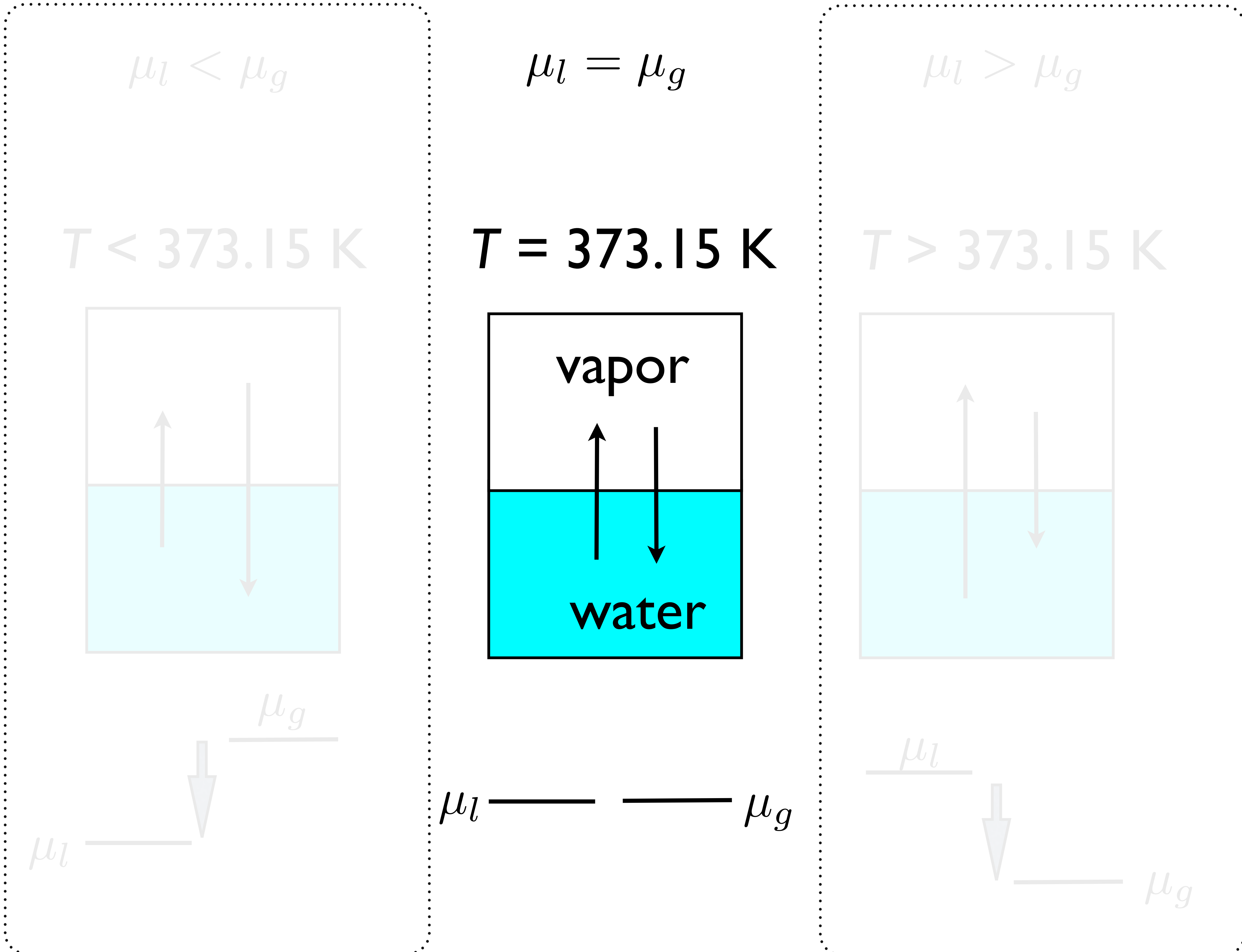
$+\mu_l$

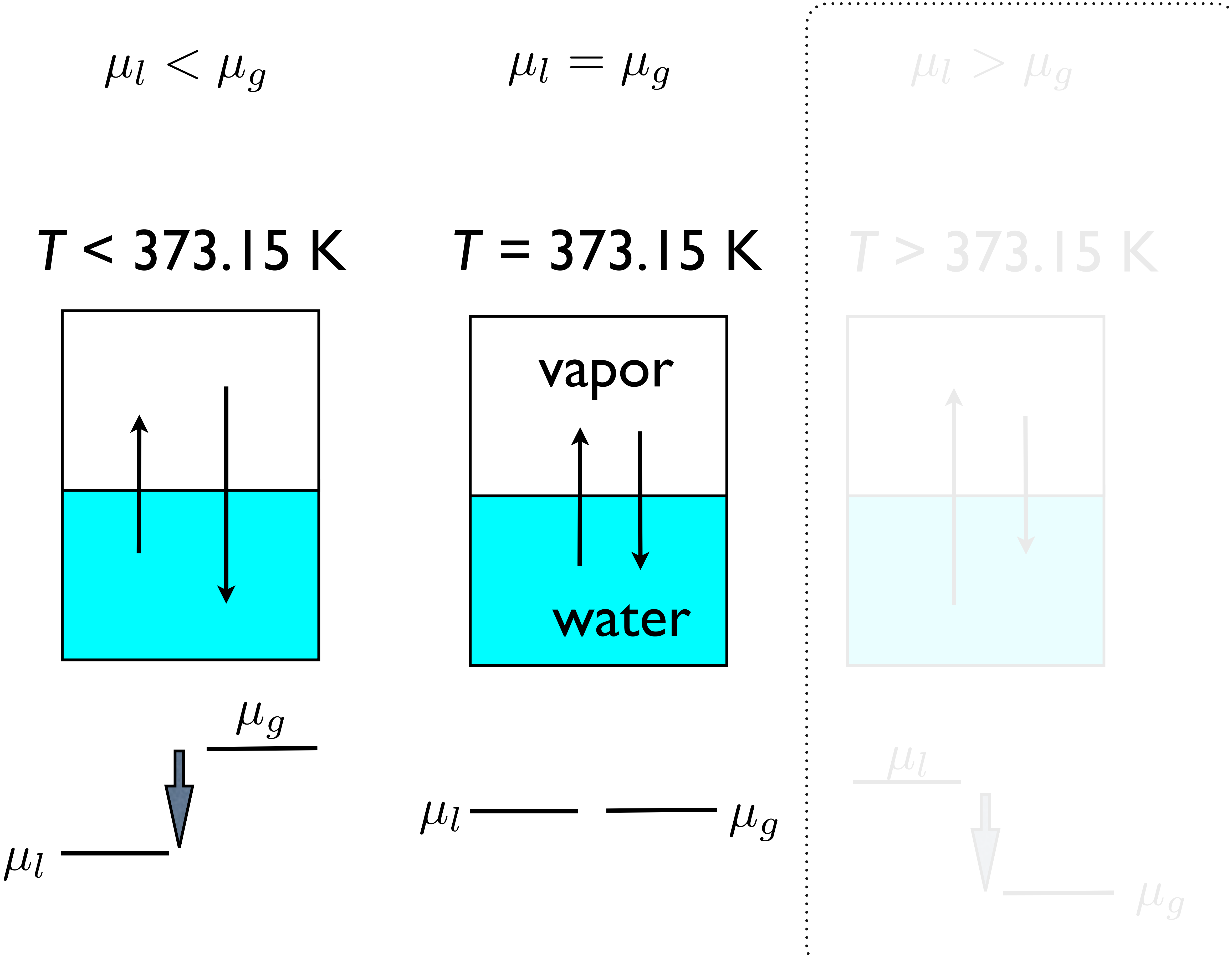



$-\mu_g$
$+\mu_g$
$+\mu_l$
$-\mu_l$



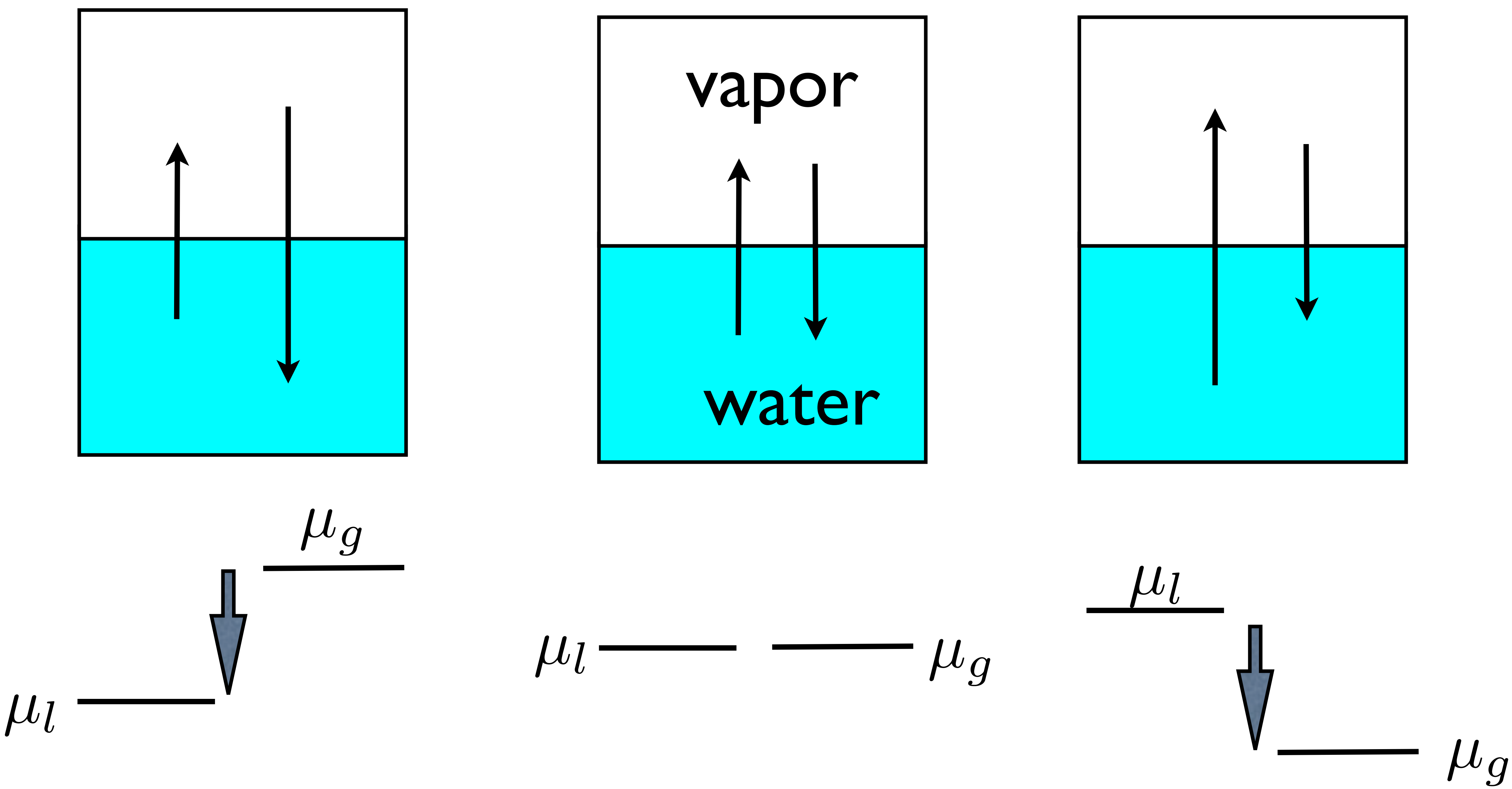
$-\mu_g$
$+\mu_l$
$+\mu_g$
$-\mu_l$


$\mu_l < \mu_g$
T < 373.15 K
μ_g
μ_l
$\mu_l = \mu_g$
T = 373.15 K
vapor
water
μ_l
μ_g
$\mu_l > \mu_g$
T > 373.15 K
μ_l
μ_g


$\mu_l < \mu_g$
$\mu_l = \mu_g$
$\mu_l > \mu_g$
T < 373.15 K
T = 373.15 K
T > 373.15 K
vapor
water
μ_g
μ_l
μ_l
μ_g
μ_l
μ_g

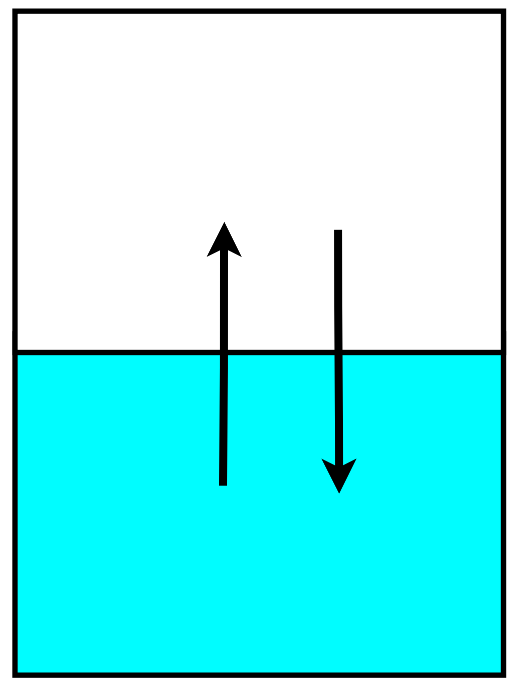
$\mu_l < \mu_g$ $\mu_l = \mu_g$ $\mu_l > \mu_g$

T < 373.15 K *T* = 373.15 K *T* > 373.15 K



相(phase)の数 $p = 2$ (Liquid, Gas)

373.15 K



相平衡の条件

$$\mu_g = \mu_l$$

$$T_g = T_l$$

$$P_g = P_l$$

式の数:3

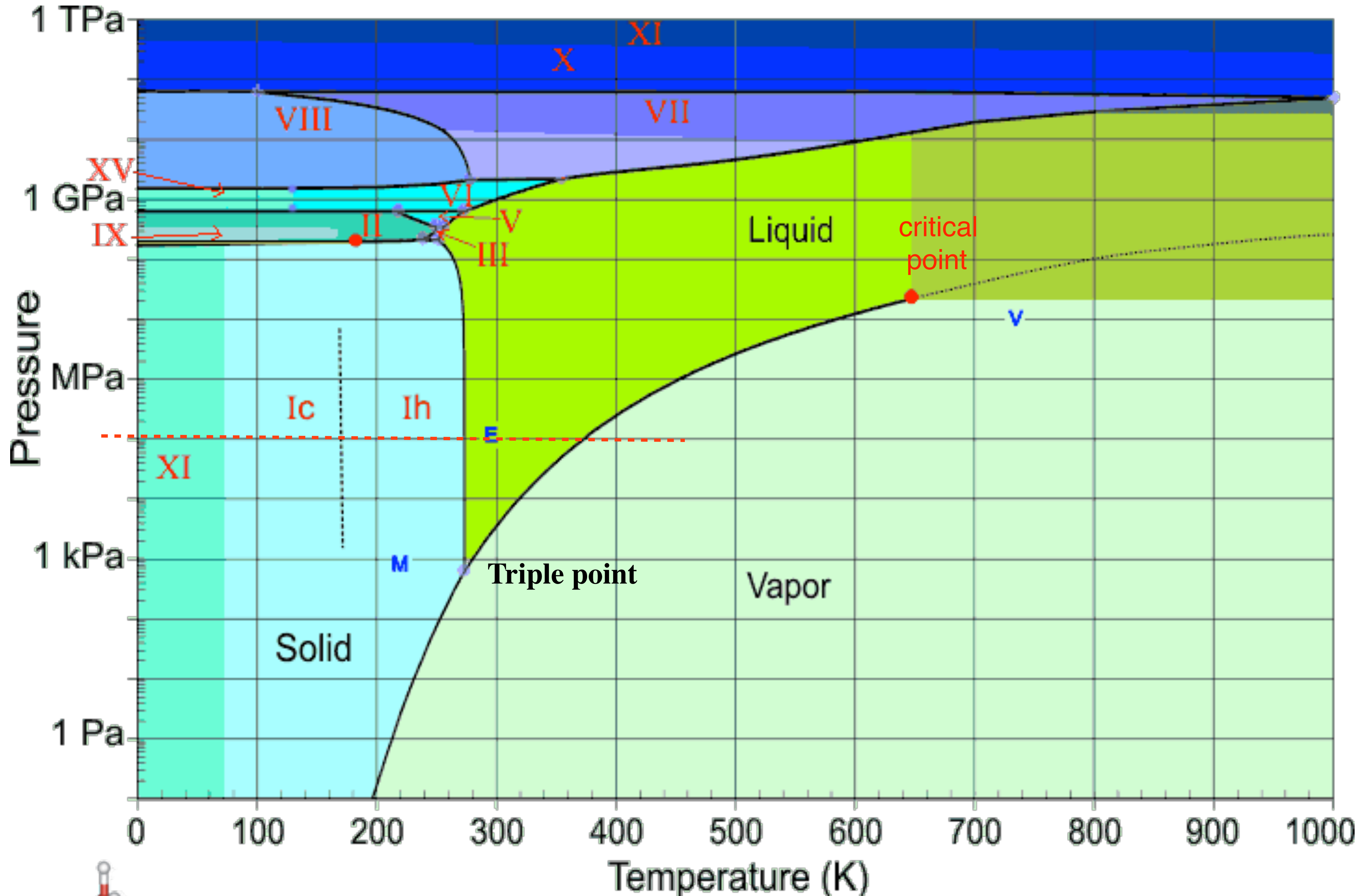
T_g, P_g

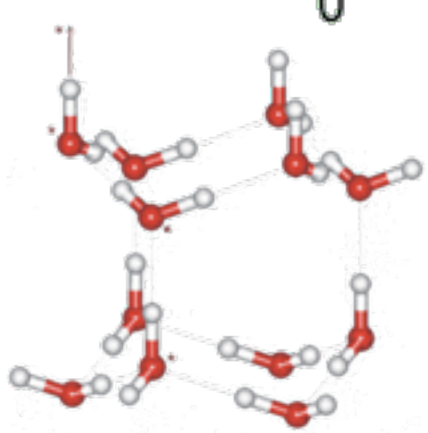
T_l, P_l

未知数 : 4

未知数 - 式の数 = 1

Water 相図：１成分





Ice Ih

Triple point

0.000611657 MPa 0.010°C

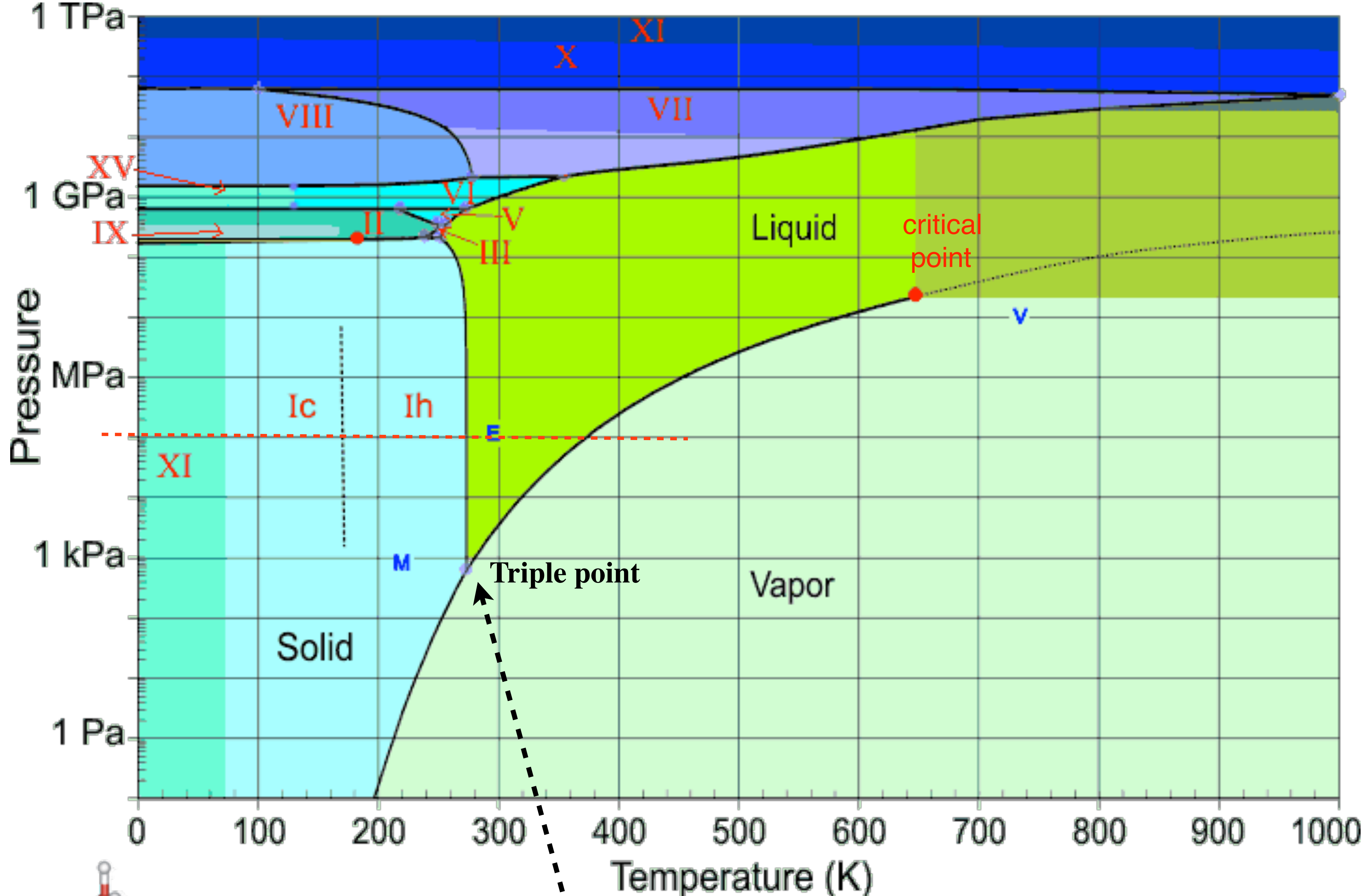
三重点

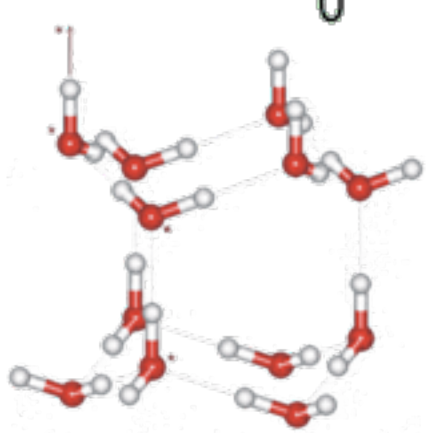
critical point

647.096 K, 22.064 MPa

臨界点

Water 相図： 1 成分





Ice Ih

Triple point

0.000611657 MPa 0.010°C

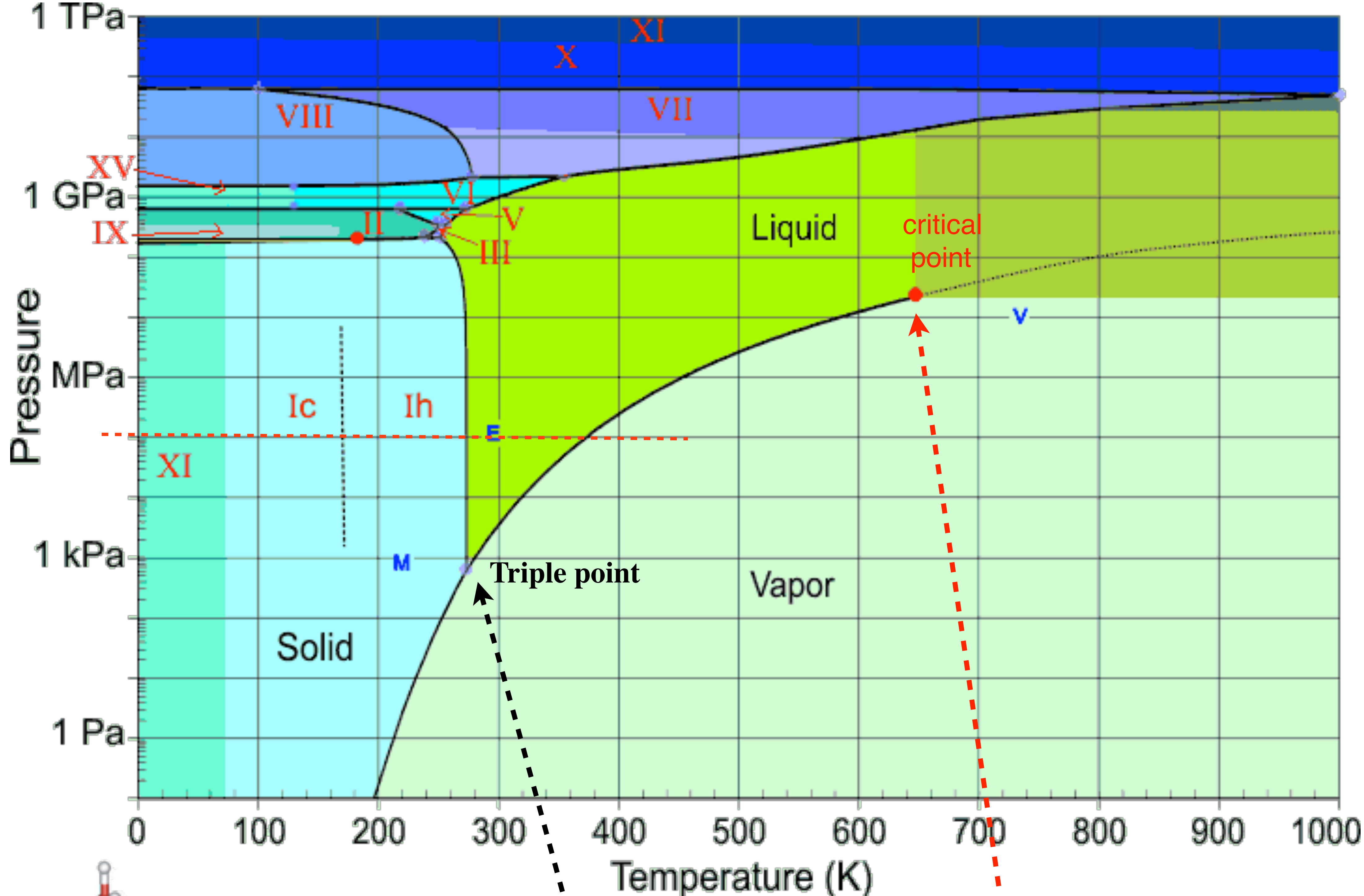
三重点

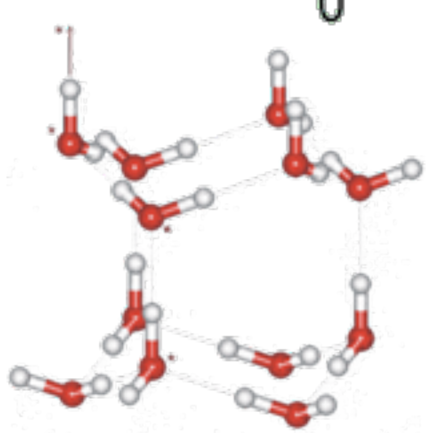
critical point

647.096 K, 22.064 MPa

臨界点

Water 相図：１成分





Ice Ih

Triple point

0.000611657 MPa 0.010°C

三重点

critical point

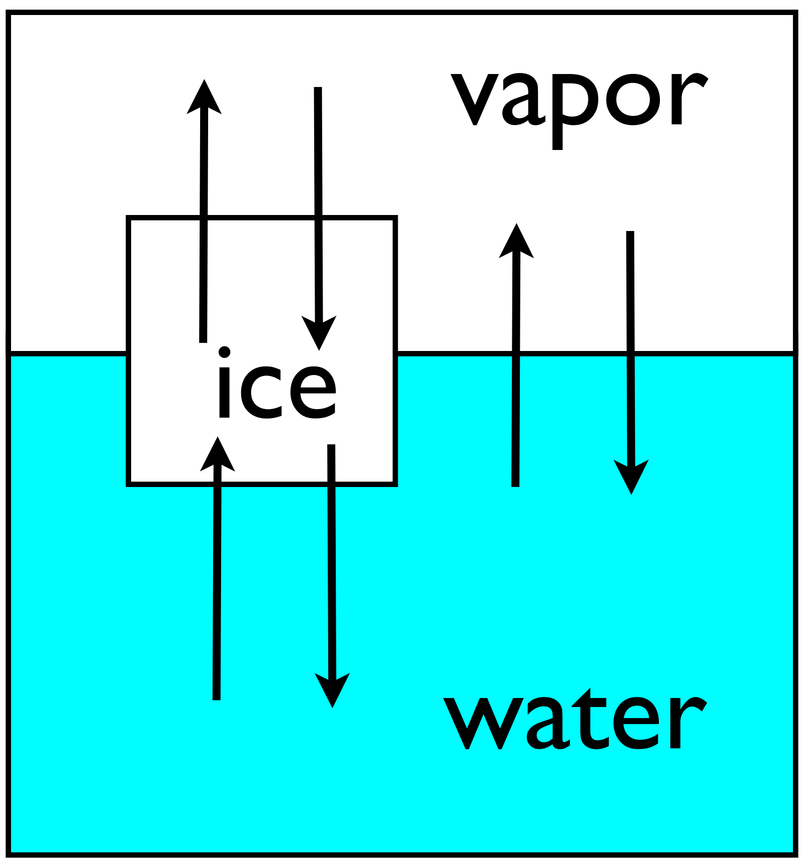
647.096 K, 22.064 MPa

臨界点

3相系

固体, 液体, 気体

例：H_2O　1成分(n=1)　max phase p=3 (S, L, G)



式の数

$\mu_g = \mu_l = \mu_s : 2$

$T_g = T_l = T_s : 2$

$P_g = P_l = P_s : 2$

計 3(p-1)

未知数

$T_g, T_l, T_s : 3$

$P_g, P_l, P_s : 3$

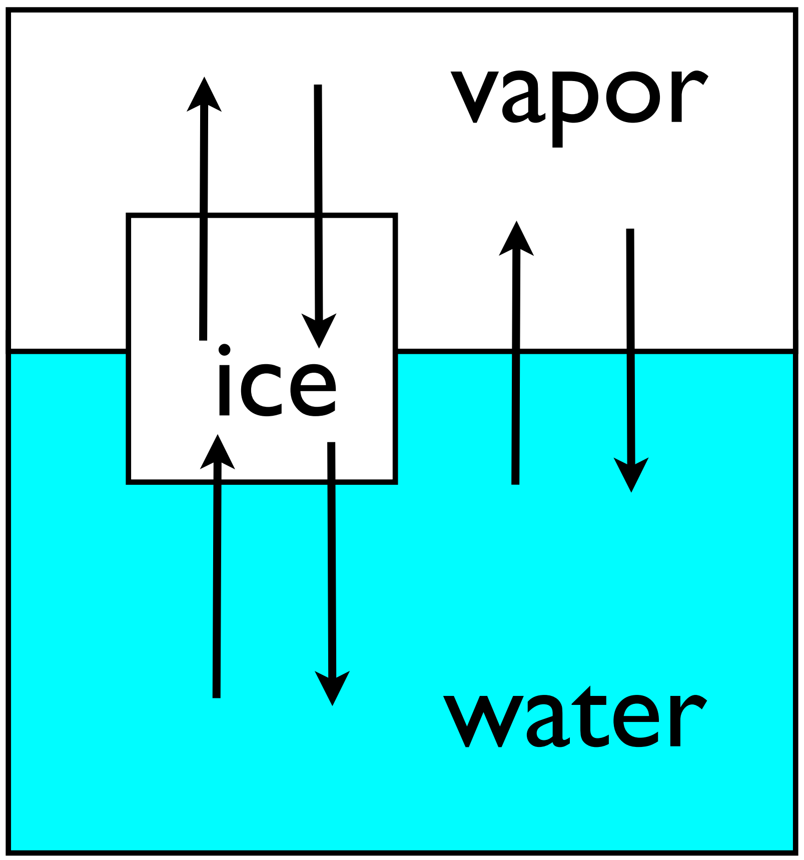
計 2p

自由度 $f = 2p\text{-}3(p\text{-}1) = 3\text{-}\ p$

３相系

固体，　液体，　気体

例：H_2O　　１成分(n=1)　　　max phase p=3 (S, L, G)



式の数

$$\mu_g = \mu_l = \mu_s : 2$$

$$T_g = T_l = T_s : 2$$

$$P_g = P_l = P_s : 2$$

計 3(p-1)

未知数

$$T_g, T_l, T_s : 3$$

$$P_g, P_l, P_s : 3$$

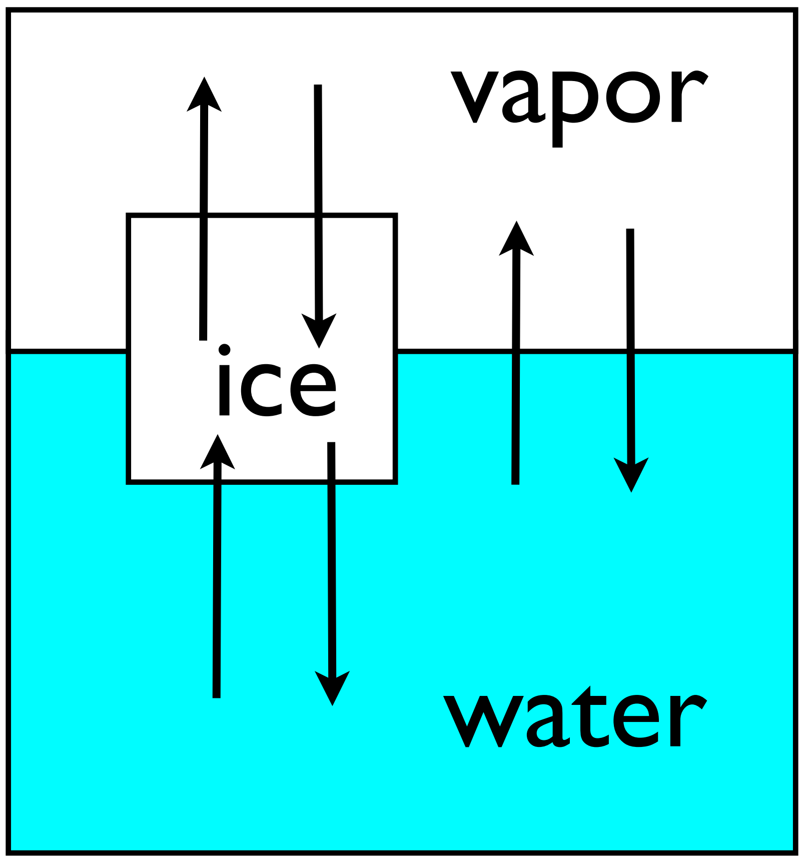
計 2p

自由度 f = 2p-3(p-1) = 3- p

3相系

固体，液体，気体

例：H_2O　1成分(n=1)　　max phase p=3 (S, L, G)



式の数

$$\mu_g = \mu_l = \mu_s : 2$$

$$T_g = T_l = T_s : 2$$

$$P_g = P_l = P_s : 2$$

計 3(p-1)

未知数

$$T_g, T_l, T_s : 3$$

$$P_g, P_l, P_s : 3$$

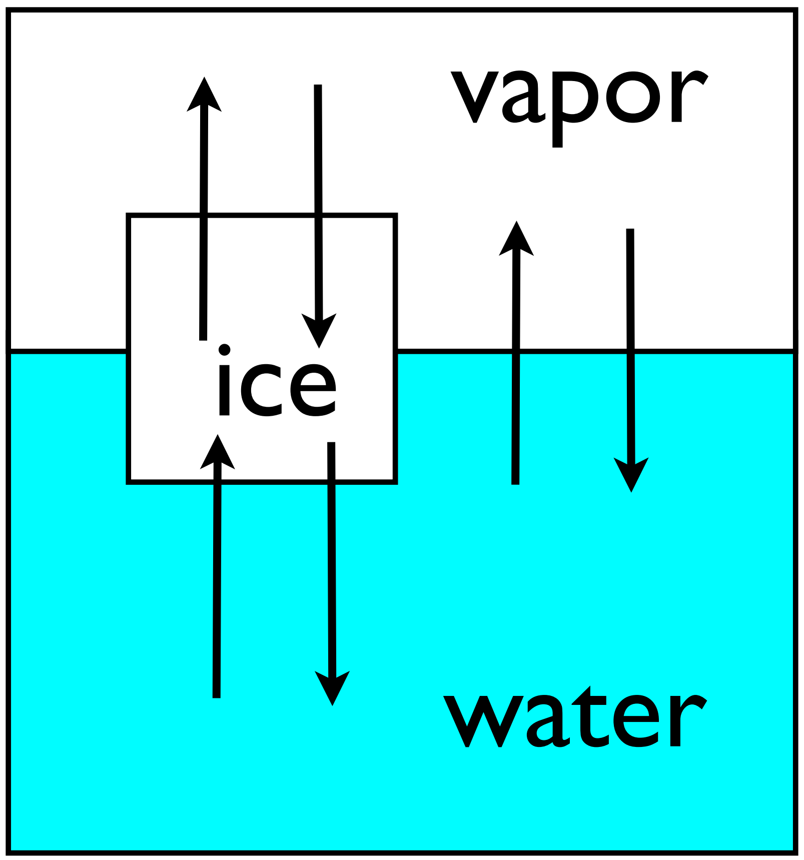
計 2p

自由度 f = 2p-3(p-1) = 3- p

３相系

固体，液体，気体

例：H_2O　１成分(n=1)　max phase p=3 (S, L, G)



式の数

$$\mu_g = \mu_l = \mu_s : 2$$

$$T_g = T_l = T_s : 2$$

$$P_g = P_l = P_s : 2$$

計 3(p-1)

未知数

$$T_g, T_l, T_s : 3$$

$$P_g, P_l, P_s : 3$$

計 2p

自由度 f = 2p-3(p-1) = 3- p

単相：$p = 1$, 自由度 $f = 3\text{-}p = 2$ →面で存在

二相共存：$p = 2$, 自由度 $f = 3\text{-}p = 1$ →線で存在

三相共存：$p = 3$, 自由度 $f = 3\text{-}p = 0$ →点で存在

単相：$p = 1$, 自由度 $f = 3\text{-}p = 2$ →面で存在

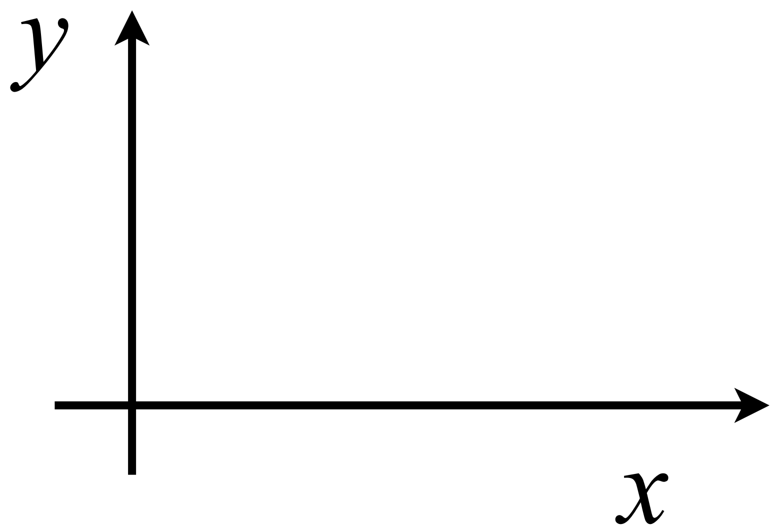
二相共存： $p = 2$, 自由度 $f = 3\text{-}p = 1$ →線で存在

三相共存： $p = 3$, 自由度 $f = 3\text{-}p = 0$ →点で存在

単相：$p = 1$, 自由度 $f = 3\text{-}p = 2$ →面で存在

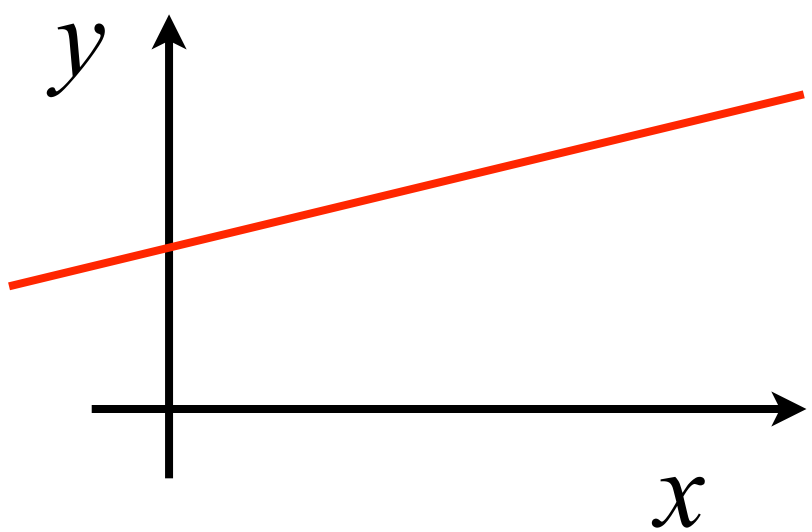
二相共存： $p = 2$, 自由度 $f = 3\text{-}p = 1$ →線で存在

三相共存： $p = 3$, 自由度 $f = 3\text{-}p = 0$ →点で存在



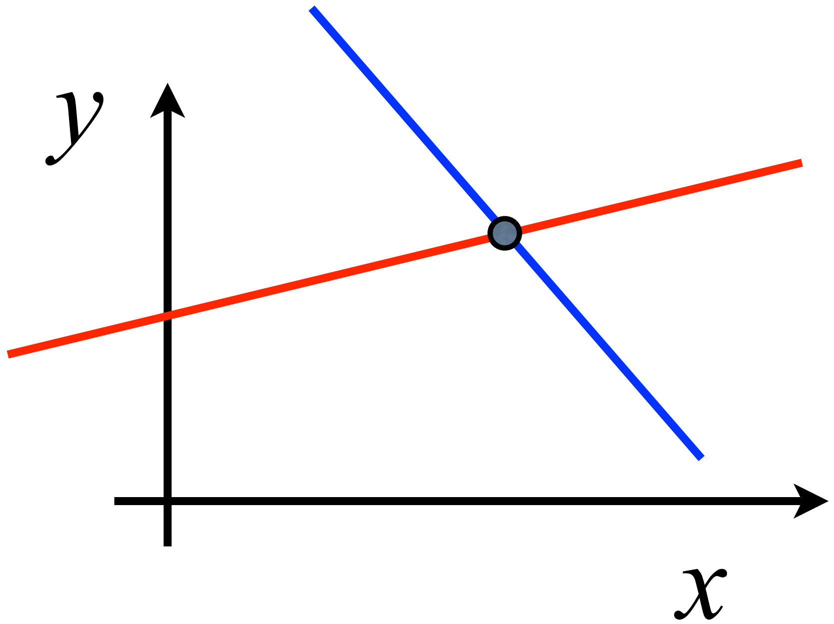
未知数2： x,y

式0:なし　$f = 2$　平面内（面）



未知数2： x,y

式1: $y = a\,x + b$　$f = 1$　（線）



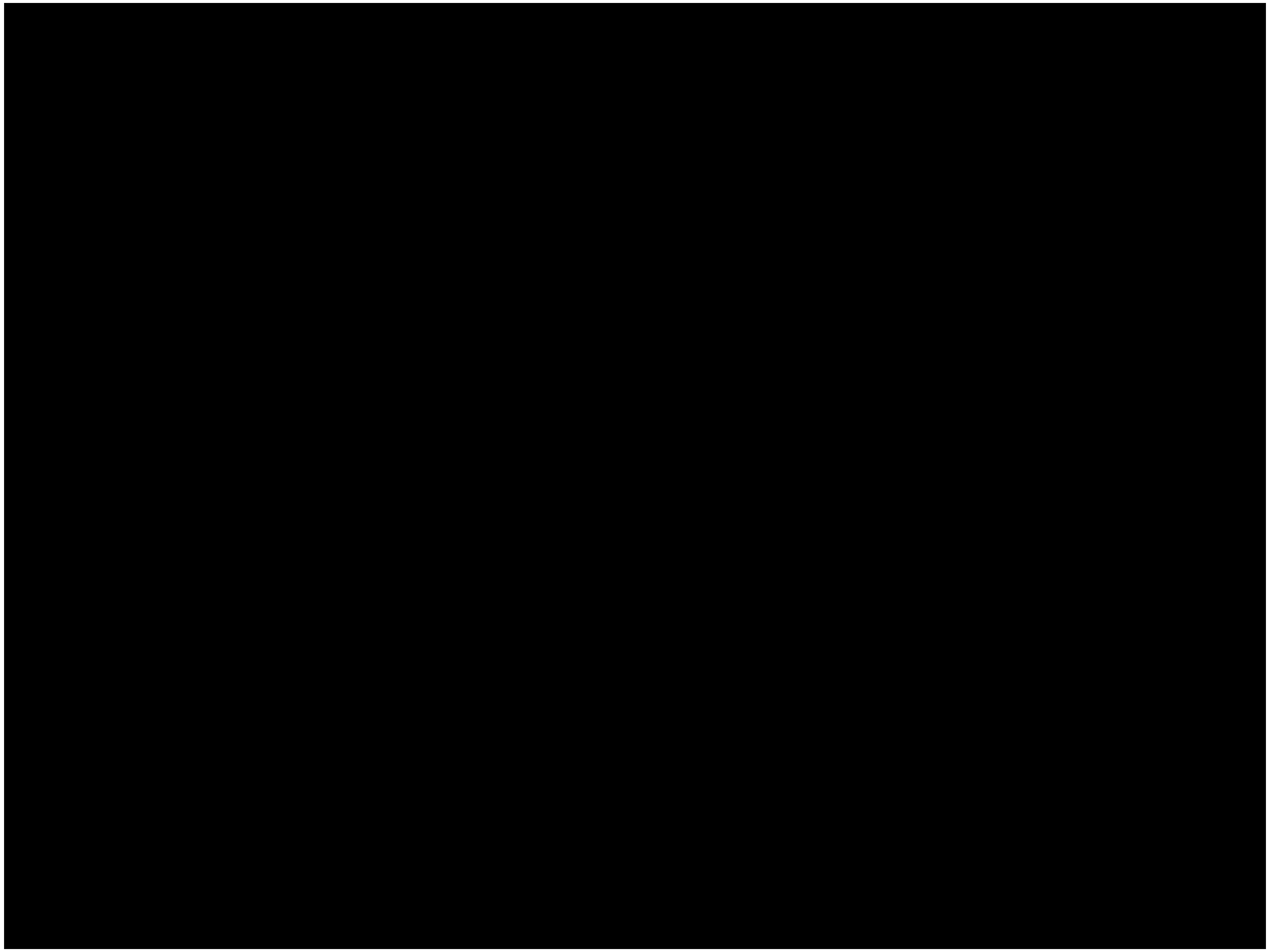
未知数2： x,y

式2: $y = a\,x + b,\ y = c\,x + d$

$f = 0$　（点）

https://www.youtube.com/watch?v=xYKT1MWNr4w

二酸化炭素超臨界流体ビデオ(音声有り）



http://riodb.ibase.aist.go.jp/SCF/sdb/scf/lecture/lecvideo/lecvideo.html

1成分:相律

unknown: $(T, P) \times$ (number of phases: p) = 2p
未知数

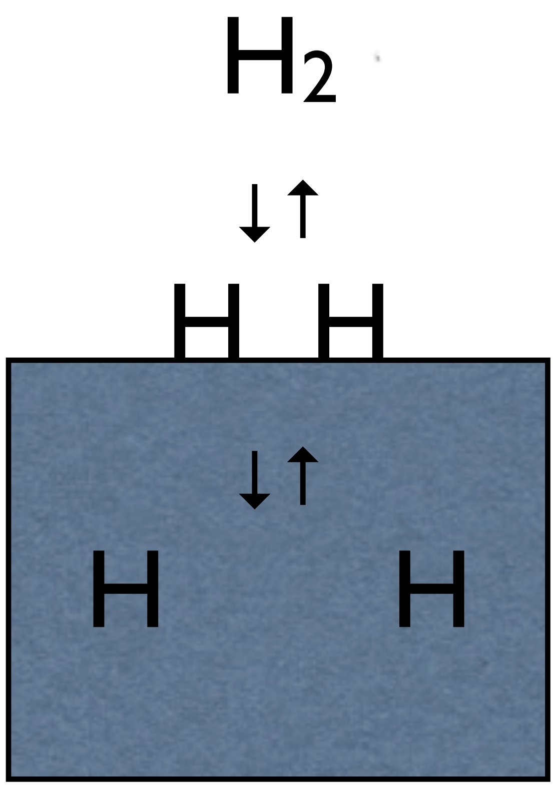
number of equations:
式の数 $(\mu, T, P) \times$ (number of phases - 1) = 3 (p-1)

$$f = 2p - 3(p-1) = 3 - p$$

$$p = 1, f = 3 - 1 = 2 \rightarrow \text{plane}$$
$$p = 2, f = 3 - 2 = 1 \rightarrow \text{line}$$
$$p = 3, f = 3 - 3 = 0 \rightarrow \text{point}$$

Zr-H：２成分

気相との水素化物相との平衡



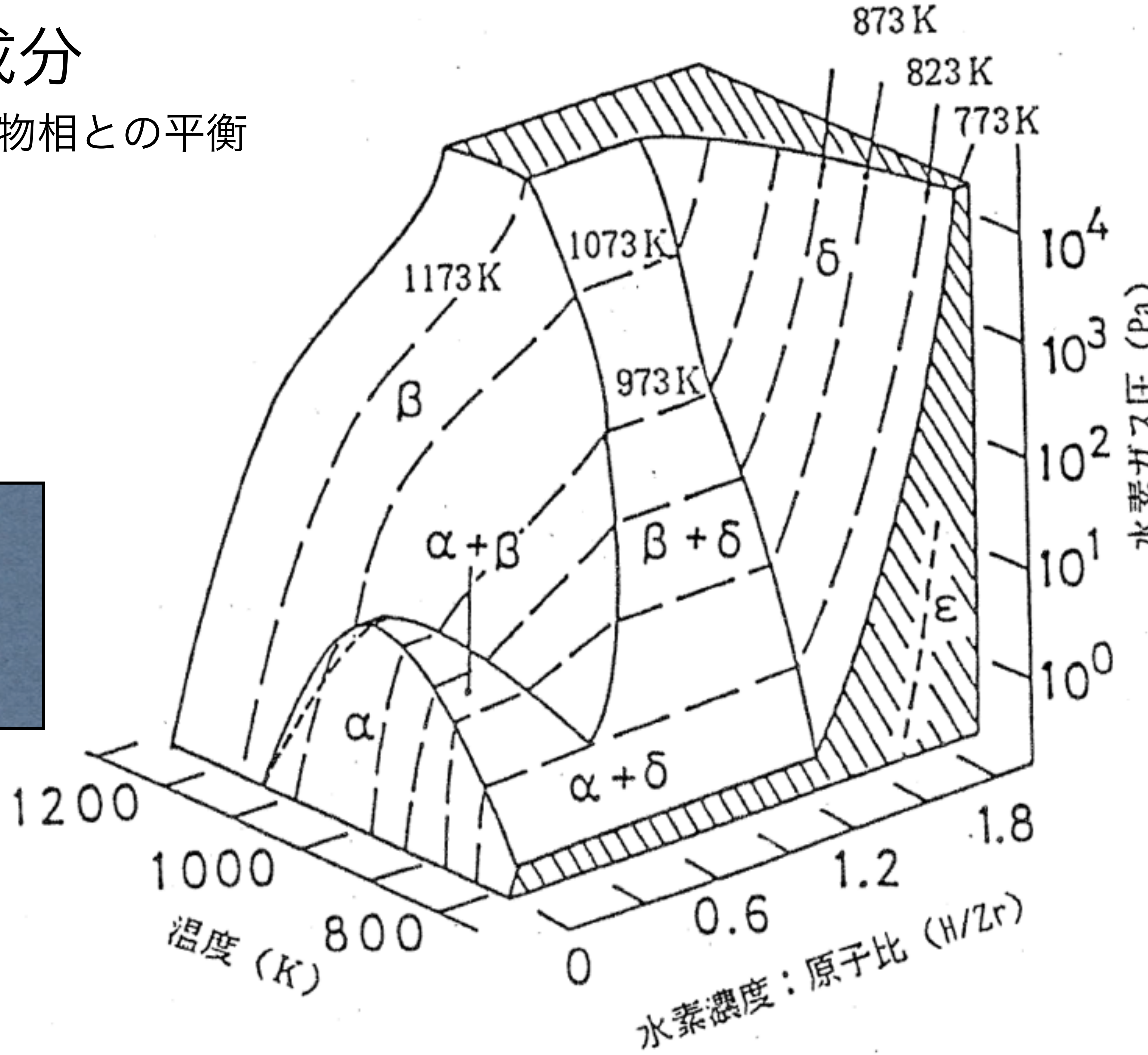


図 3－8 水素－ジルコニウム系の３次元相図

未知数：　$2[(T, P)] \times$相の数$p = 2p$

$+$

組成X [n(成分)-1]×相の数$p = (n\text{-}1)p$

例：１成分で組成は意味がない

２成分では片方の組成を決めれば他方が決まる。

式の数:　$[(T, P)]$: $2 \times (p - 1) = 2(p - 1)$

$+$

$[\mu]$　: $n \times (p - 1) = n(p - 1)$

Gibbsの相律

Gibbs' phase rule

$$f = 2p + (n-1)p - [2(p-1) + n(p-1)]$$
$$= n + 2 - p$$

未知数：　$2[(T, P)] \times$相の数$p = 2p$

$+$

組成$X\ [n$(成分)-1$] \times$相の数$p = (n\text{-}1)p$

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組成 $X\,[n$(成分)-1$] \times$ 相の数 $p = (n\text{-}1)p$

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＋

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＋

$[\mu]$　　: $n\times(p - 1) = n(p - 1)$

Gibbsの相律

Gibbs' phase rule

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未知数：　$2[(T, P)] \times$ 相の数 $p = 2p$

＋

組成 X $[n$(成分)-1$] \times$ 相の数 $p = (n\text{-}1)p$

例：１成分で組成は意味がない

２成分では片方の組成を決めれば他方が決まる。

式の数:　$[(T, P)]$: $2 \times (p - 1) = 2(p - 1)$

＋

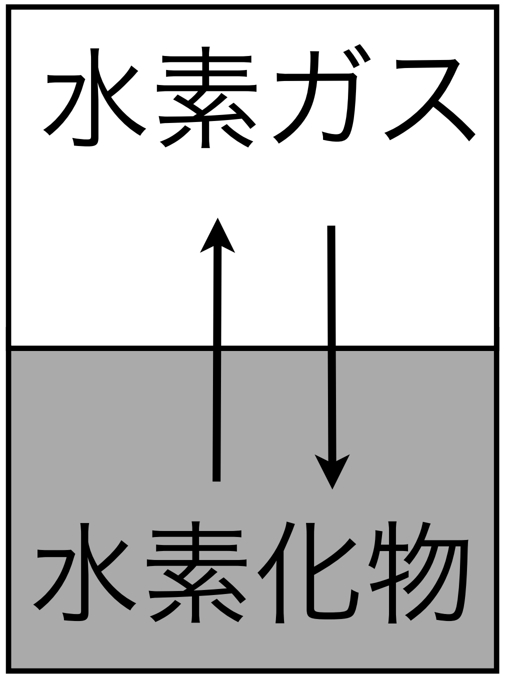
$[\mu]$　　: $n \times (p - 1) = n(p - 1)$

Gibbsの相律

Gibbs' phase rule

$$
\begin{aligned}
f &= 2p + (n-1)p - [2(p-1) + n(p-1)] \\
&= n + 2 - p
\end{aligned}
$$

水素ガス相を忘れないこと



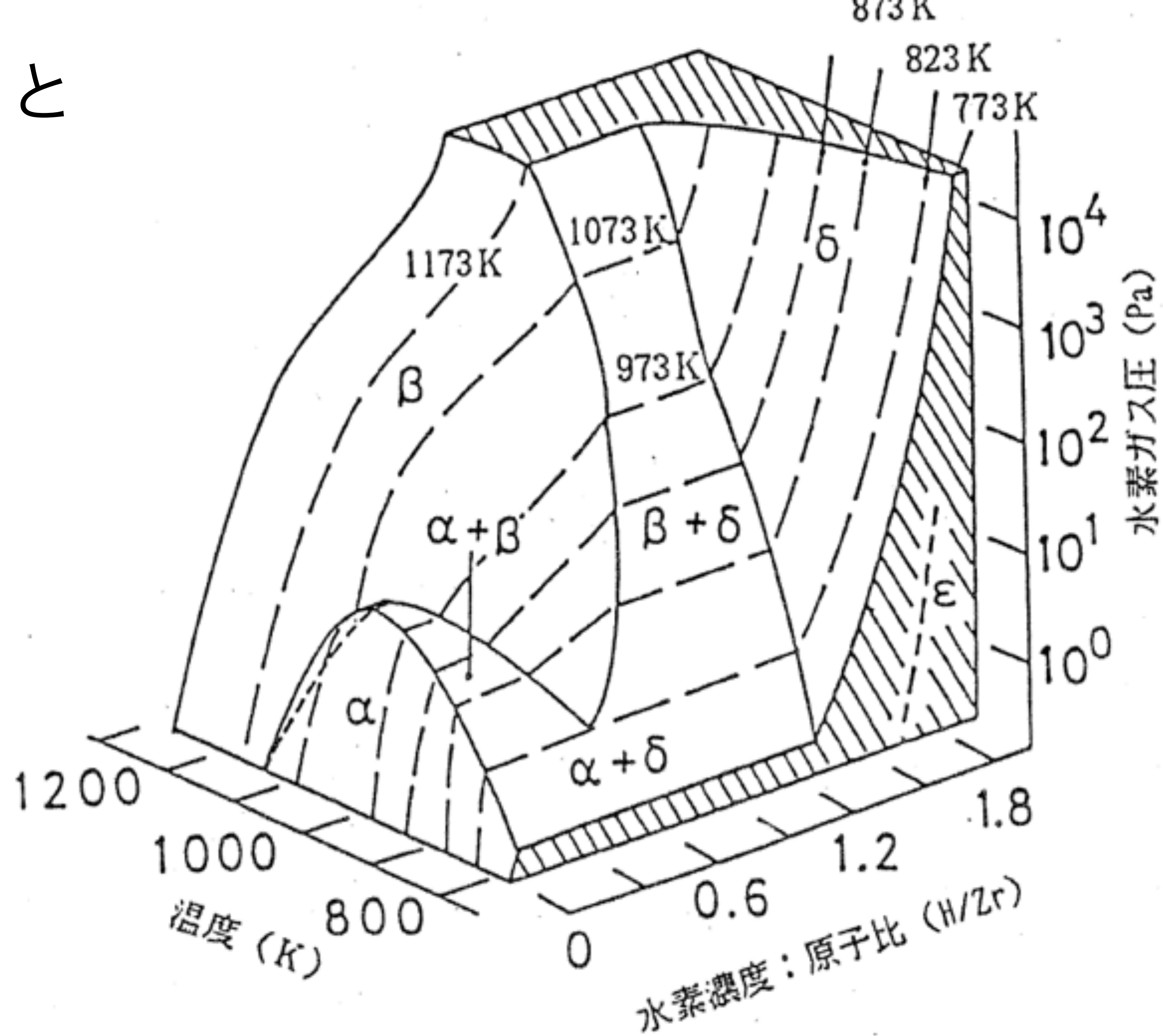


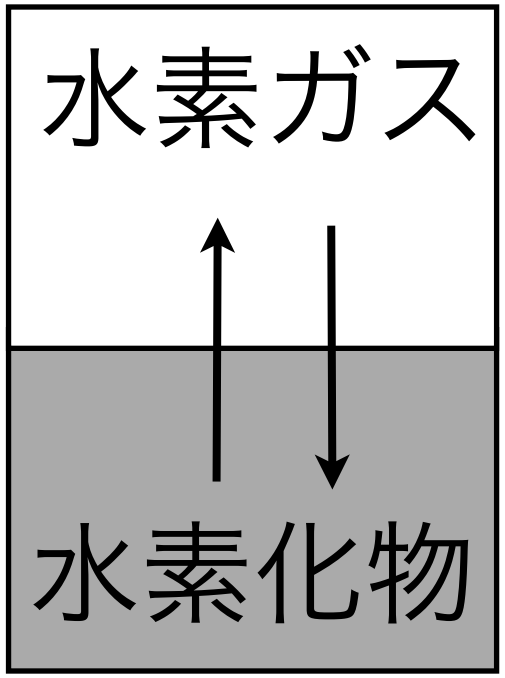
図 3−8 水素−ジルコニウム系の3次元相図

$$n = 2, p = 2, f = 2$$

$$n = 2, p = 3, f = 1$$

$$n = 2, p = 4, f = 0$$

水素ガス相を忘れないこと



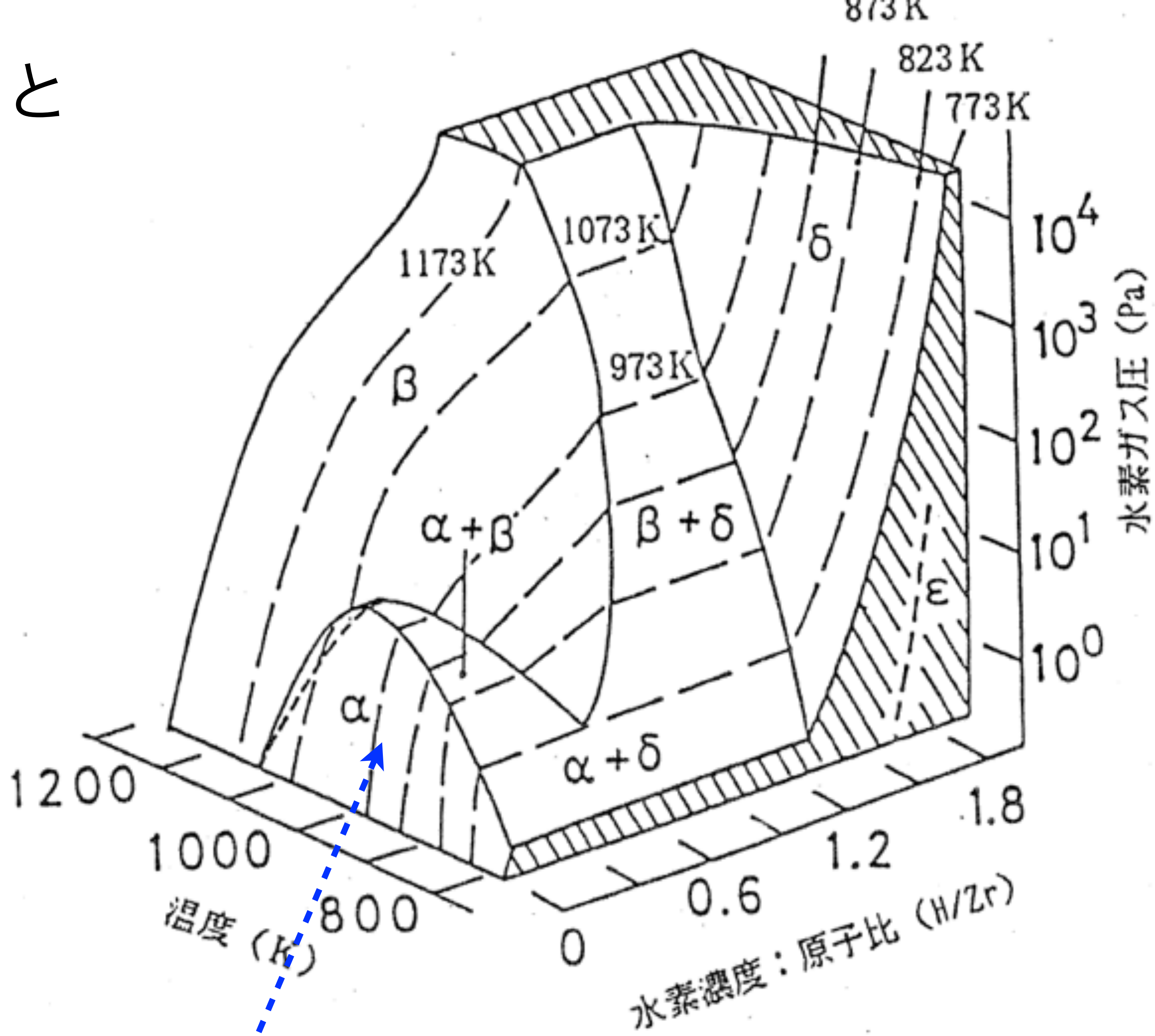


図 3−8 水素−ジルコニウム系の3次元相図

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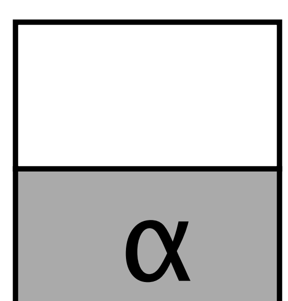
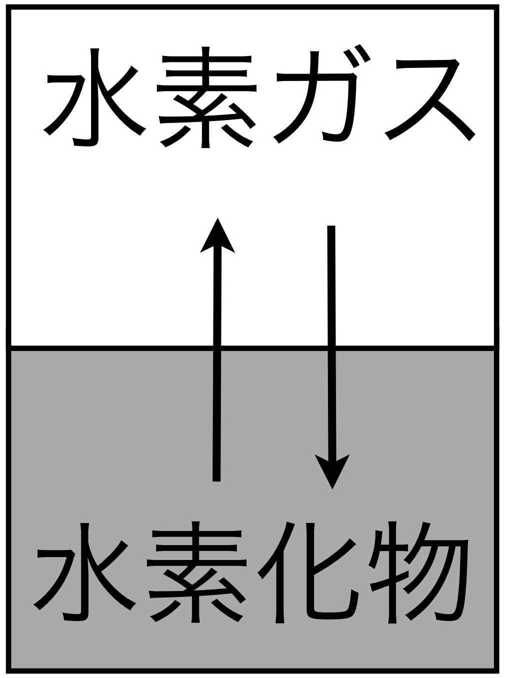


水素ガス相を忘れないこと



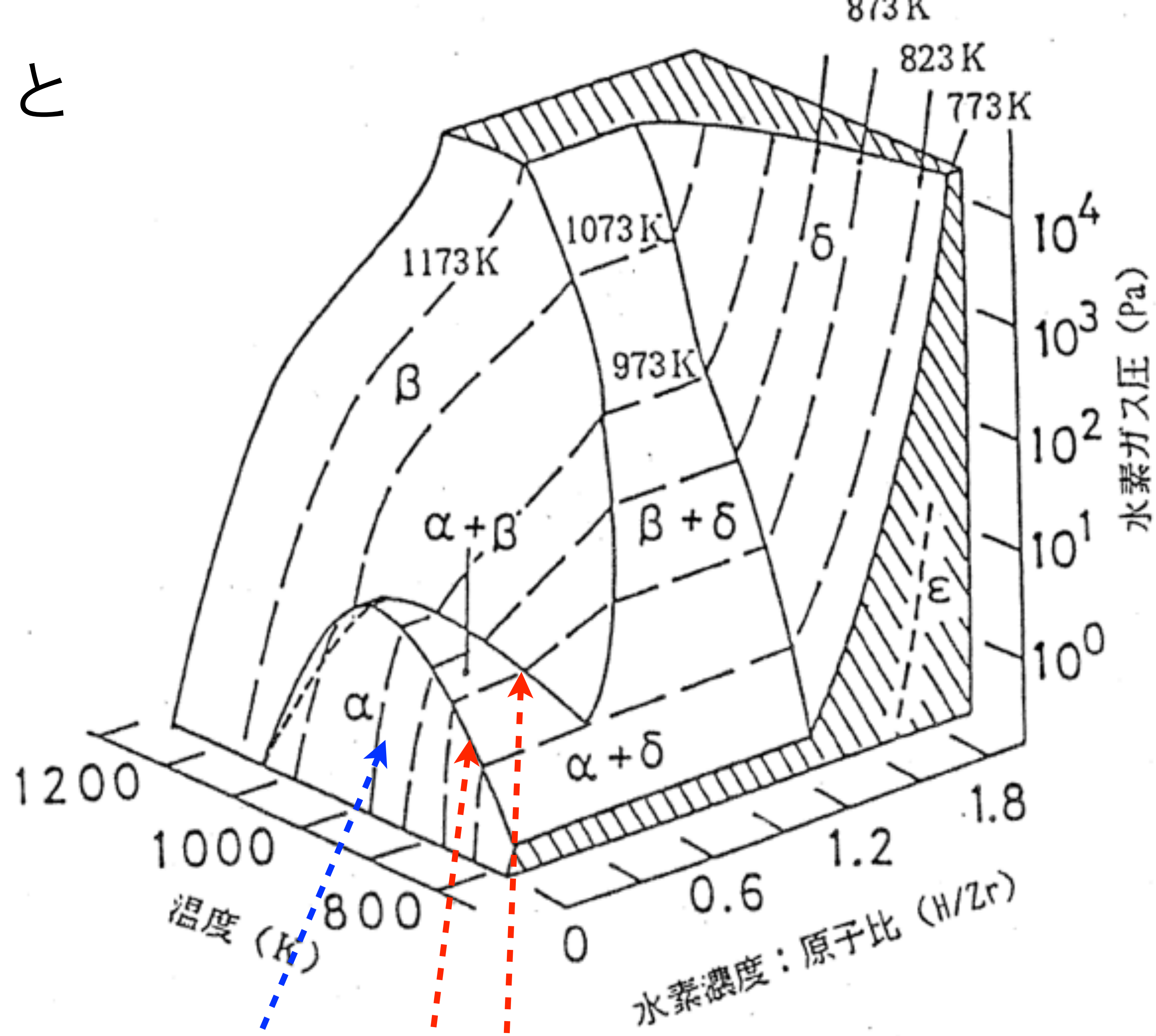
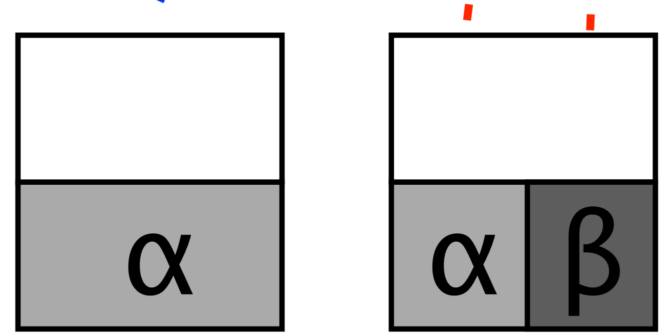


図 3－8 水素－ジルコニウム系の３次元相図

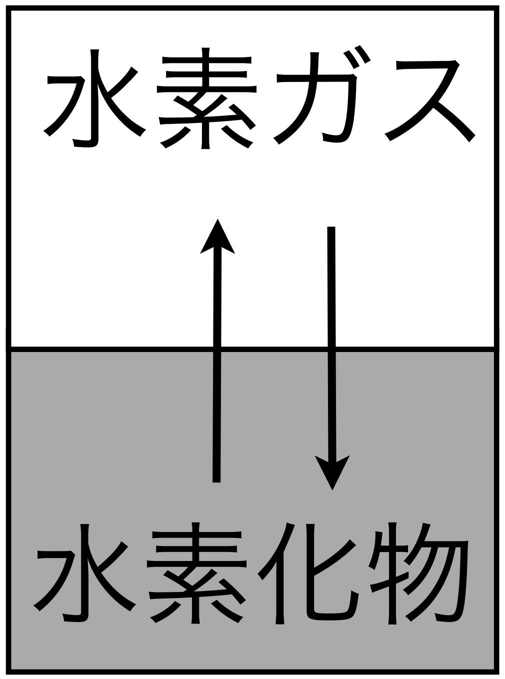
$$n = 2, p = 2, f = 2$$

$$n = 2, p = 3, f = 1$$

$$n = 2, p = 4, f = 0$$



水素ガス相を忘れないこと



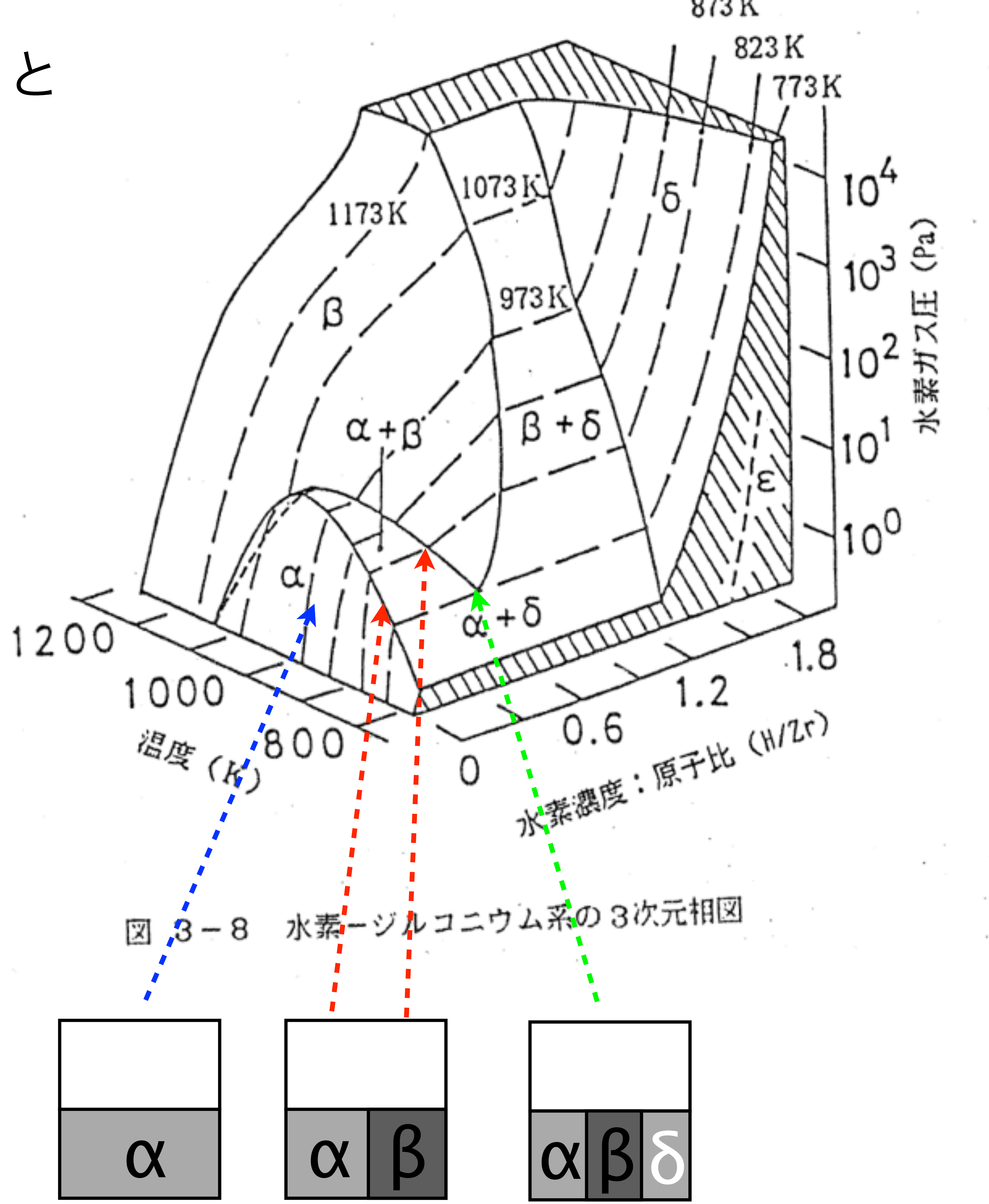


図 3−8 水素−ジルコニウム系の３次元相図

$$n = 2, p = 2, f = 2$$

$$n = 2, p = 3, f = 1$$

$$n = 2, p = 4, f = 0$$

理想気体状態方程式

分子間に相互作用なし

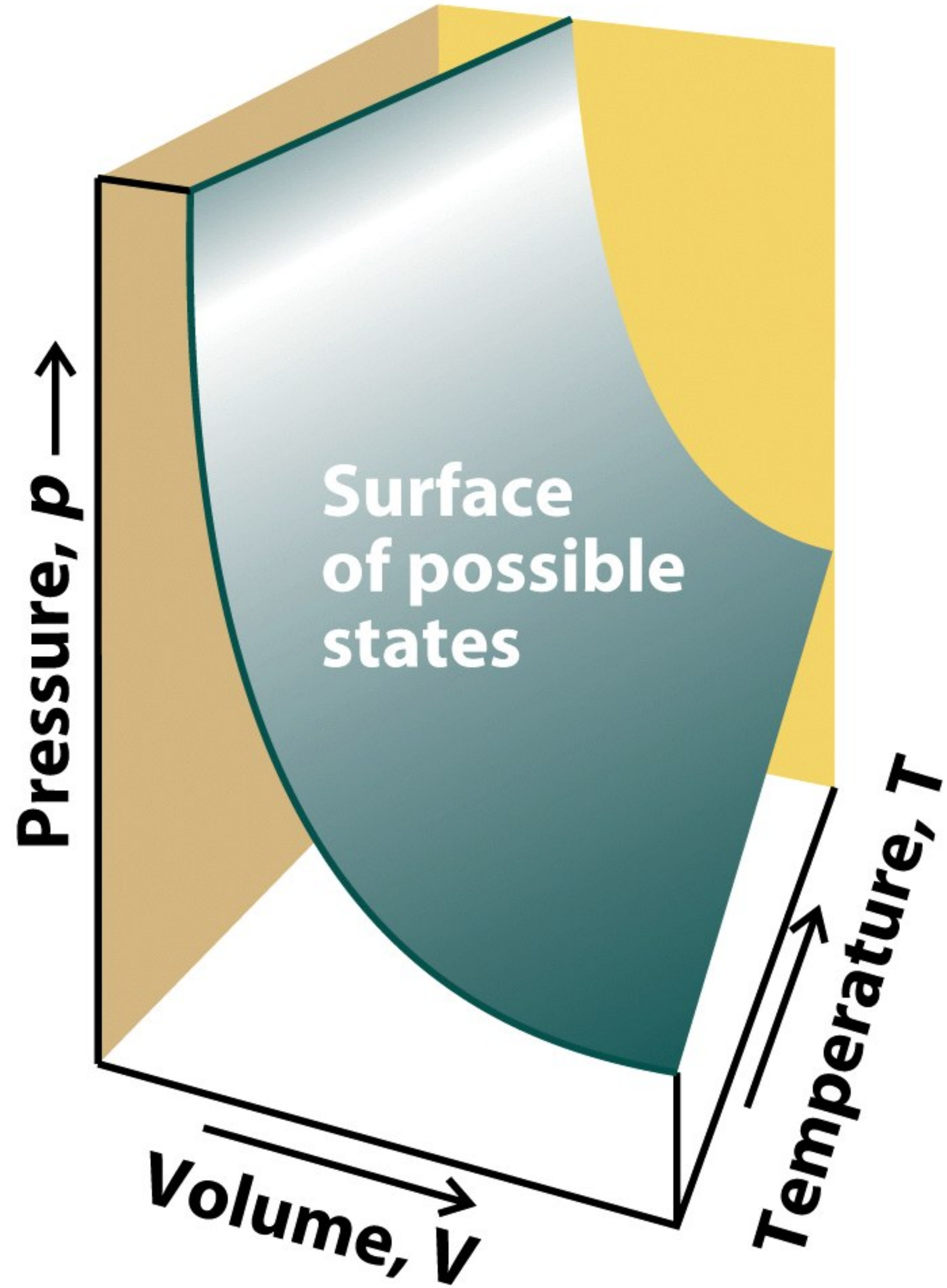


Figure 1-8
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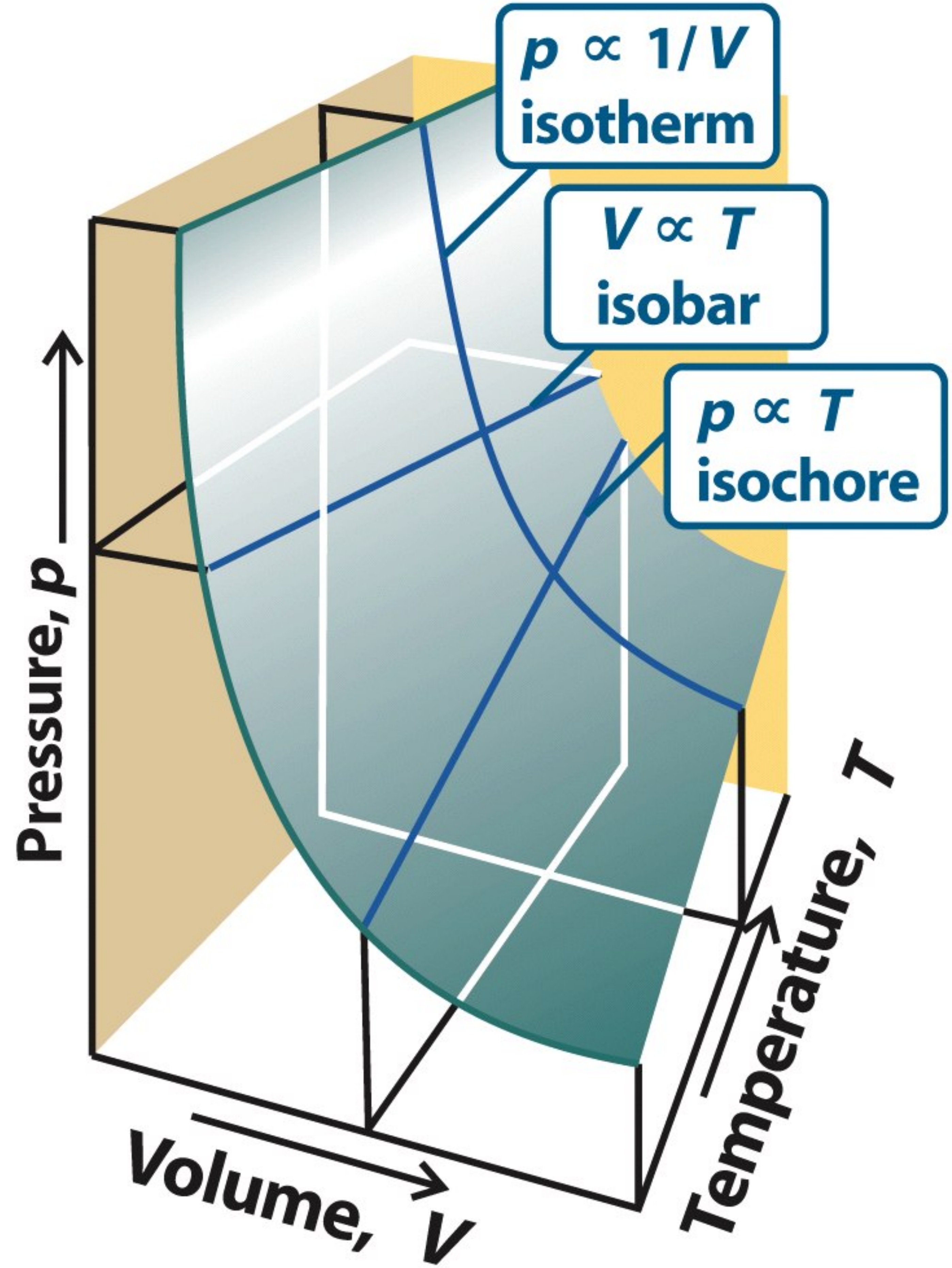

Figure 1-9

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van der Waals 状態方程式

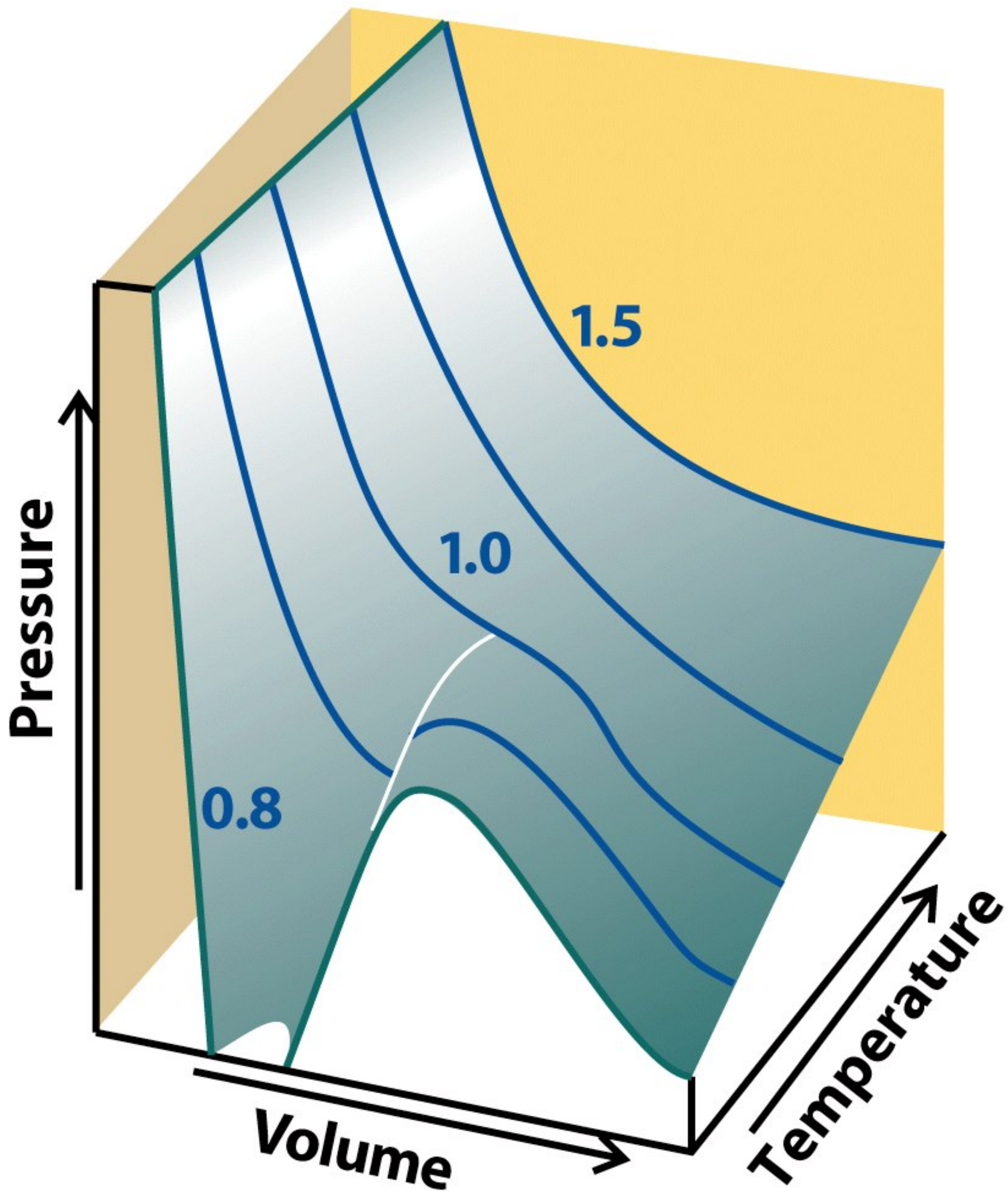

Figure 1-17
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分子間に引力

低温，体積小で

液体に

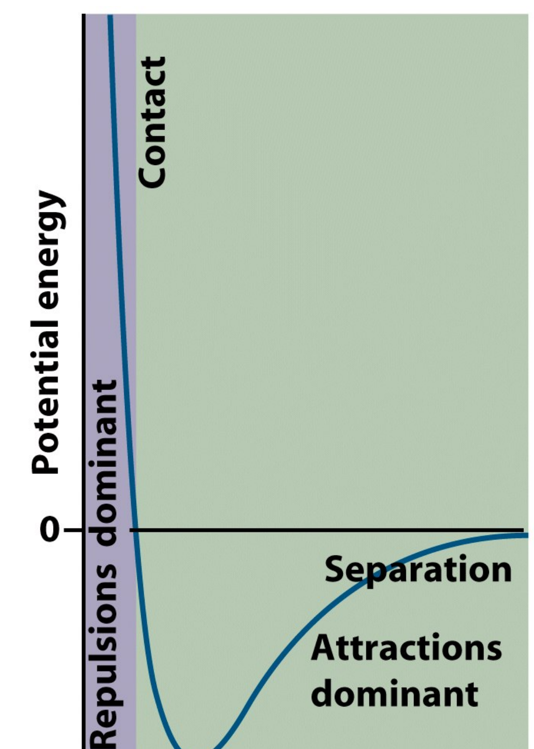

Figure 1-13
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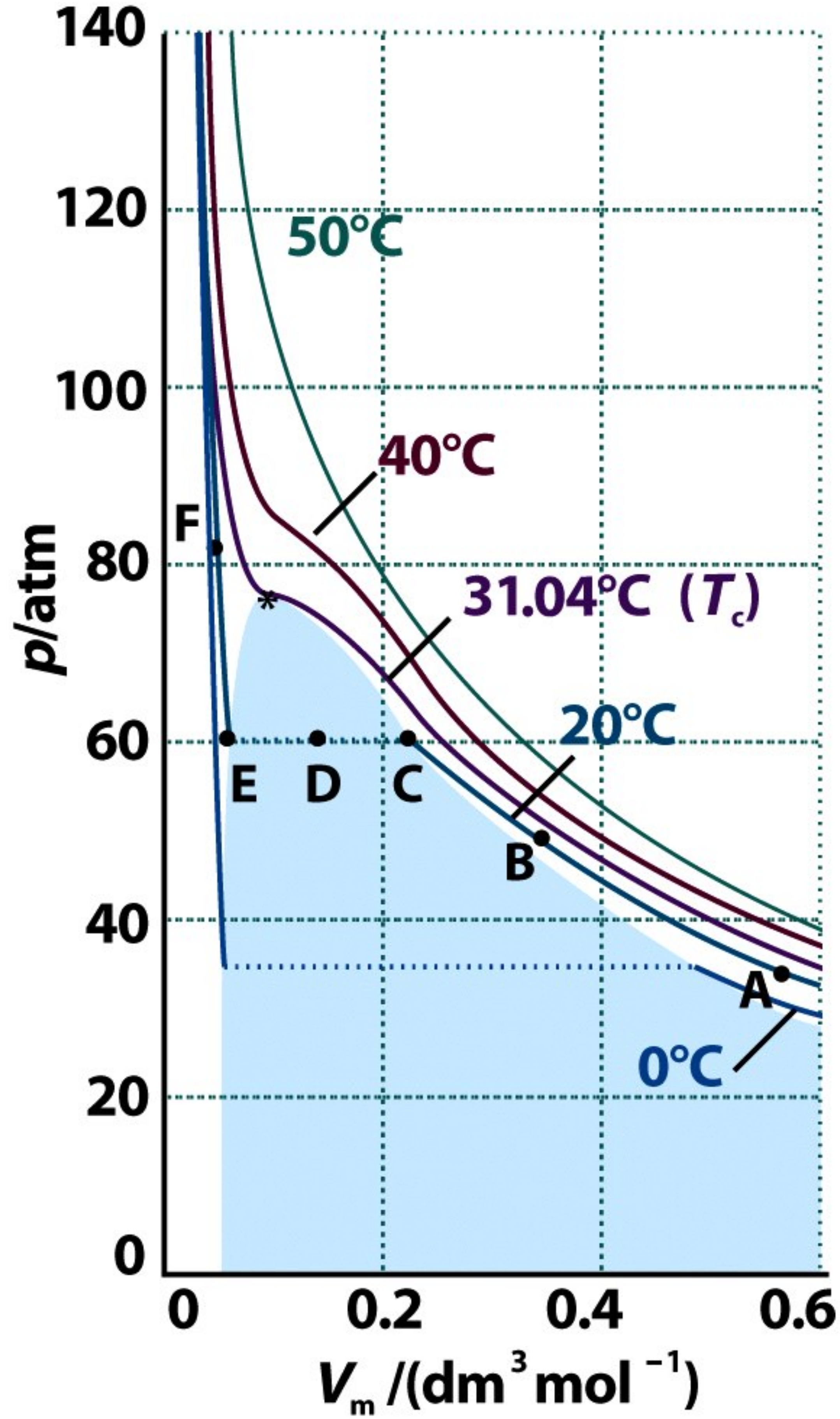

Figure 1-15
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CO_2 気液相図

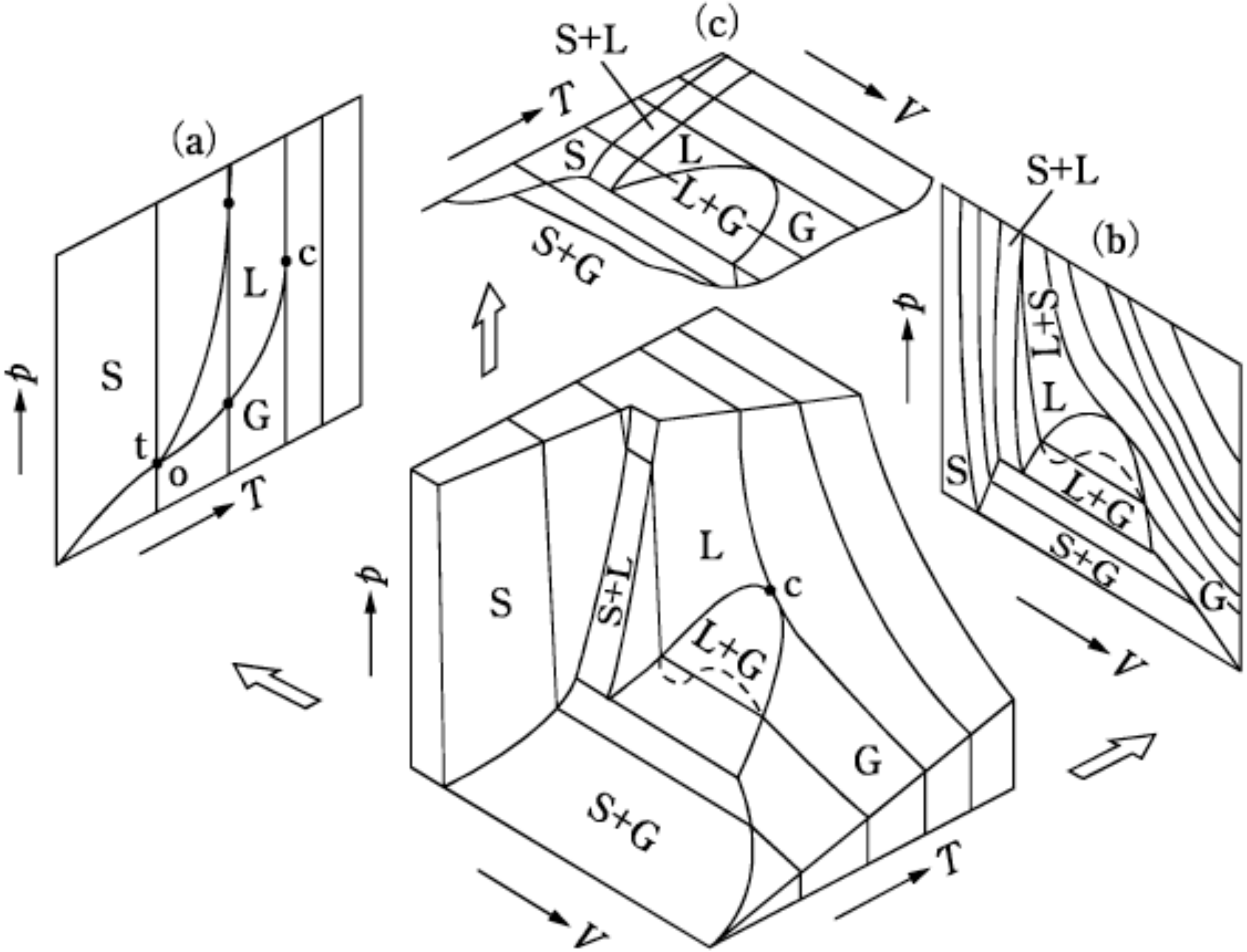


図 9.1　一成分系の p-V-T 関係

(a)　p-T 平面への投影図
(b)　p-V 平面への投影図
(c)　T-V 平面への投影図
S：固相，L：液相，G：気相.

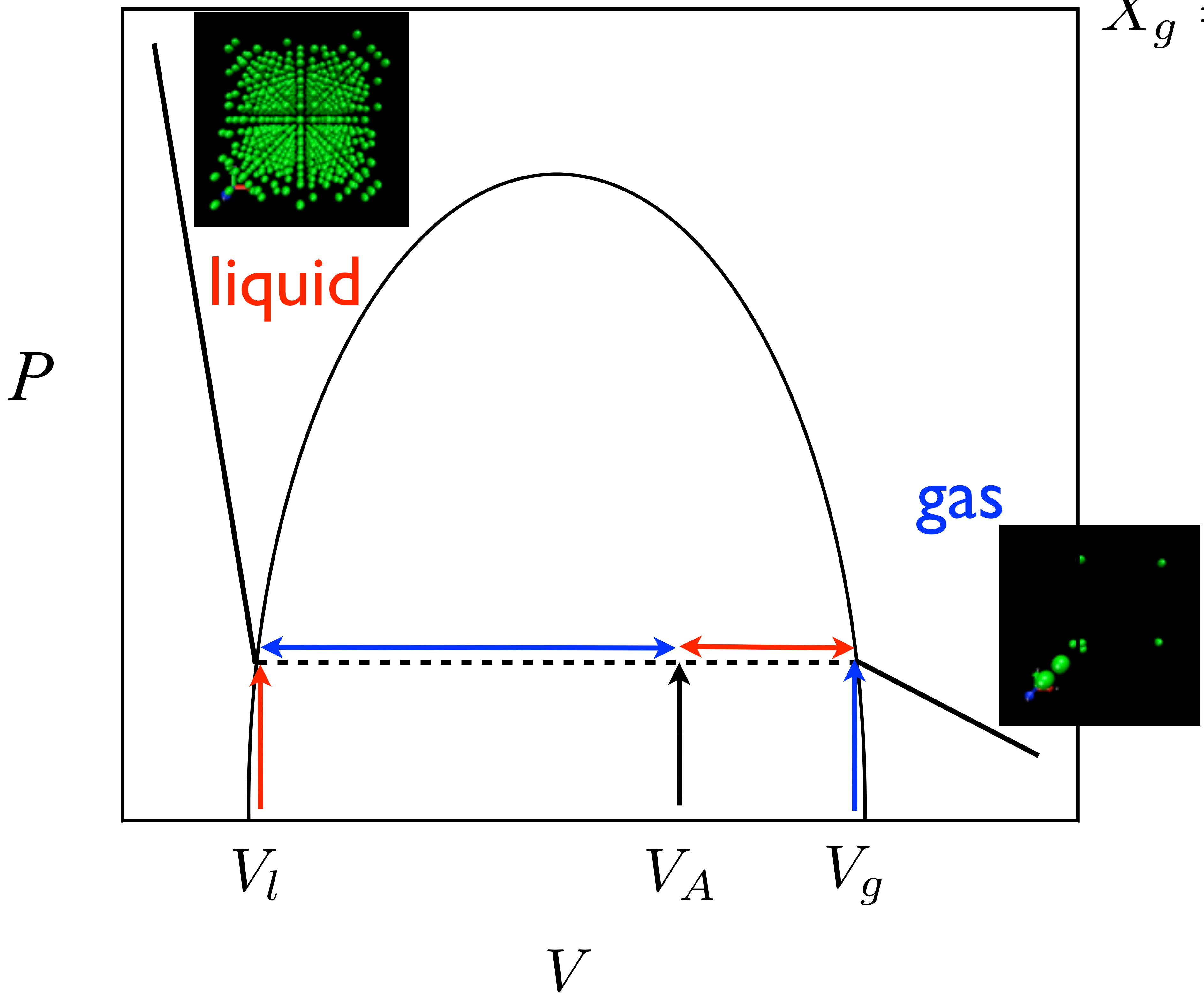
$$1 = X_l + X_g$$

$$V_A = V_l X_l + V_g X_g$$

てこの原理

$$X_l = \frac{V_g - V_A}{V_g - V_l}$$

$$X_g = \frac{V_A - V_l}{V_g - V_l}$$



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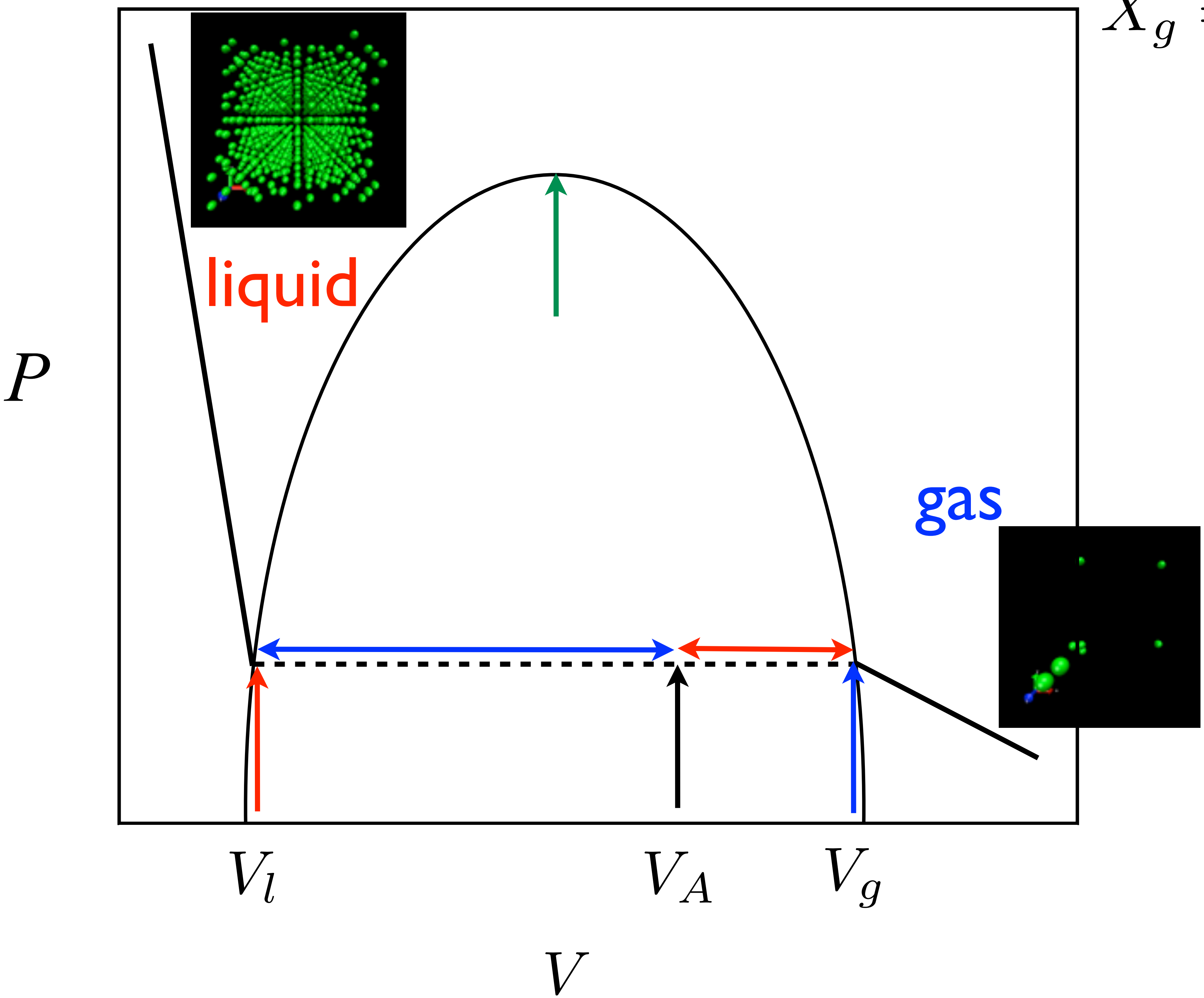


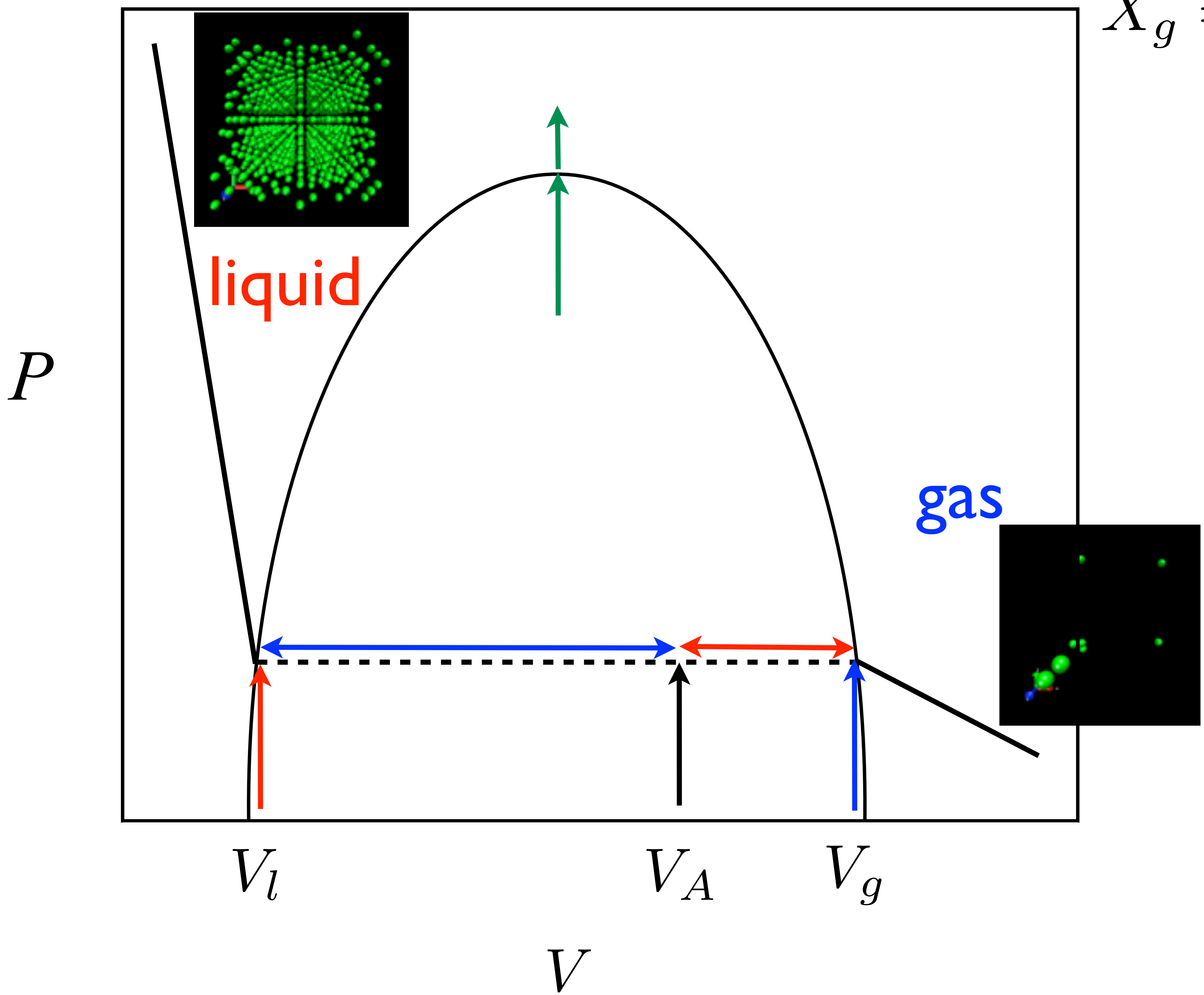
$$1 = X_l + X_g$$

$$V_A = V_l X_l + V_g X_g$$

てこの原理

$$X_l = \frac{V_g - V_A}{V_g - V_l}$$

$$X_g = \frac{V_A - V_l}{V_g - V_l}$$



同次関数についてのEulerの定理

示量変数　extensive　V, S, N

系を倍の大きさにしたら倍になるもの

示強変数　intensive　P, T, μ

系を倍の大きさにしても変わらないもの

$$G(T,P):\ dG = -SdT + VdP$$

$$A(T,V):\ dA = -SdT + PdV$$

示量変数と示強変数は対になる

同次関数についてのEulerの定理

示量変数　**extensive**　V, S, N

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$$A(T,V):\ dA = -SdT + PdV$$

示量変数と示強変数は対になる

$$f(\lambda x_1, \lambda x_2, ...) = \lambda f(x_1, x_2, ...)$$

一次の同次式

x_1,x_2は示量変数

$$f(\lambda x_1, \lambda x_2, ...) = \lambda f(x_1, x_2, ...)$$

$$u_i \equiv \lambda x_i$$

$$f(u_1, u_2, ...) = \lambda f(x_1, x_2, ...)$$

$$\left[\frac{\partial f(u_1, u_2, ...)}{\partial \lambda}\right]_{x_1, x_2, ...} = f(x_1, x_2, ...)$$

上式をλで微分

$$\left[\frac{\partial f(u_1, u_2, ...)}{\partial \lambda}\right]_{x_1, x_2, ...} = \sum_i \left[\frac{\partial f(u_1, u_2, ...)}{\partial u_i}\right]_{u_j(\neq u_i)} \left(\frac{\partial u_i}{\partial \lambda}\right)_{u_j(\neq u_i)}$$

$$= \sum_i \left[\frac{\partial f(u_1, u_2, ...)}{\partial u_i}\right]_{u_j(\neq u_i)} x_i$$

$$\lambda = 1$$

$$\sum_i \left[\frac{\partial f(x_1, x_2, ...)}{\partial x_i}\right]_{x_j(\neq x_i)} x_i = f(x_1, x_2, ...)$$

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$$\lambda = 1$$

$$\sum_i \left[\frac{\partial f(x_1, x_2, ...)}{\partial x_i}\right]_{x_j(\neq x_i)} x_i = f(x_1, x_2, ...)$$

$$G(T, P, \lambda n_A, \lambda n_B) = \lambda G(T, P, n_A, n_B)$$

$$\left(\frac{\partial G}{\partial n_A}\right)_{T,P,n_B} n_A + \left(\frac{\partial G}{\partial n_B}\right)_{T,P,n_A} n_B = G(T, P, n_A, n_B)$$

$$G = n_A \mu_A + n_B \mu_B$$

$$G(T, P, \lambda n_A, \lambda n_B) = \lambda G(T, P, n_A, n_B)$$

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$$G = n_A\mu_A + n_B\mu_B$$

$$A(T,\lambda V,\lambda n_A,\lambda n_B) = \lambda A(T,V,n_A,n_B)$$

$$\left(\frac{\partial A}{\partial n_A}\right)_{T,V,n_B} n_A + \left(\frac{\partial A}{\partial n_B}\right)_{T,V,n_A} n_B + \left(\frac{\partial A}{\partial V}\right)_{T,n_A,N_B} V = A(T,V,n_A,n_B)$$

$$A(T,V,n_A,n_B) = \mu'_A n_A + \mu'_B n_B - PV$$

$$G = A + PV$$

$$\mu_A = \mu'_A, \quad \mu_B = \mu'_B$$

$$A(T,V,n_A,n_B) = \mu_A n_A + \mu_B n_B - PV = \mu_A n_A + \mu_B n_B + V\left(\frac{\partial A}{\partial V}\right)_{T,n_\mathrm{A},n_\mathrm{B}}$$

$$G(T,P,\lambda n_A,\lambda n_B)=\lambda G(T,P,n_A,n_B)$$

$$\left(\frac{\partial G}{\partial n_A}\right)_{T,P,n_B} n_A+\left(\frac{\partial G}{\partial n_B}\right)_{T,P,n_A} n_B=G(T,P,n_A,n_B)$$

$$G=n_A\mu_A+n_B\mu_B$$

$$A(T,\lambda V,\lambda n_A,\lambda n_B)=\lambda A(T,V,n_A,n_B)$$

$$\left(\frac{\partial A}{\partial n_A}\right)_{T,V,n_B} n_A+\left(\frac{\partial A}{\partial n_B}\right)_{T,V,n_A} n_B+\left(\frac{\partial A}{\partial V}\right)_{T,n_A,N_B} V=A(T,V,n_A,n_B)$$

$$A(T,V,n_A,n_B)=\mu'_A n_A+\mu'_B n_B-PV$$

$$G=A+PV$$

$$\mu_A=\mu'_A,\quad \mu_B=\mu'_B$$

$$A(T,V,n_A,n_B)=\mu_A n_A+\mu_B n_B-PV=\mu_A n_A+\mu_B n_B+V\left(\frac{\partial A}{\partial V}\right)_{T,n_\mathrm{A},n_\mathrm{B}}$$

$$G(T,P,\lambda n_A,\lambda n_B) = \lambda G(T,P,n_A,n_B)$$

$$\left(\frac{\partial G}{\partial n_A}\right)_{T,P,n_B} n_A + \left(\frac{\partial G}{\partial n_B}\right)_{T,P,n_A} n_B = G(T,P,n_A,n_B)$$

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$$\left(\frac{\partial A}{\partial n_A}\right)_{T,V,n_B} n_A + \left(\frac{\partial A}{\partial n_B}\right)_{T,V,n_A} n_B + \left(\frac{\partial A}{\partial V}\right)_{T,n_A,N_B} V = A(T,V,n_A,n_B)$$

$$A(T,V,n_A,n_B) = \mu'_A n_A + \mu'_B n_B - PV$$

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$$A(T,V,n_A,n_B) = \mu'_A n_A + \mu'_B n_B - PV$$

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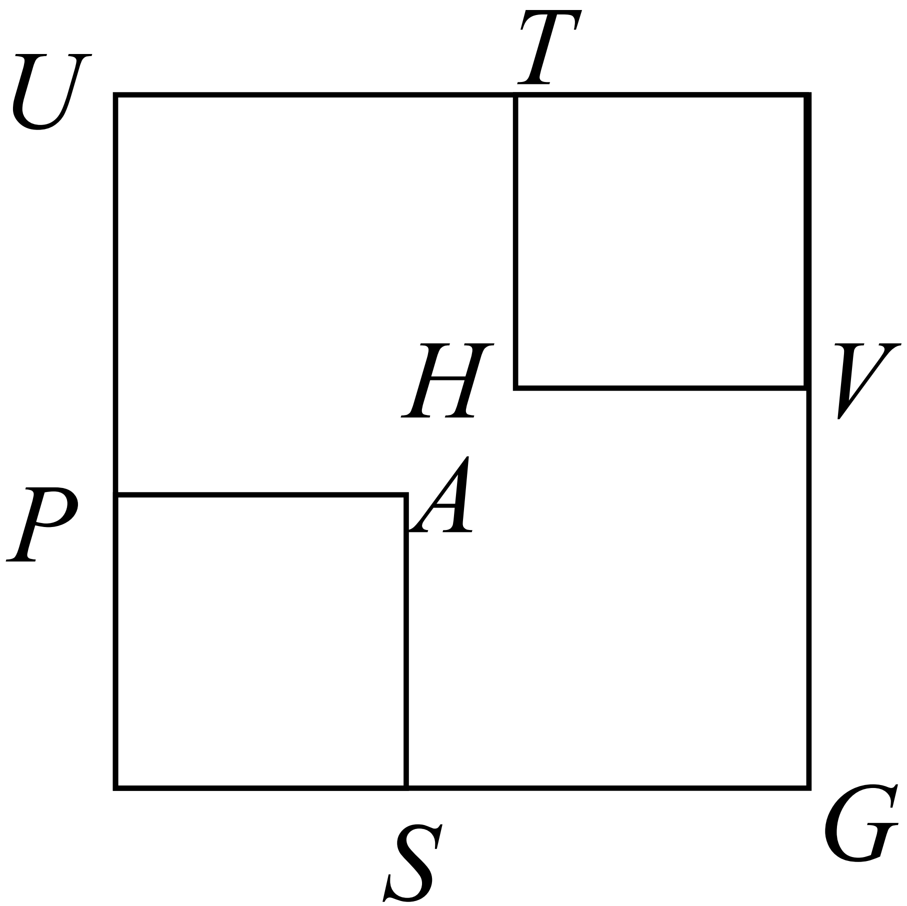
$$A(T,V,n_A,n_B) = \mu_A n_A + \mu_B n_B - PV = \mu_A n_A + \mu_B n_B + V\left(\frac{\partial A}{\partial V}\right)_{T,n_\mathrm{A},n_\mathrm{B}}$$



$$dA = -SdT - PdV$$
$$= \left(\frac{\partial A}{\partial T}\right)_V dT + \left(\frac{\partial A}{\partial V}\right)_T dV$$

$$\mu_\mathrm{A} = \left(\frac{\partial G}{\partial n_\mathrm{A}}\right)_{T,P} = \left(\frac{\partial A}{\partial n_\mathrm{A}}\right)_{T,V}$$
$$\mu_\mathrm{B} = \left(\frac{\partial G}{\partial n_\mathrm{B}}\right)_{T,P} = \left(\frac{\partial A}{\partial n_\mathrm{B}}\right)_{T,V}$$

Gibbs-Duhem equation

$$G(P, T, n_{\mathrm{A}}, n_{\mathrm{B}})$$

$$dG = \left(\frac{\partial G}{\partial P}\right)_{T, n_{\mathrm{A}}, n_{\mathrm{B}}} dP + \left(\frac{\partial G}{\partial T}\right)_{P, n_{\mathrm{A}}, n_{\mathrm{B}}} dT$$

$$+ \left(\frac{\partial G}{\partial n_{\mathrm{A}}}\right)_{T, P, n_{\mathrm{B}}} dn_{\mathrm{A}} + \left(\frac{\partial G}{\partial n_{\mathrm{B}}}\right)_{T, P, n_{\mathrm{A}}} dn_{\mathrm{B}}$$

$$= V dP - S dT + \mu_{\mathrm{A}} dn_{\mathrm{A}} + \mu_{\mathrm{B}} dn_{\mathrm{B}}$$

$$(dG)_{T,P} = \mu_{\mathrm{A}} dn_{\mathrm{A}} + \mu_{\mathrm{B}} dn_{\mathrm{B}} \qquad (*)$$

一方

$$G = n_{\mathrm{A}}\mu_{\mathrm{A}} + n_{\mathrm{B}}\mu_{\mathrm{B}}$$

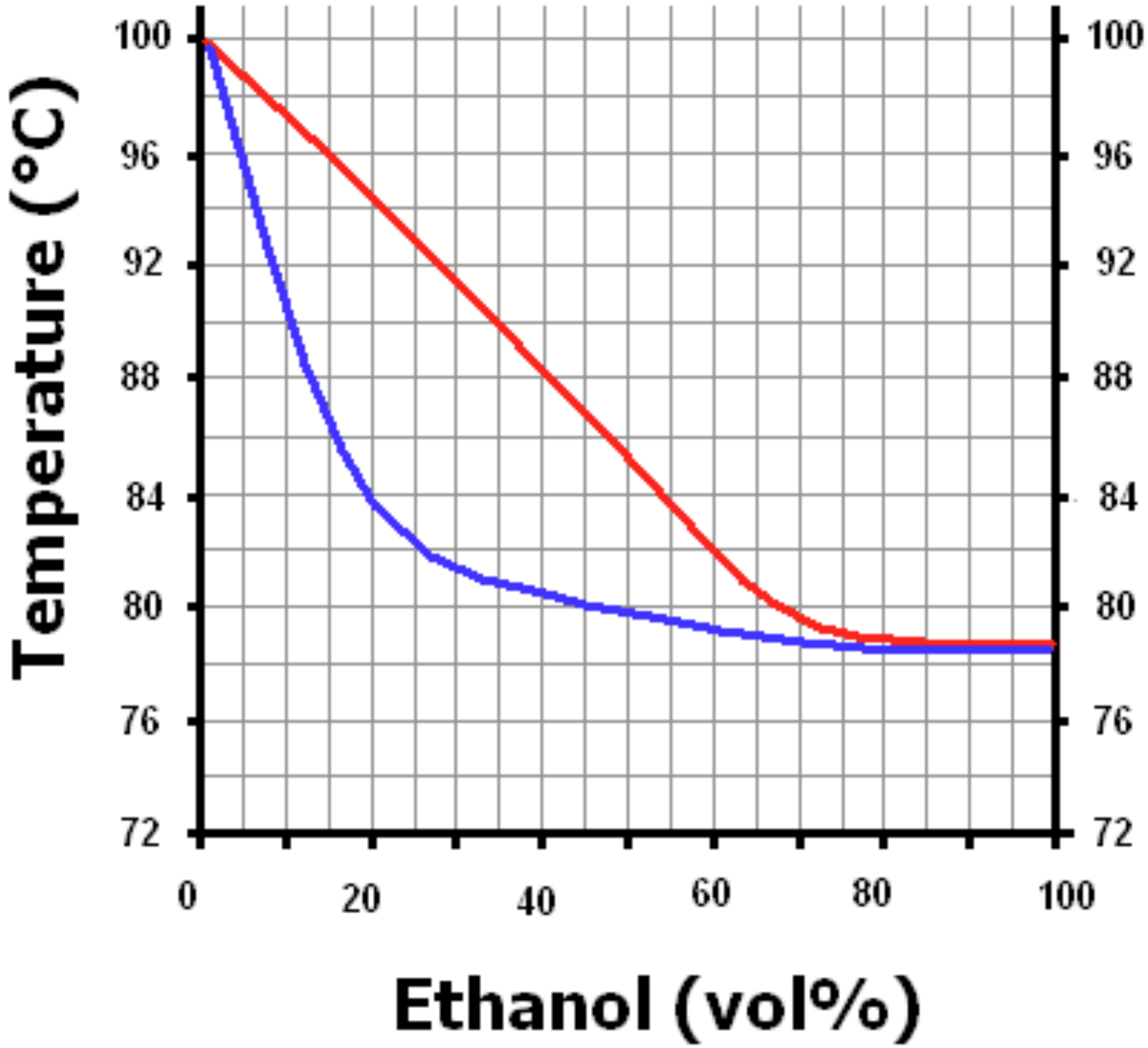
$$dG = \mu_{\mathrm{A}}dn_{\mathrm{A}} + n_{\mathrm{A}}d\mu_{\mathrm{A}} + \mu_{\mathrm{B}}dn_{\mathrm{B}} + n_{\mathrm{B}}d\mu_{\mathrm{A}}$$

(*) より

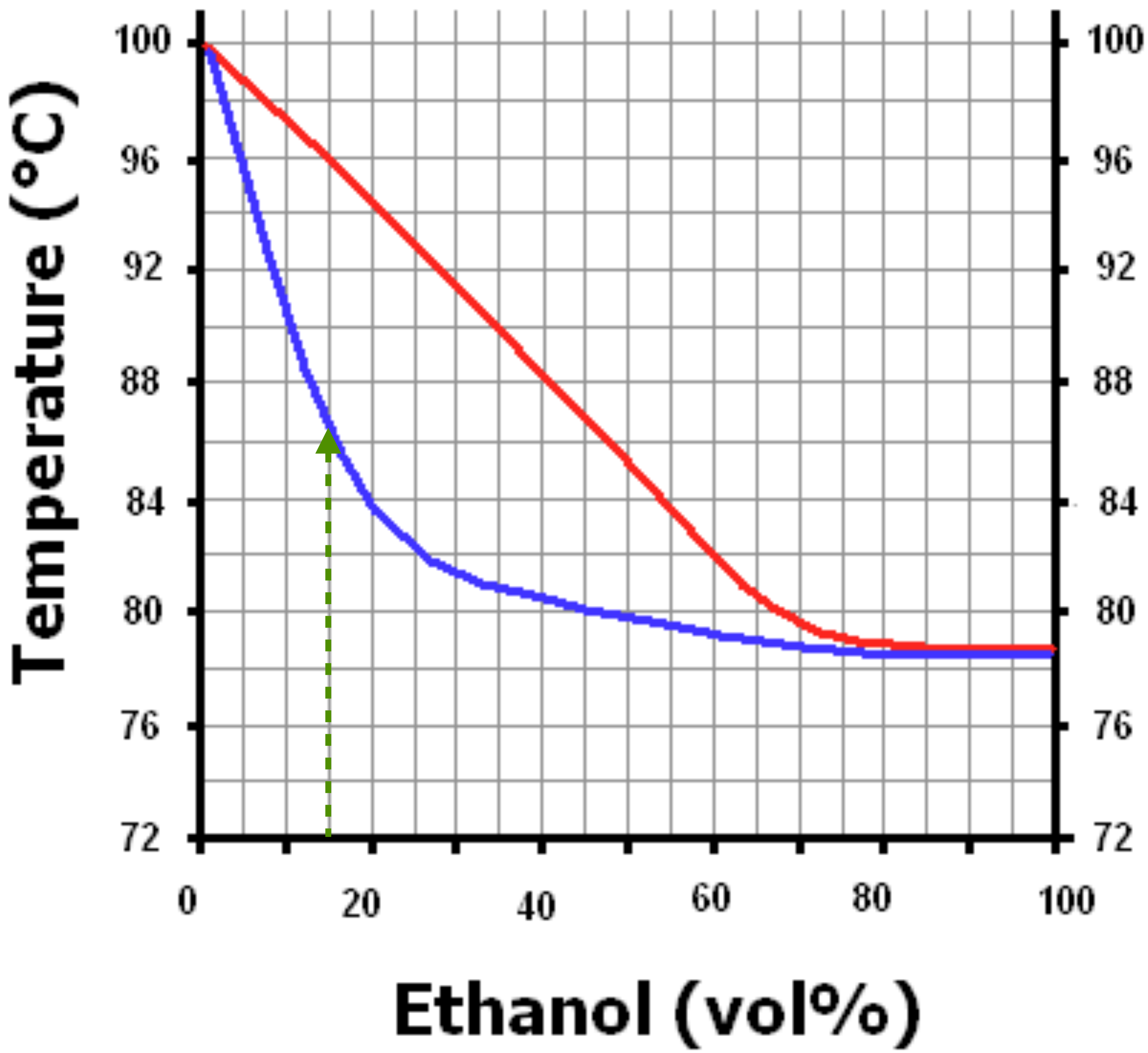
$$(dG)_{T,P} = \mu_{\mathrm{A}}dn_{\mathrm{A}} + \mu_{\mathrm{B}}dn_{\mathrm{B}}$$

$$0 = n_{\mathrm{A}}d\mu_{\mathrm{A}} + n_{\mathrm{B}}d\mu_{\mathrm{A}}, \quad (T, P : \mathrm{constant})$$

Gibbs-Duhem equation



A phase diagram (NOTE: VERY INACCURATE DATA) representing the boiling point of a mixture of ethanol and water, and the composition of the vapour phase.



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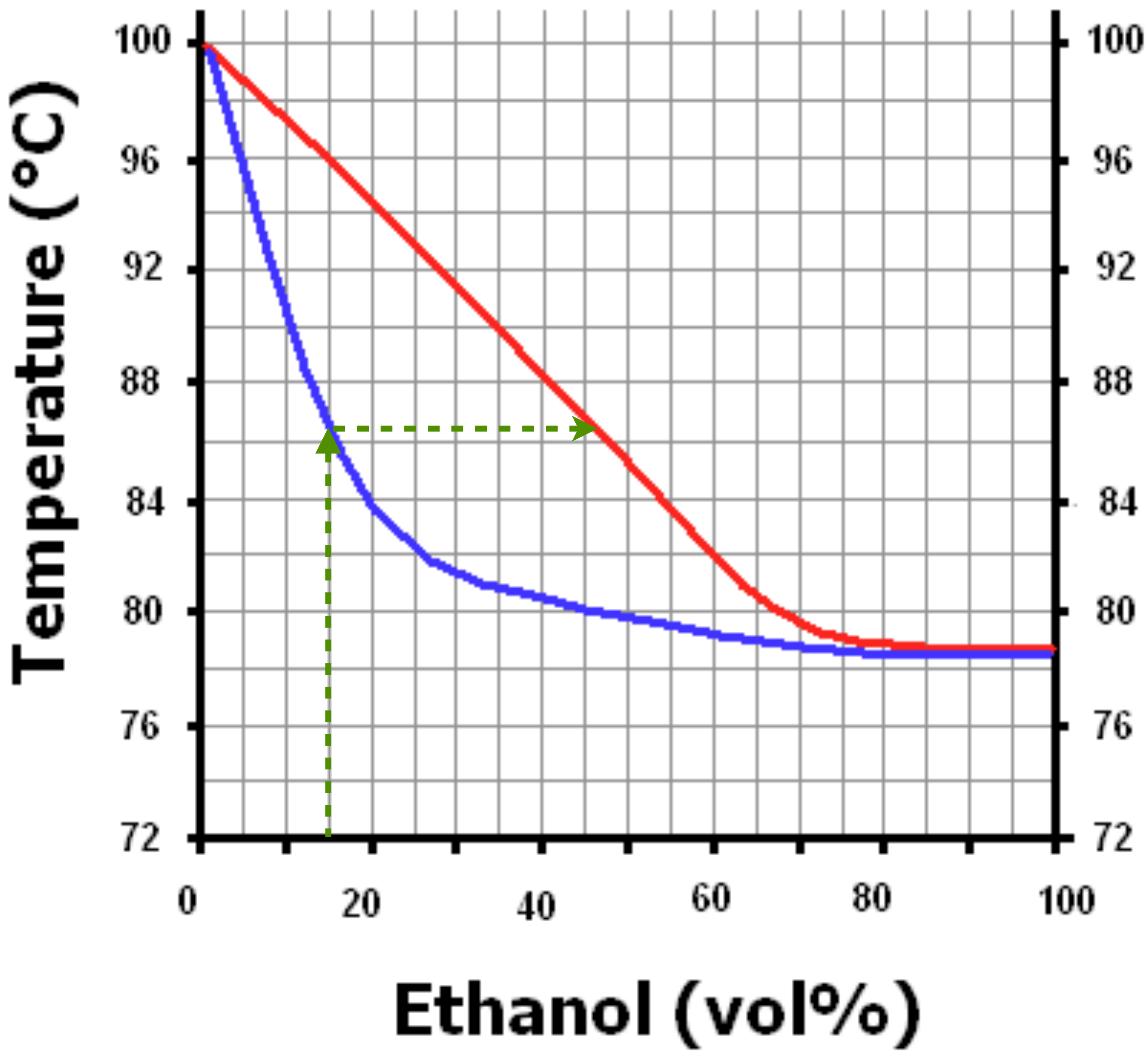

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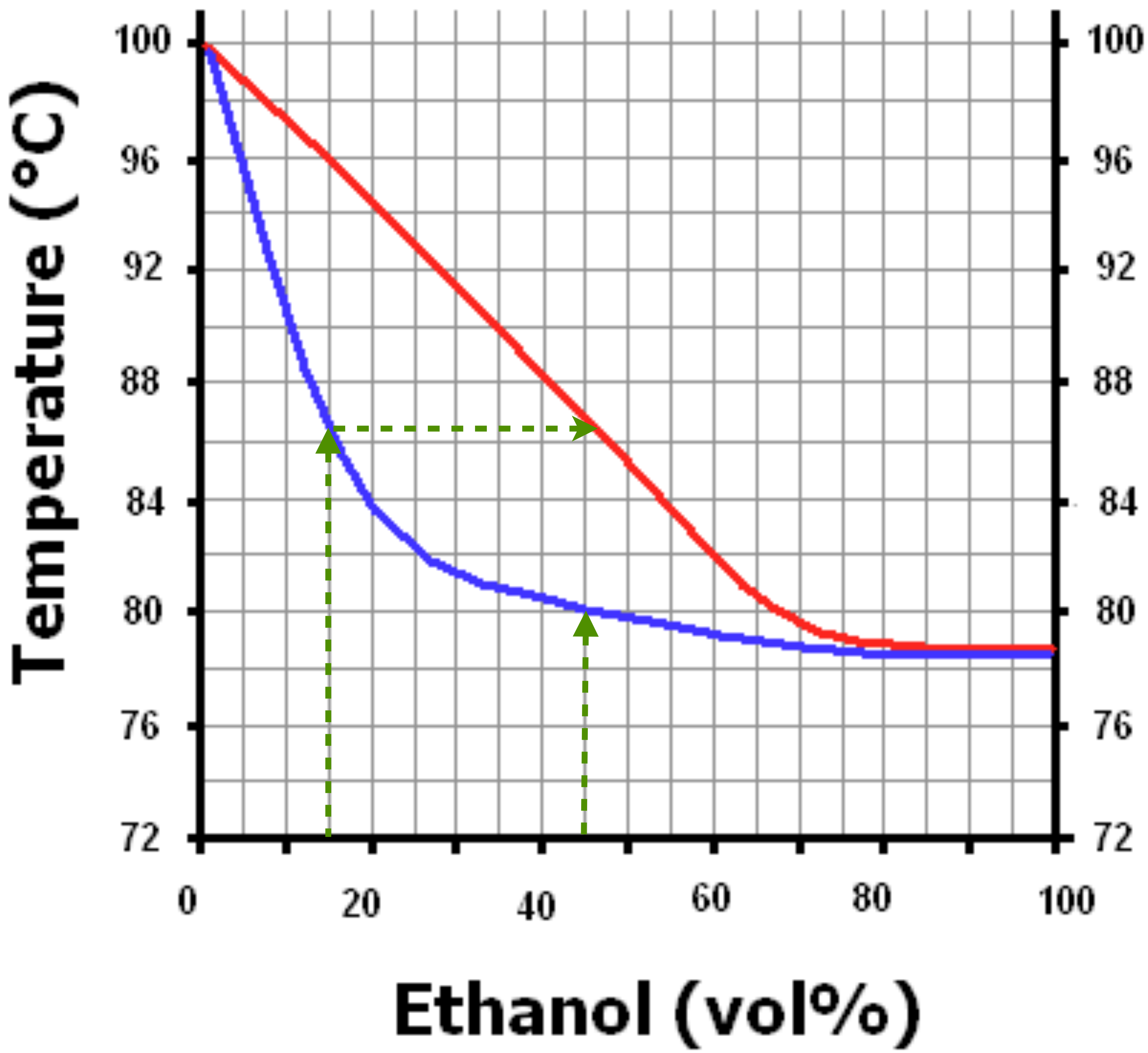

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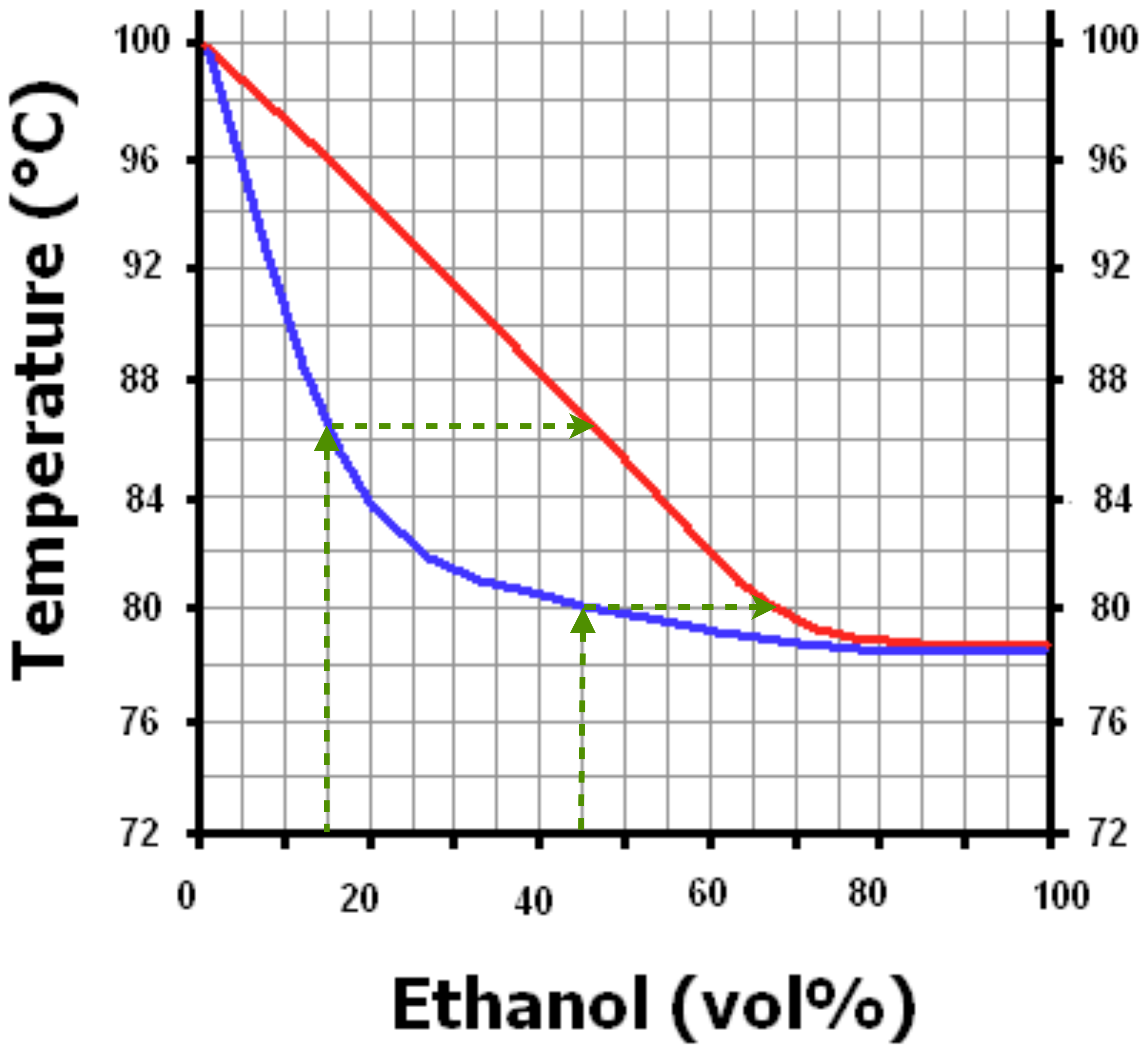
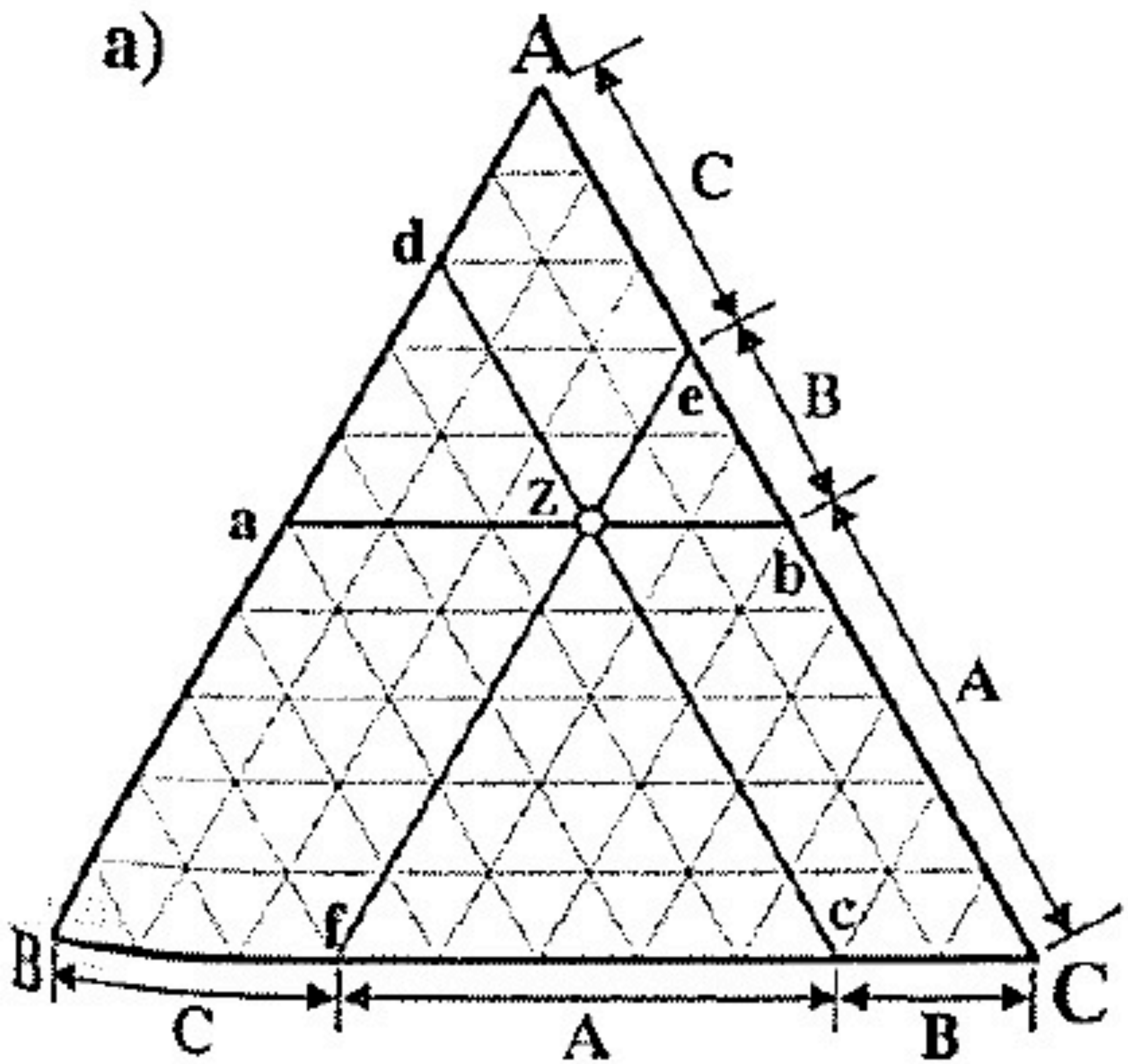


A phase diagram (NOTE: VERY INACCURATE DATA) representing the boiling point of a mixture of ethanol and water, and the composition of the vapour phase.

三元系での組成の読み方

Fig.2 a) に示すように、点Zを通り、組成三角形の各辺に平行な線、ab、cd、efを引いてみよう。これらの線の各辺との交点から、直ちに各成分濃度を知ることができる。例えば、BfまたはAeから、Cの濃度は30％であることがわかる。

a)



また、Fig.2 b) のように各頂点から点Zを通る直線を引くと、各線の辺との交点、g、h、iは点Zにおける成分濃度比を与える。例えばBg：gC＝60：40なので、ZにおけるBとCの濃度比は2：3である。このことから、線Ag上では、BとCの濃度比は常に2：3で一定であることが理解されよう。B