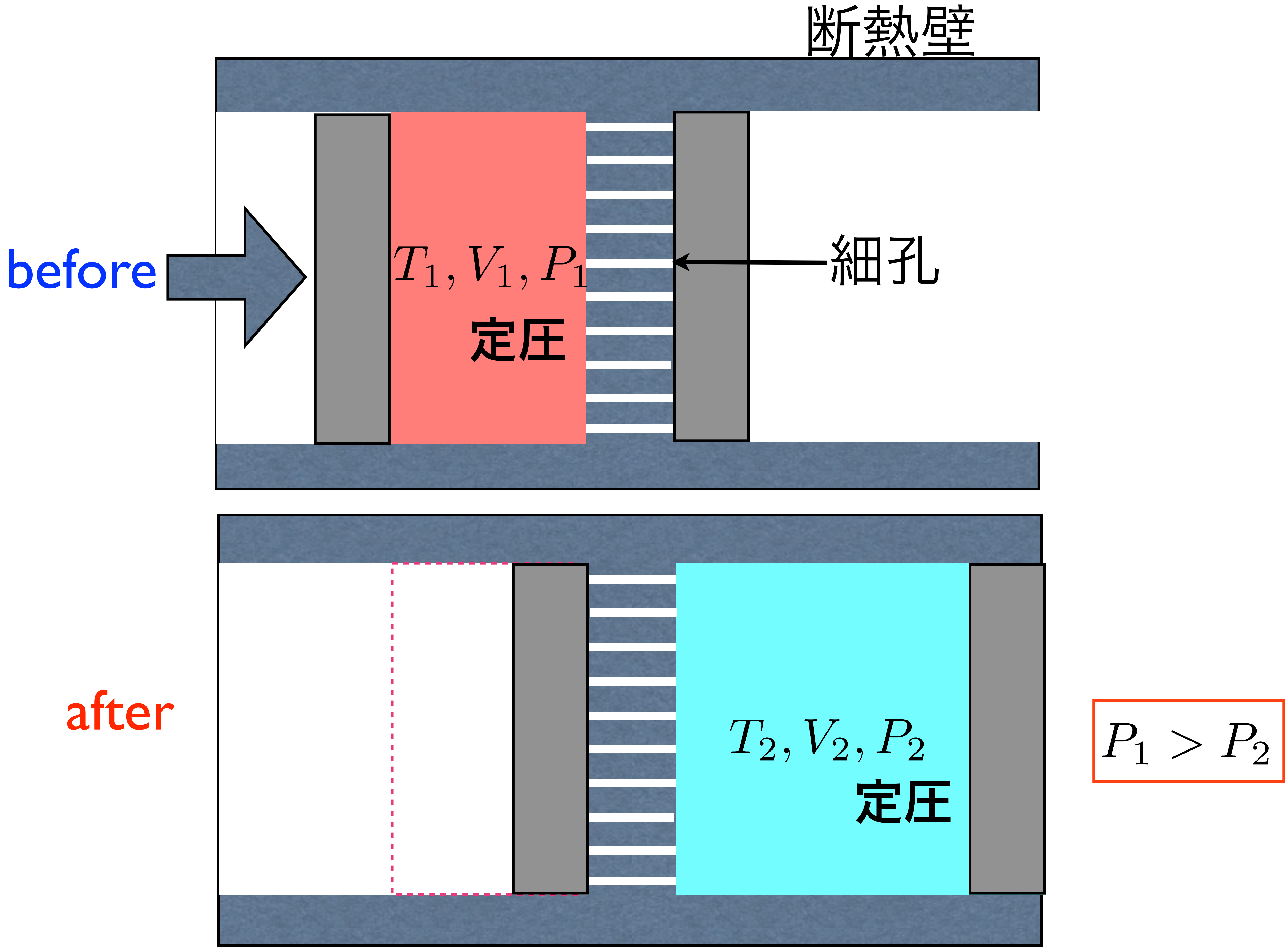
Joule−Thomson(Kelvin) ：ガスの液化に使う



internal energy

	after	before
left:	0	U_1
right:	U_2	0
total :	$U_2 - U_1$	

気体が存在しなければU=0

work

left:	$+P_1V_1$
right:	$-P_2V_2$
total:	$+P_1V_1 - P_2V_2$

気体は仕事をされた
気体は仕事をした

$dQ = 0$：断熱過程

$$U_2 - U_1 = +P_1V_1 - P_2V_2$$

$$U_1 + P_1V_1 = U_2 + P_2V_2$$

$$H_1 = H_2$$

等エンタルピー過程

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等エンタルピー過程

何の変数で全微分形を書いてよい！

UP THAS VGで書く変数(自然な変数）を使うのがBEST！

$$dH = TdS + VdP$$

$$H = H(S, P)$$

$$H = H(T, P) \quad \rightarrow \mu_{\mathrm{JT}}$$

↑Sが$S(T,P)$であればOK

理想気体のSは，以下のように書かれる

$$S(T,V) = C_V \ln \frac{T}{T^*} + nR \ln \frac{V}{V^*}$$

$$* : \text{a reference state}$$

$$PV = nRT, \quad P^*V^* = nRT^*$$

$$S(T,P) = C_V \ln \frac{T}{T^*} + nR \ln \left(\frac{nRT}{P} \frac{P^*}{nRT^*} \right)$$

$$= (C_V + nR) \ln \frac{T}{T^*} + nR \ln \frac{P^*}{P}$$

$$= C_P \ln \frac{T}{T^*} - nR \ln \frac{P}{P^*}$$

↑Sは$S(T,P)$で示された

P一定でTを変化するのとP一定でSを変化は同じ

$H(P,T):$

$$dH = \left(\frac{\partial H}{\partial P}\right)_T dP + \left(\frac{\partial H}{\partial T}\right)_P dT = 0$$

$$\mu_{\mathrm{JT}} \equiv \left(\frac{\partial T}{\partial P}\right)_H = -\left(\frac{\partial H}{\partial P}\right)_T / \underbrace{\left(\frac{\partial H}{\partial T}\right)_P}_{=C_P}$$

$$dH = TdS + VdP$$

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

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

$$\left(\frac{\partial H}{\partial P}\right)_T = -T\left(\frac{\partial V}{\partial T}\right)_P + V = -T\frac{nR}{P} + V = 0$$

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別解

$$dH = TdS + VdP$$

$$S = S(T, P)$$

$$dS = \left(\frac{\partial S}{\partial T}\right)_P dT + \left(\frac{\partial S}{\partial P}\right)_T dP$$

$$dH = T\left(\frac{\partial S}{\partial T}\right)_P dT + \left[T\left(\frac{\partial S}{\partial P}\right)_T + V\right] dP$$

$$TdS = dQ, \quad T\left(\frac{\partial S}{\partial T}\right)_P = C_P dT$$

$$dG = -SdT + VdP \rightarrow \left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P$$

$$dH = C_P dT + \left[-T\left(\frac{\partial V}{\partial T}\right)_P + V\right] dP$$

$$\mu_{\mathrm{JT}} = \left(\frac{\partial T}{\partial P}\right)_H = \left[-T\left(\frac{\partial V}{\partial T}\right)_P + V\right] / C_P$$

$$V = \frac{nRT}{P}, \quad -T\frac{nR}{P} + V = -V + V = 0$$

理想気体では

JT過程で

温度は変化しないが

実在気体では下がる

ガスの液化に使われている

Joule-Thomson coefficients for various gases at atmospheric pressure.

https://en.wikipedia.org/wiki/Joule%E2%80%93Thomson_effect

$$P_1 > P_2$$

If the gas temperature is	then μ_{JT} is	since ∂P is	thus ∂T must be	so the gas
below the inversion temperature	positive	always negative	negative	cools
above the inversion temperature	negative	always negative	positive	warms

For an ideal gas, μ_{JT} is always equal to zero: ideal gases neither warm nor cool upon being expanded at constant enthalpy.

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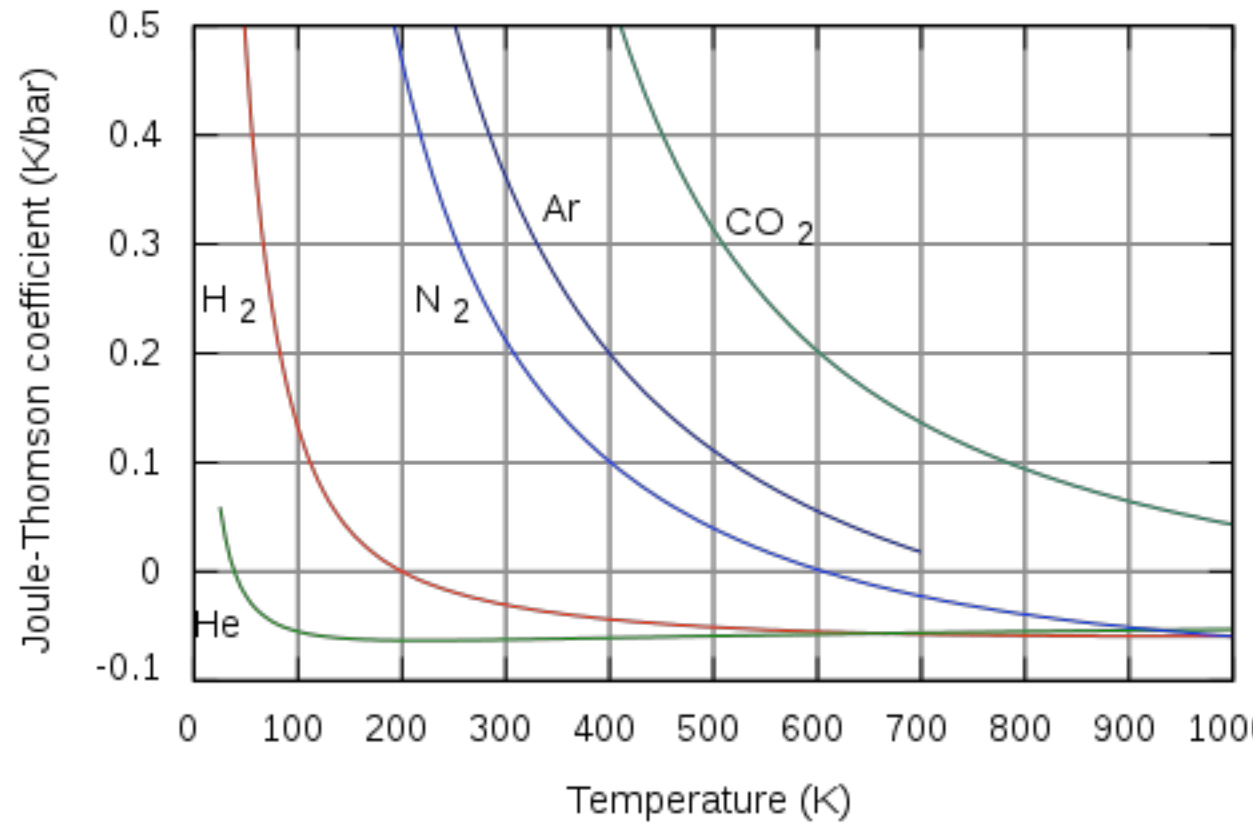

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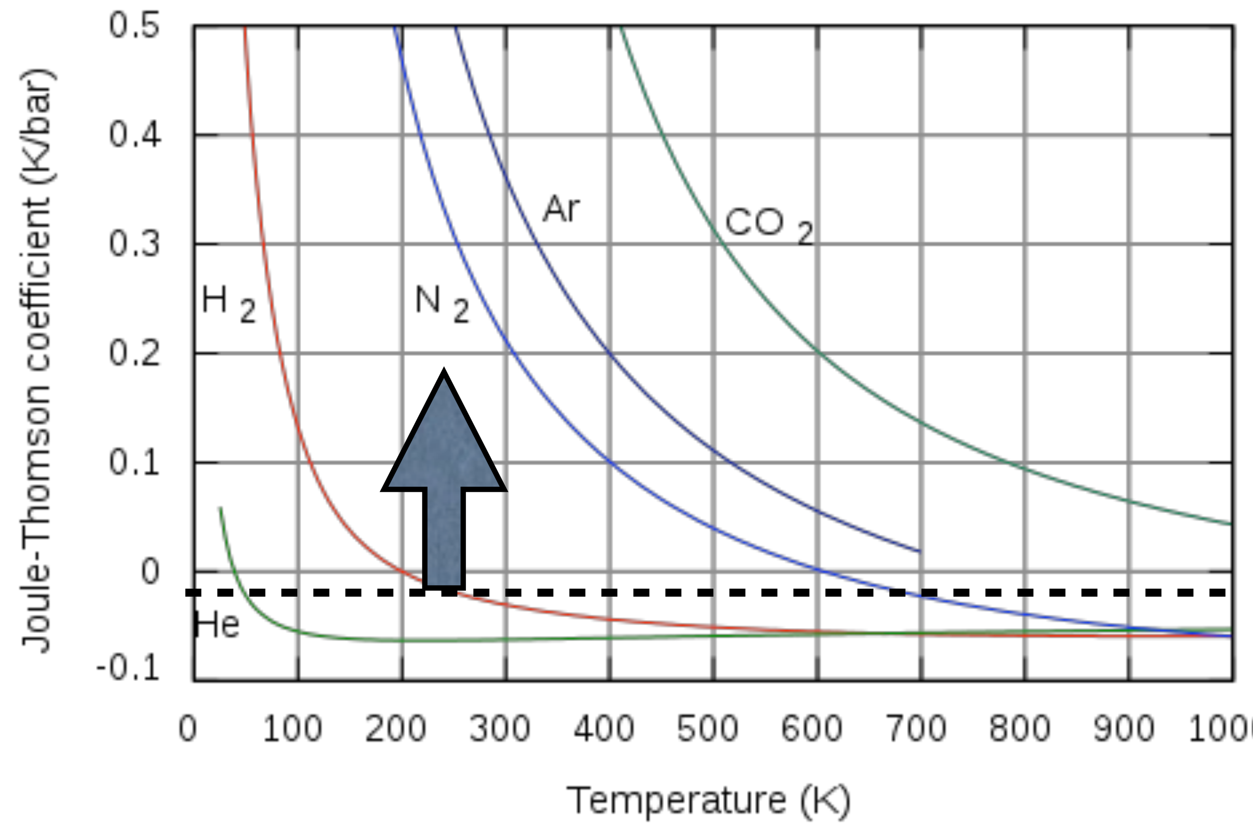

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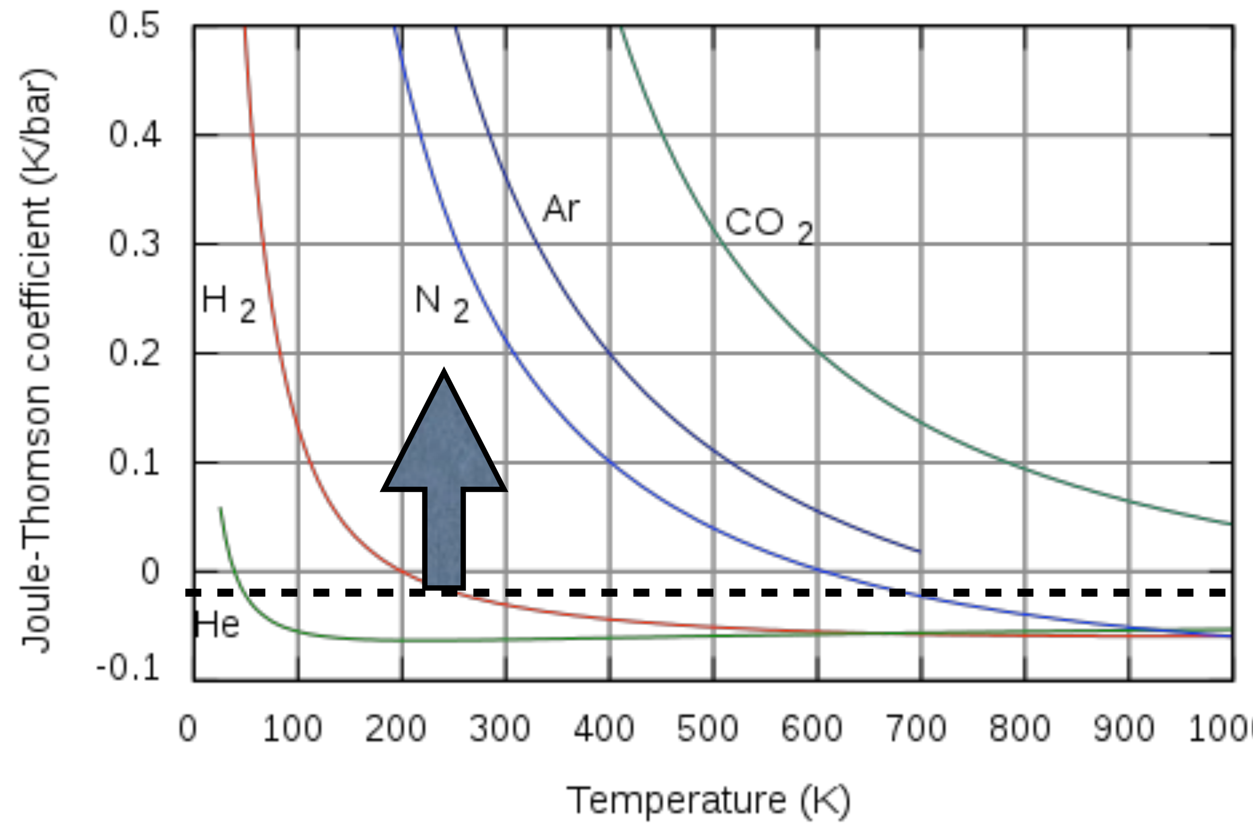

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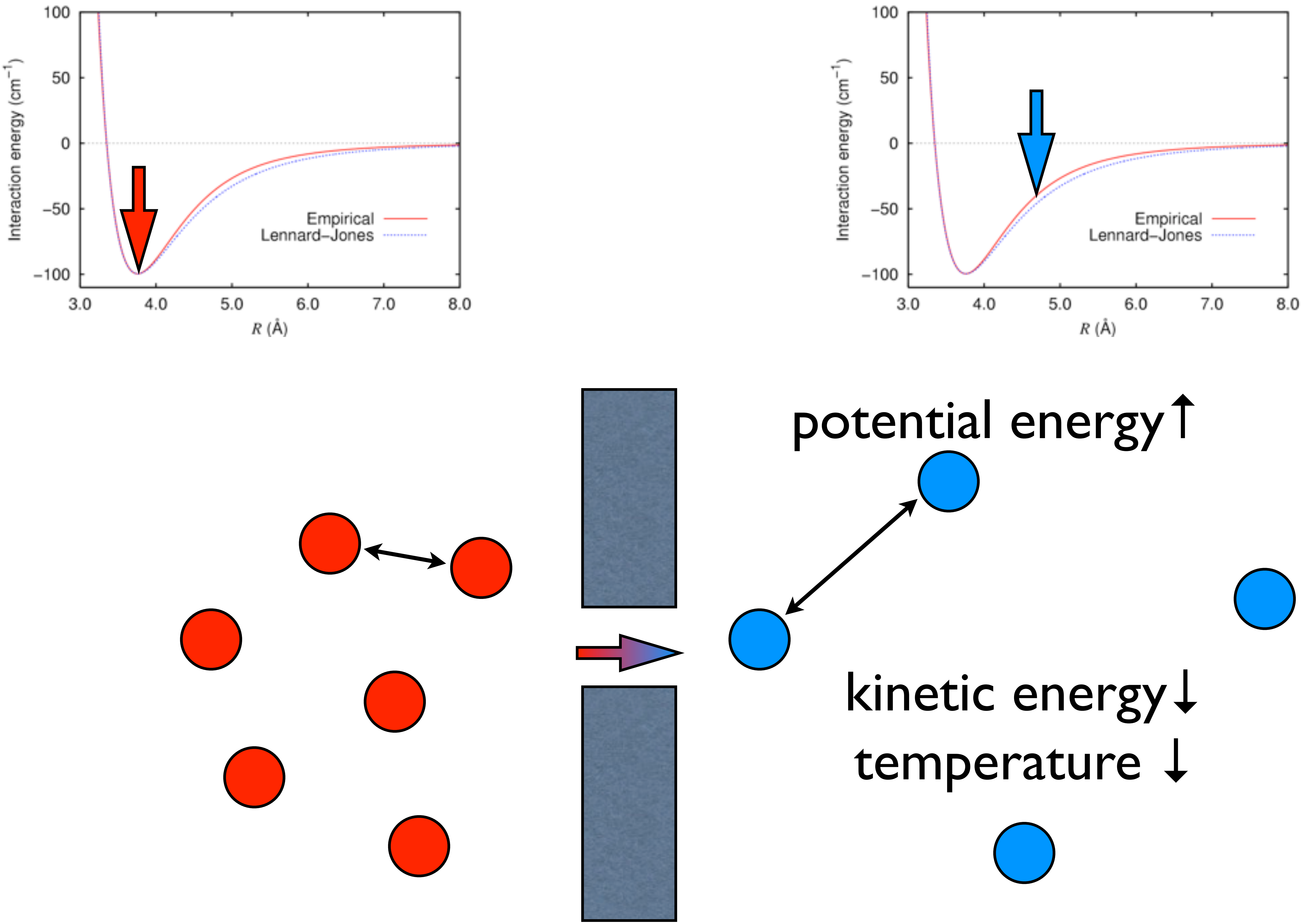
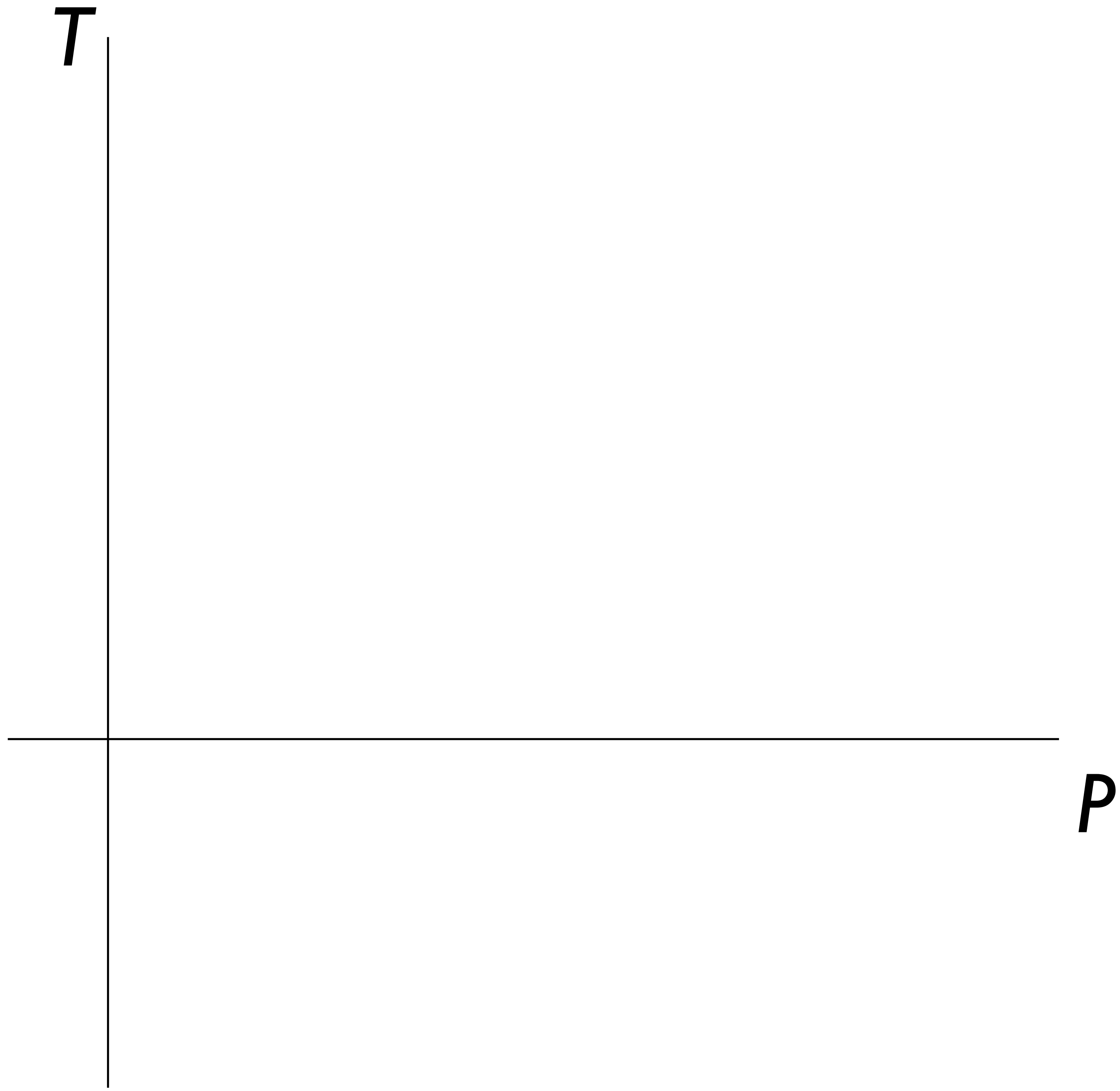
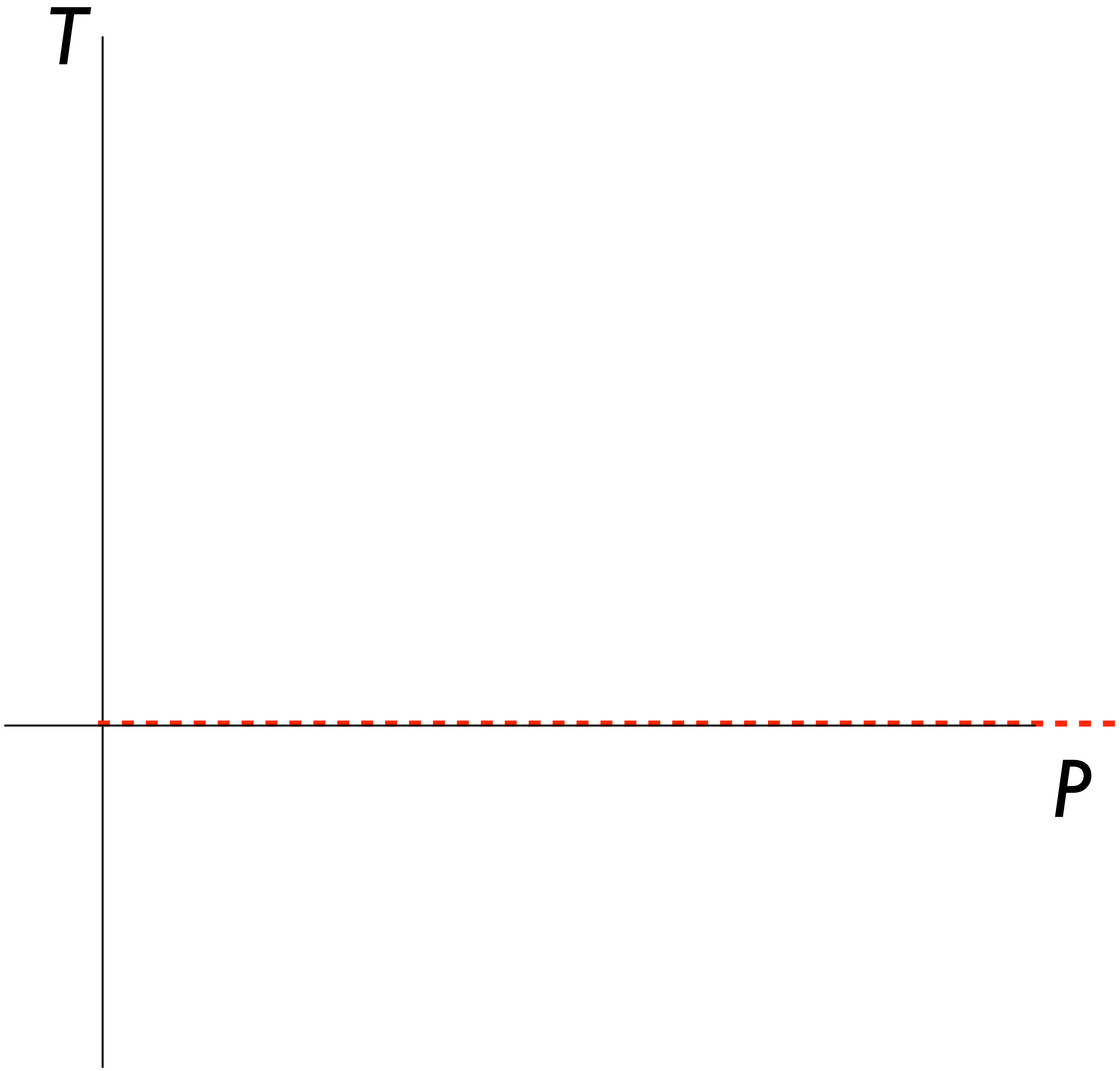
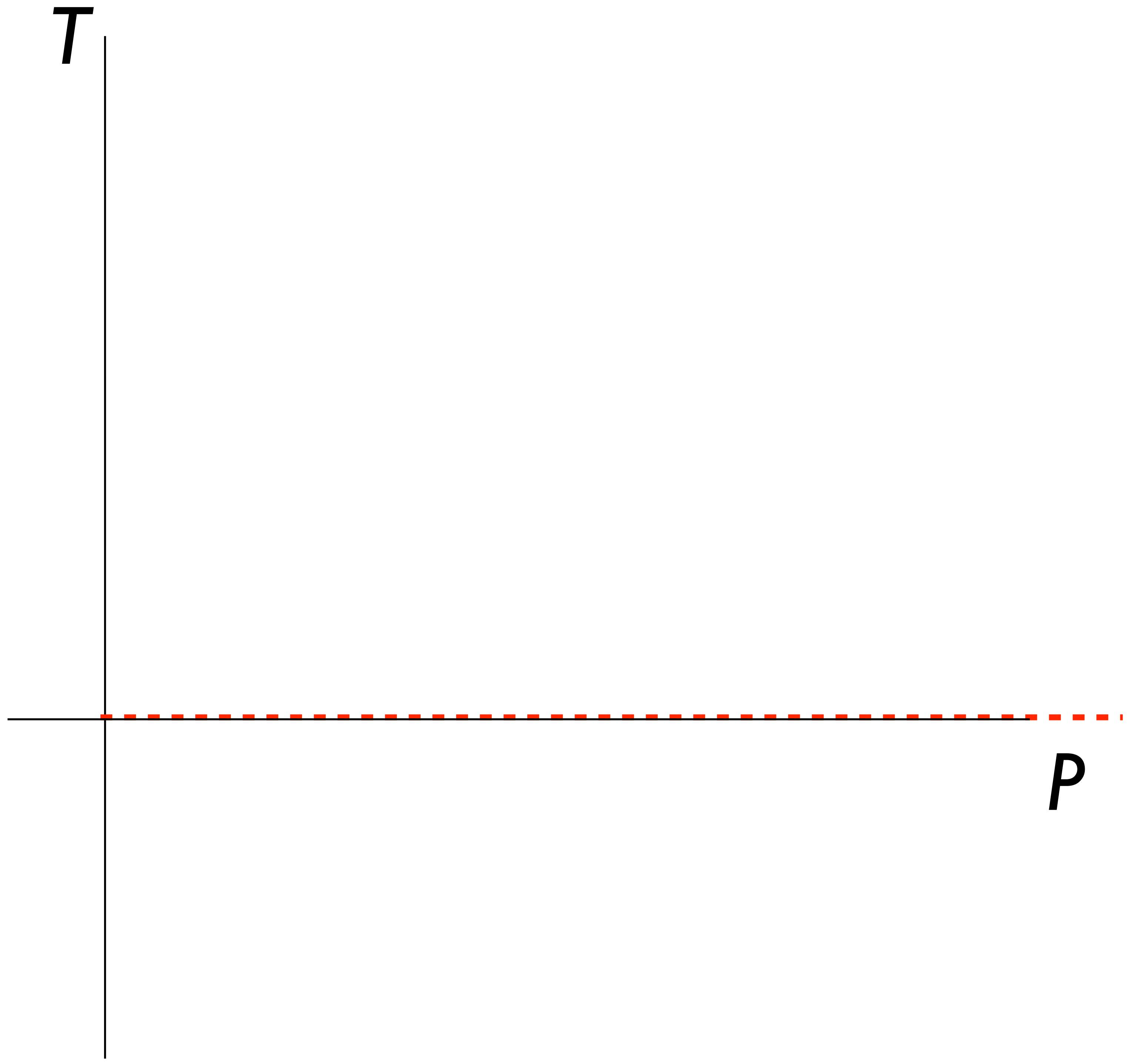
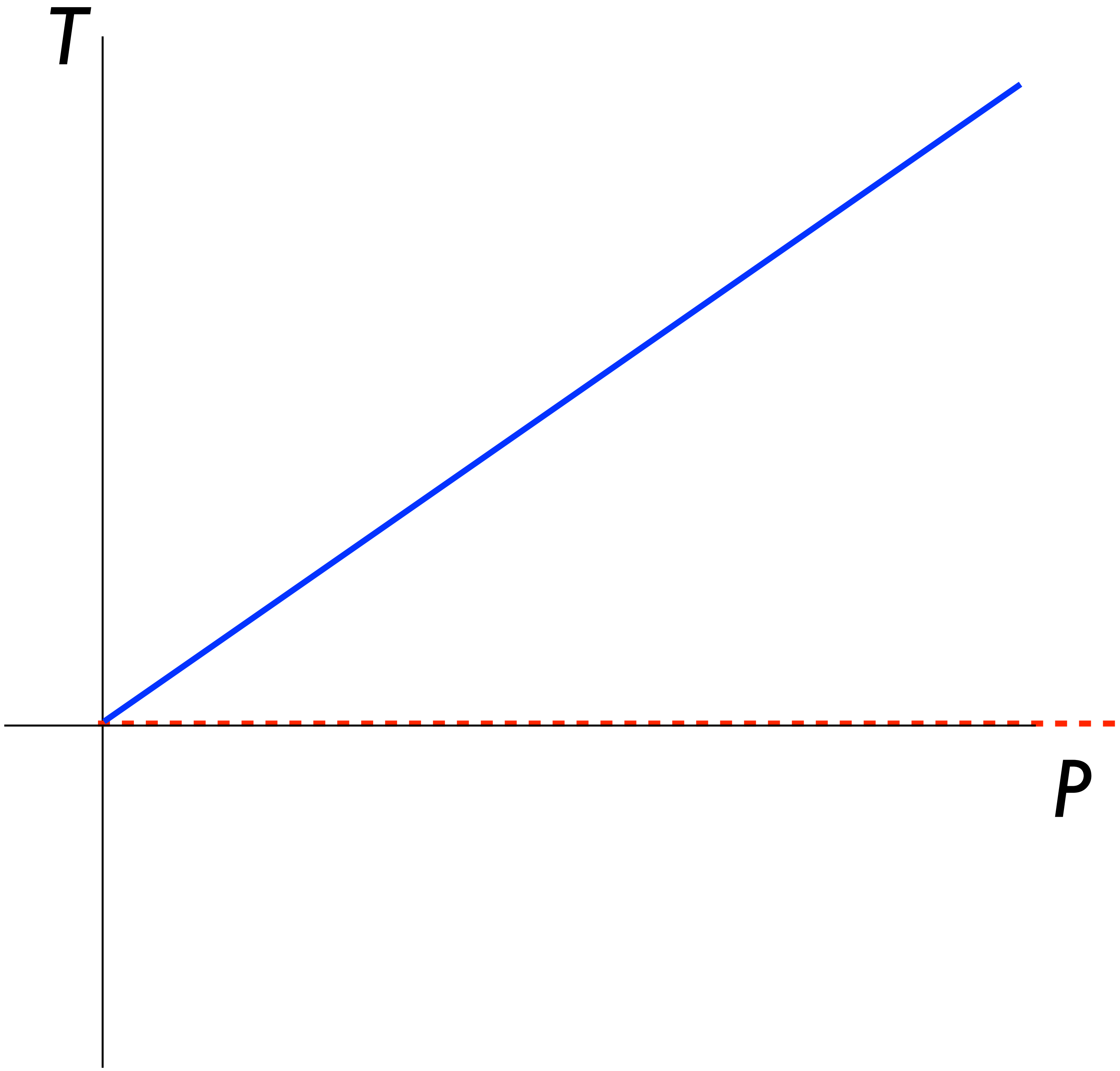

Interaction energy (cm^{-1})
100
50
0
−50
−100
3.0
4.0
5.0
6.0
7.0
8.0
R (Å)
Empirical
Lennard–Jones
potential energy↑
kinetic energy↓
temperature ↓


T
P


T
P



$$\left(\frac{\partial T}{\partial P}\right)_H = 0$$



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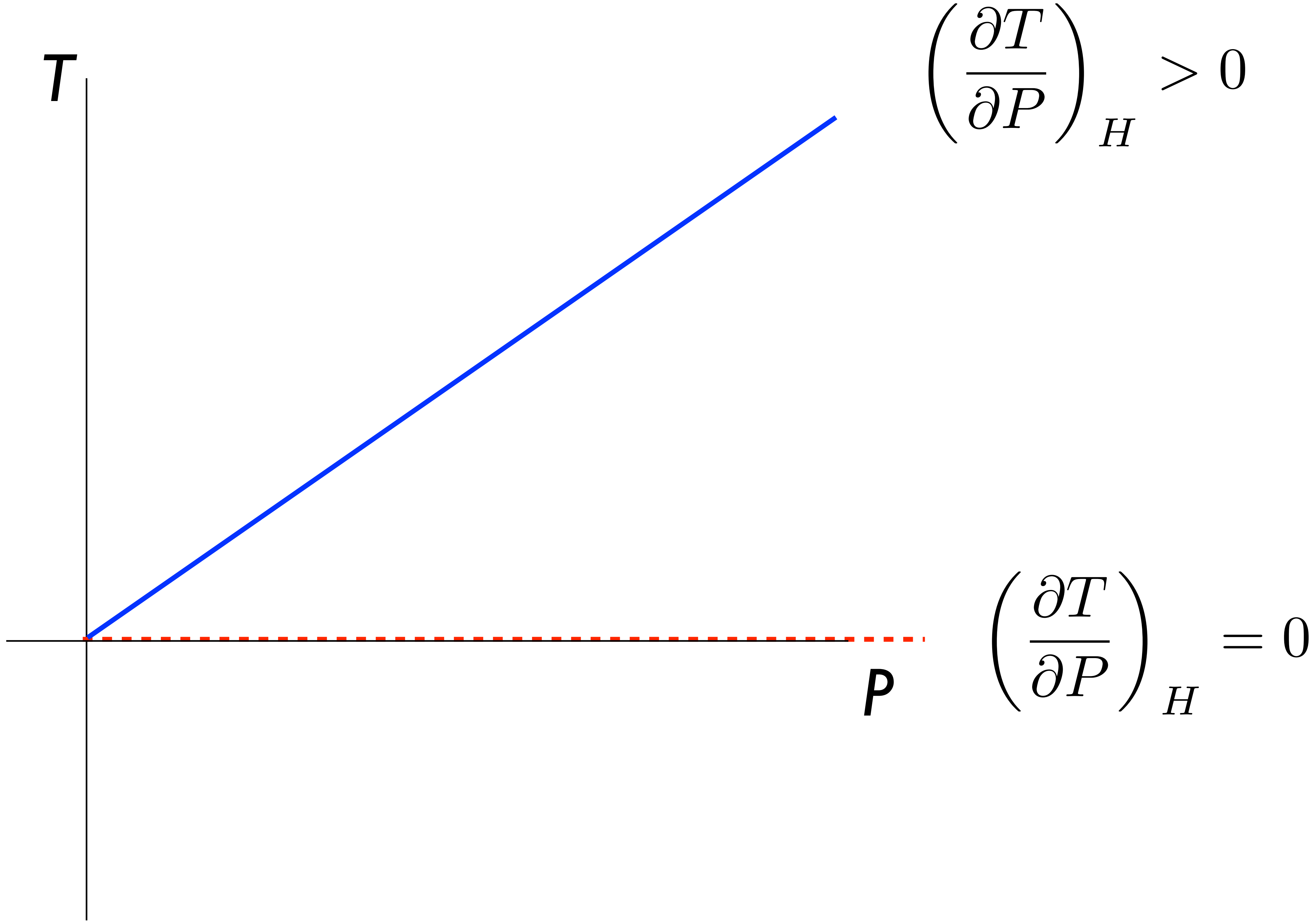
T
P
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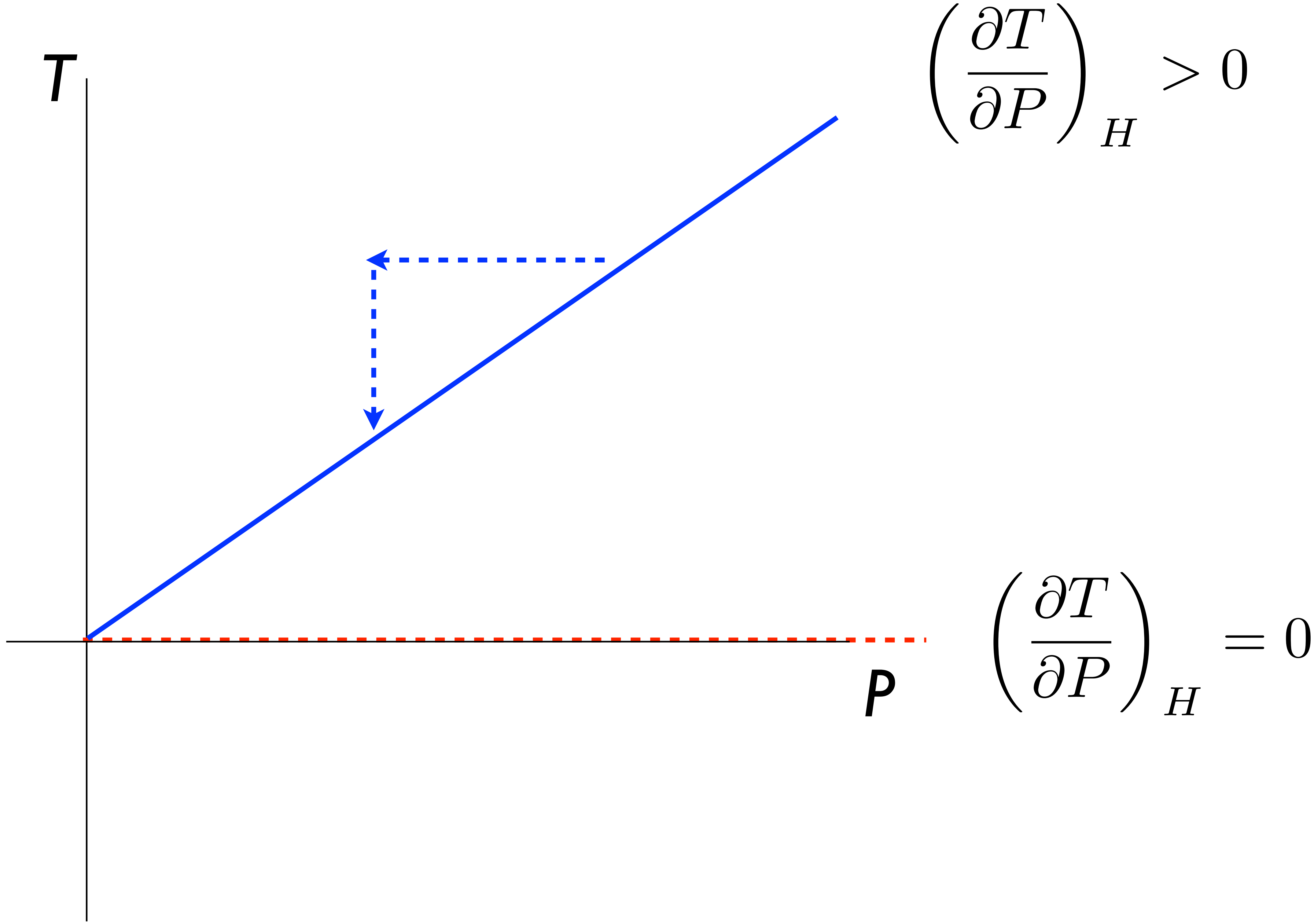
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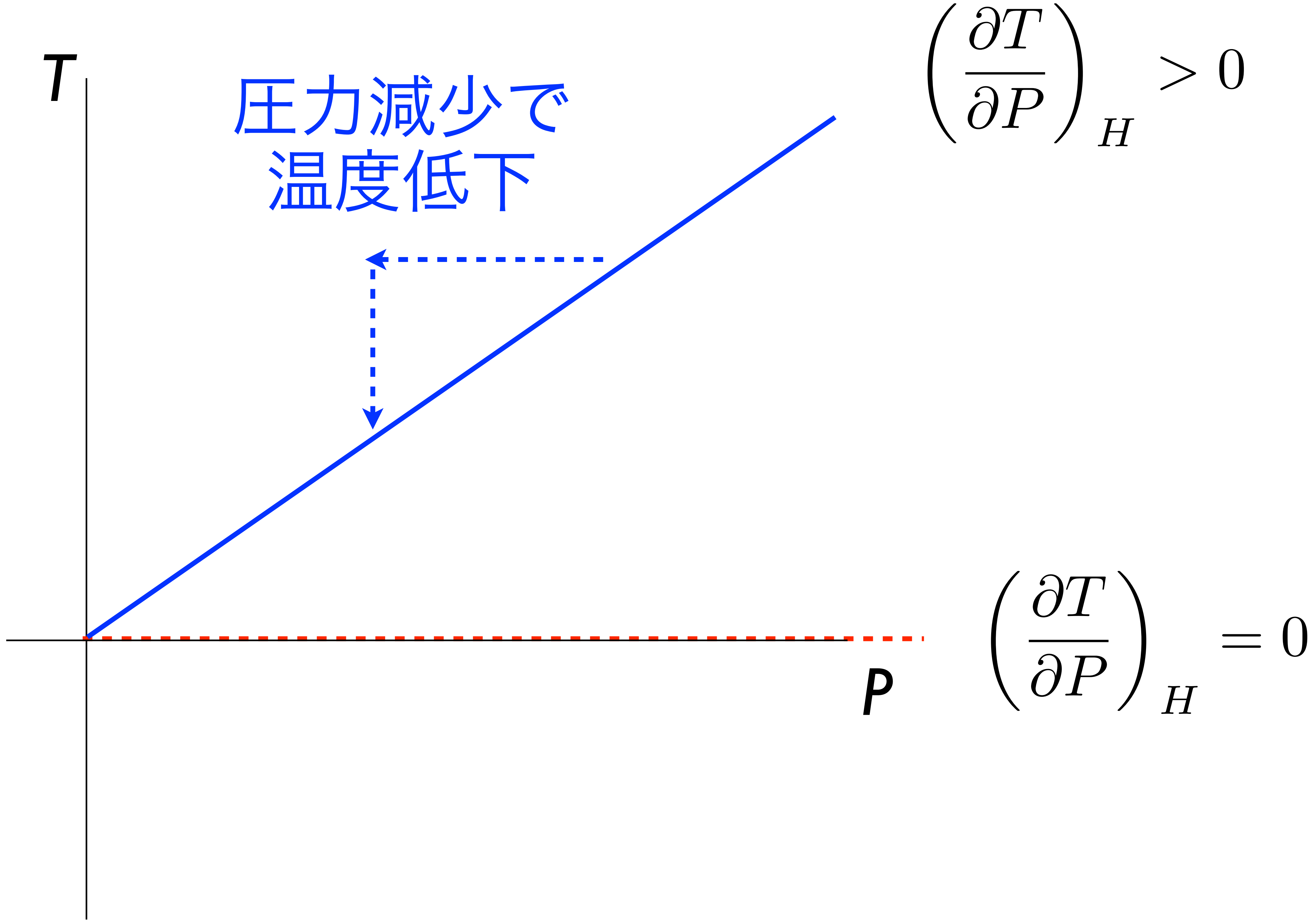
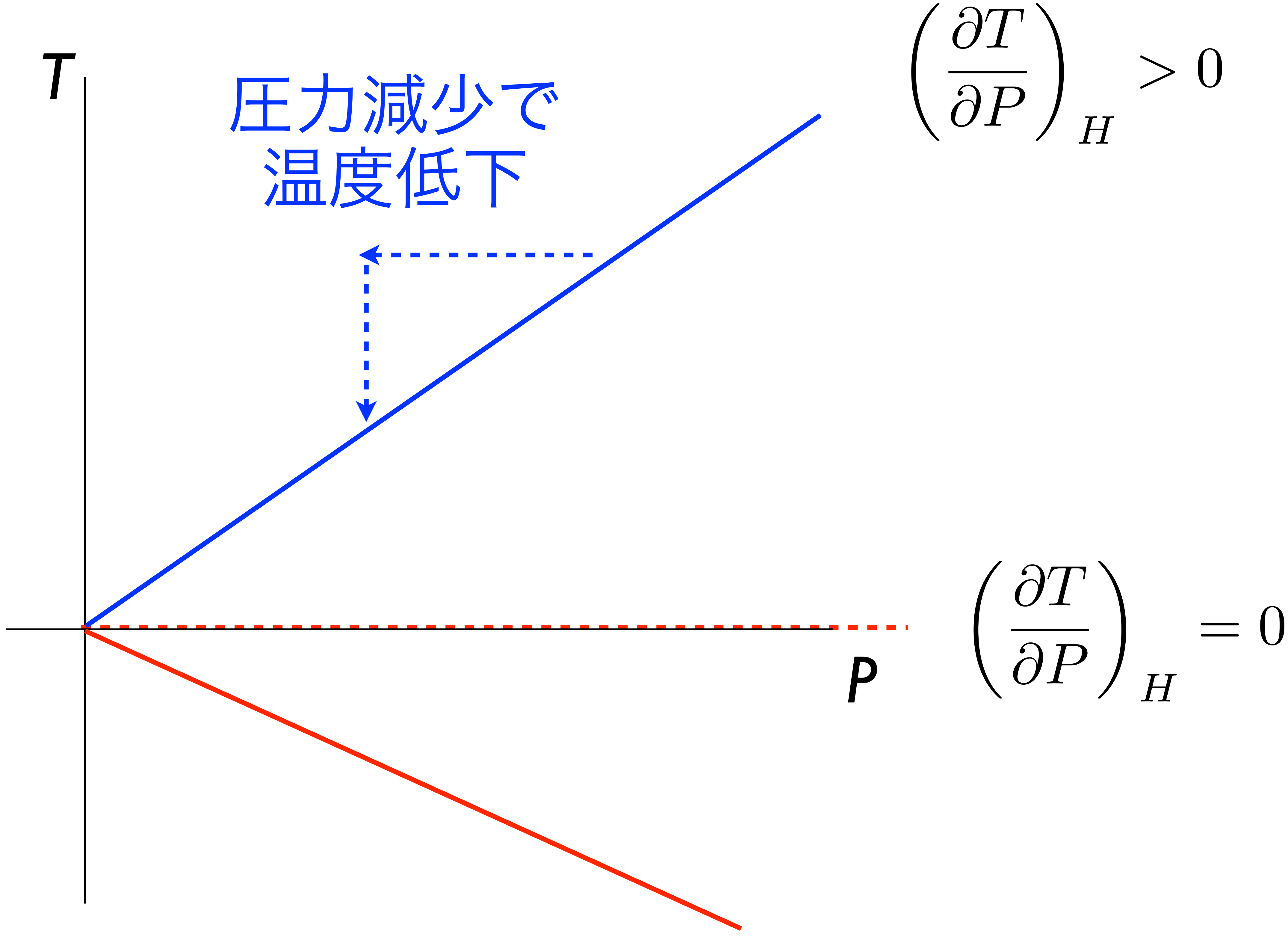
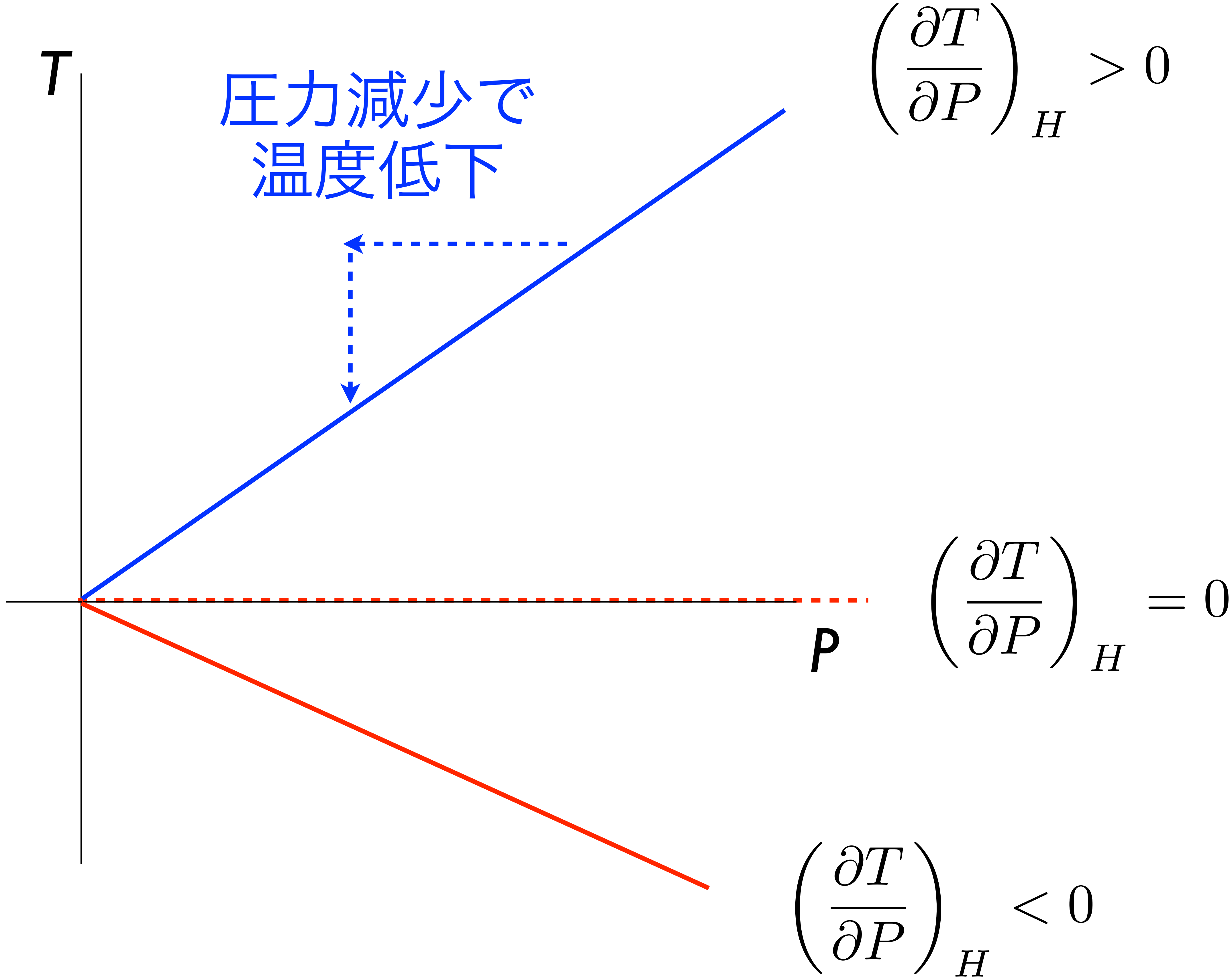

T
圧力減少で
温度低下
P
$\left(\frac{\partial T}{\partial P}\right)_H > 0$
$\left(\frac{\partial T}{\partial P}\right)_H = 0$



T
圧力減少で
温度低下
$\left(\frac{\partial T}{\partial P}\right)_H > 0$
$\left(\frac{\partial T}{\partial P}\right)_H = 0$
P


T
圧力減少で
温度低下
P
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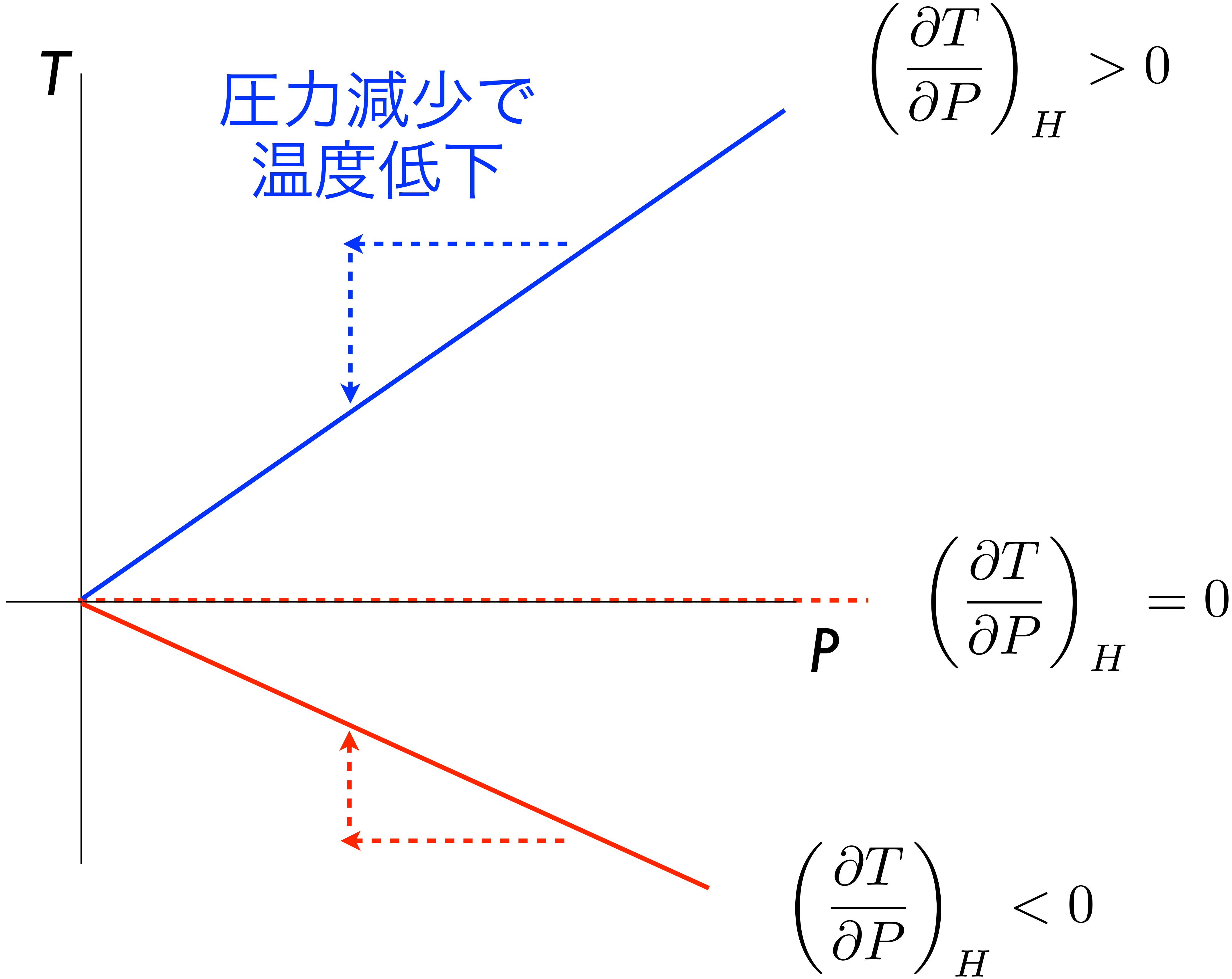
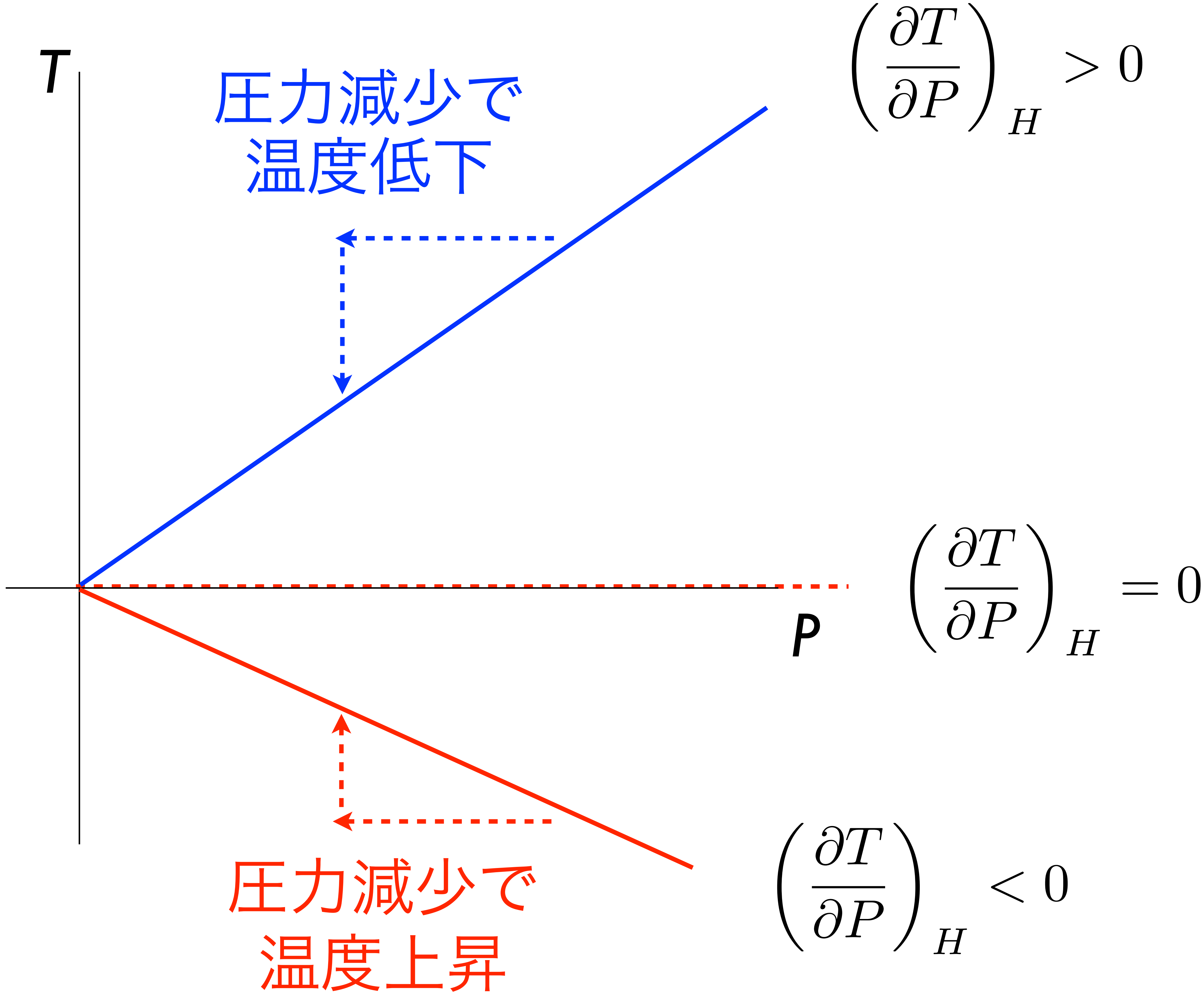
$\left(\frac{\partial T}{\partial P}\right)_H = 0$
$\left(\frac{\partial T}{\partial P}\right)_H < 0$


T
圧力減少で
温度低下
$\left(\frac{\partial T}{\partial P}\right)_H > 0$
$\left(\frac{\partial T}{\partial P}\right)_H = 0$
P
$\left(\frac{\partial T}{\partial P}\right)_H < 0$


T
P
圧力減少で
温度低下
圧力減少で
温度上昇
$\left(\frac{\partial T}{\partial P}\right)_H > 0$
$\left(\frac{\partial T}{\partial P}\right)_H = 0$
$\left(\frac{\partial T}{\partial P}\right)_H < 0$

LNG :　Liquid Natural gas　(CH_4, C_2H_6, C_3H_8, C_4H_{10})

エタンのJT係数 > 0

Experimental results for heat capacity and Joule-Thomson coefficient of ethane at zero pressure

Konrad Bier, Joachim Kunze, Gerd Maurer, Holger Sand　J. Chem. Eng. Data, 1976, 21 (1), pp 5–7　DOI: 10.1021/je60068a033

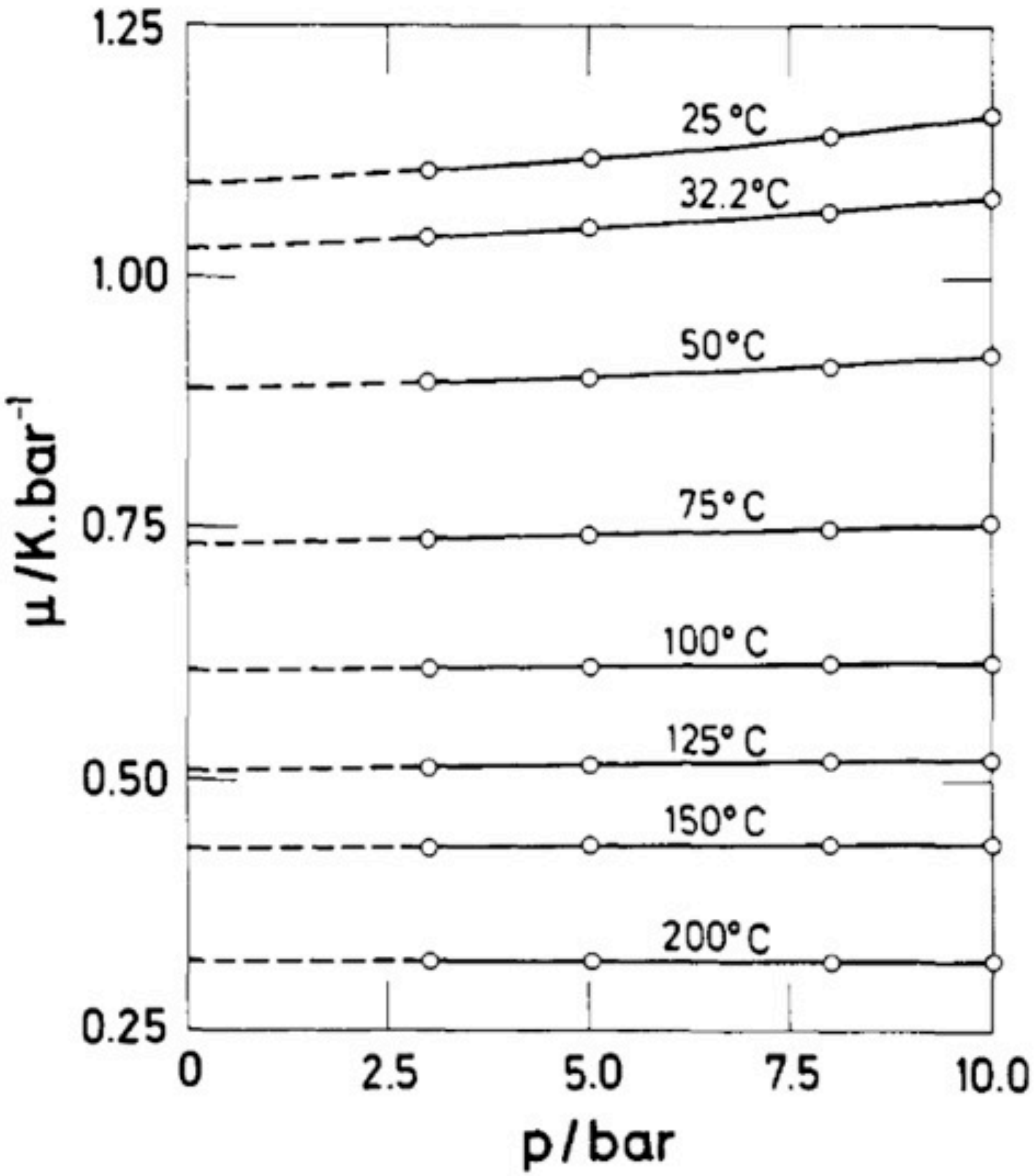


Figure 2. Experimental results for differential Joule-Thomson coefficient of ethane

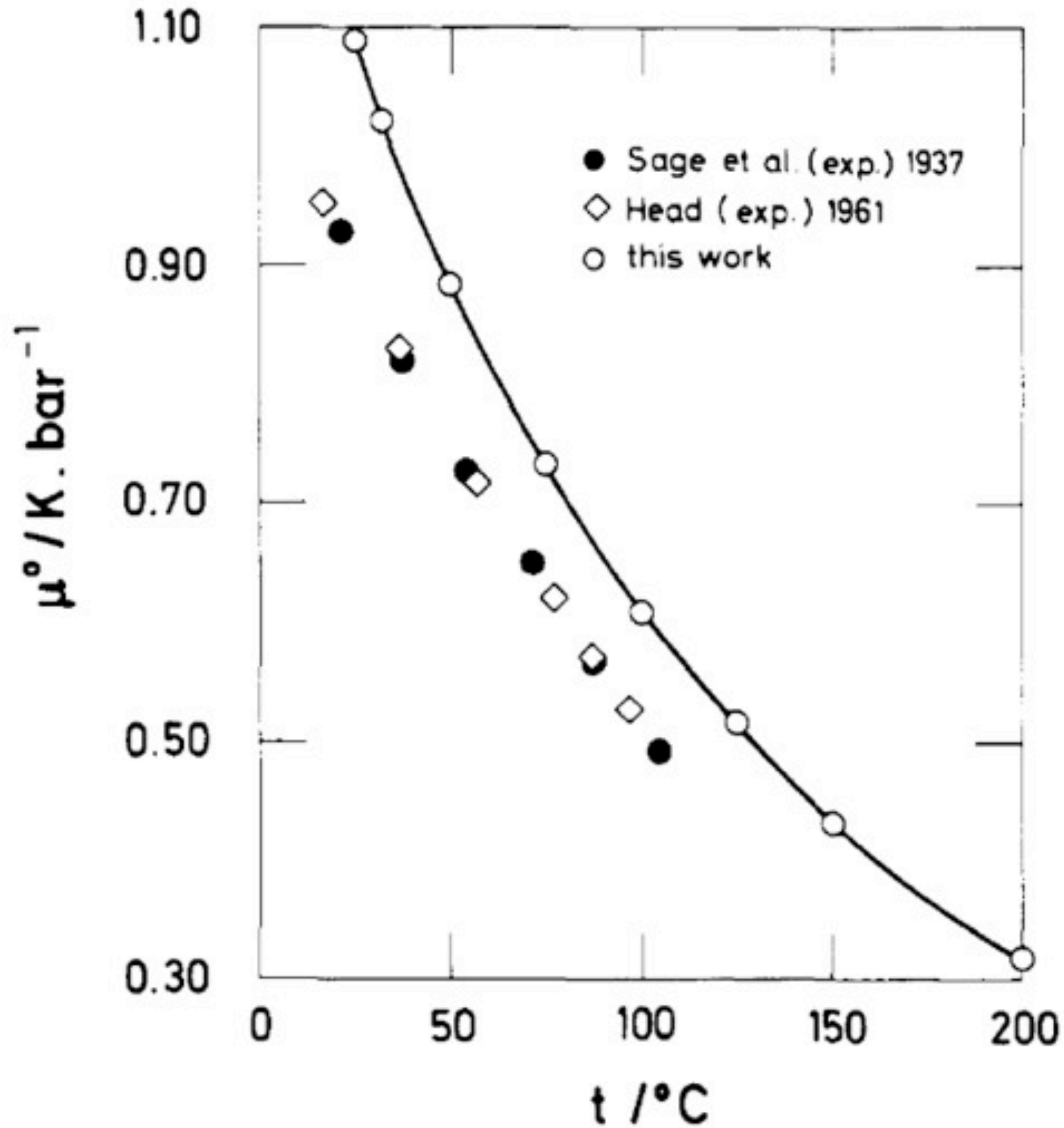


Figure 4. Differential Joule-Thomson coefficient at zero pressure of ethane

天然ガス液化の原理は、気体が膨張して密度が減少するときに、希薄な密度を維持するために内部エネルギーの一部が使用されて温度が低下するという、ジュール・トムソン効果を利用するものである

http://oilgas-info.jogmec.go.jp/pdf/0/598/200503_001a.pdf