

# PROPRIEDADES TERMODINÂMICAS: DIAGRAMAS DE EQUILÍBRIO

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## Aula passada:

2ª lei de Newton aplicada a um sistema de partículas... relação algébrica entre pressão, volume e temperatura (gases perfeitos)

Como explicitar a vinculação entre diferentes propriedades termodinâmicas para uma substância genérica ?



# Demonstração do uso de "tabelas eletrônicas"...

REFPROP (water) - NIST Reference Fluid Properties

File Edit Options Substance Calculate Plot Window Help Cautions

2: water: V/L sat. T=0,02 to 370, °C

	Temperature (°C)	Pressure (bar)	Liquid Density (kg/m <sup>3</sup> )	Vapor Density (kg/m <sup>3</sup> )	Liquid Enthalpy (kJ/kg)	Vapor Enthalpy (kJ/kg)	Liquid Entropy (kJ/kg-K)	Vapor Entropy (kJ/kg-K)
1	0,020000	0,0061210	999,79	0,0048579	0,042811	2500,9	0,00015448	9,1552
2	5,0200	0,0087379	999,92	0,0068112	21,104	2510,1	0,076556	9,0243
3	10,020	0,012298	999,65	0,0094190	42,105	2519,2	0,15138	8,8993
4	15,020	0,017080	999,05	0,012857	63,065	2528,4	0,22475	8,7798
5	20,020	0,023422	998,16	0,017334	83,998	2537,5	0,29677	8,6655
6	25,020	0,031737	997,00	0,023101	104,91	2546,5	0,36751	8,5562
7	30,020	0,042518	995,60	0,030448	125,82	2555,6	0,43703	8,4516
8	35,020	0,056352	993,98	0,039716	146,72	2564,6	0,50540	8,3513
9	40,020	0,073928	992,17	0,051294	167,62	2573,5	0,57267	8,2552
10	45,020	0,096049	990,16	0,065628	188,52	2582,5	0,63888	8,1630

1: Temperature vs. Entropy plot: water

water - H2O (CAS# 7732-18-5)

Molar mass: 18,015 kg/kmol  
Triple pt. temp.: 0,01 °C  
Normal boiling pt.: 99,974 °C  
Gas phase dipole at NBP: 1,855 debye

Critical Point:  
Temperature: 373,95 °C  
Pressure: 220,64 bar  
Density: 322, kg/m<sup>3</sup>  
Acentric factor: 0,3443

Range of applicability:  
Minimum temp.: 0,01 °C  
Maximum temp.: 1726,9 °C  
Maximum pressure: 10000, bar  
Maximum density: 1332,4 kg/m<sup>3</sup>

NIST Rec: FEQ\_Helmholtz equation of state for water of Wagner and Pruss (2002).

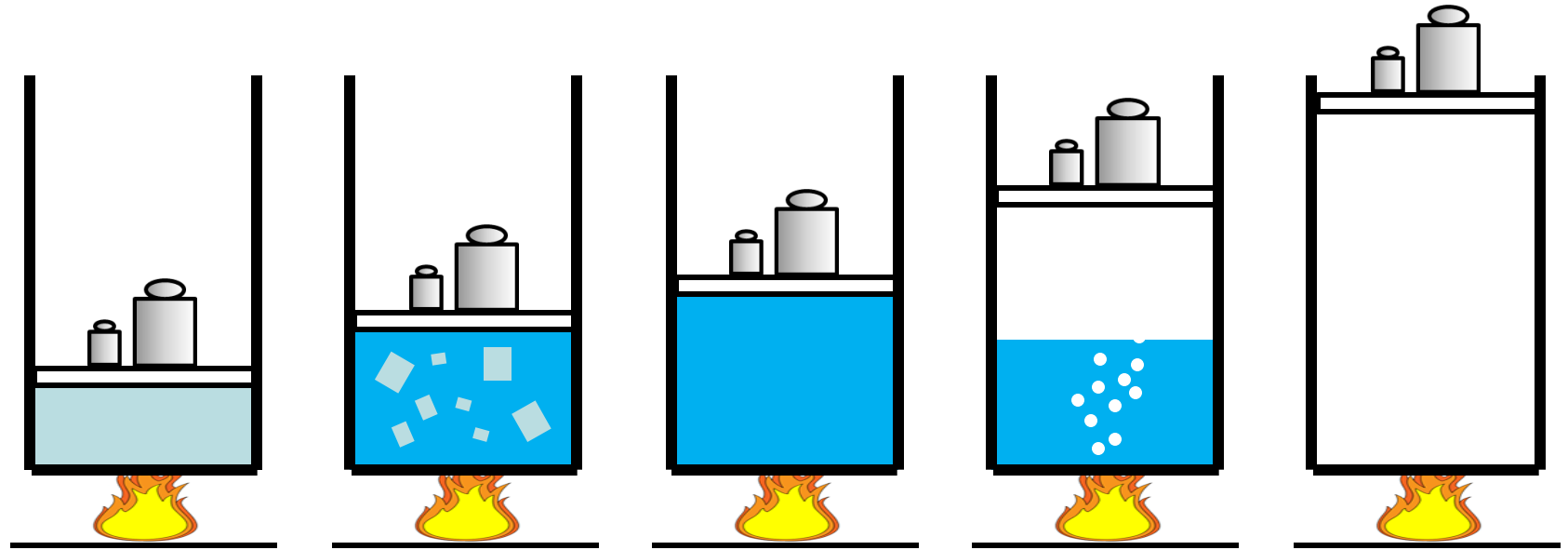
LITERATURE REFERENCE  
Wagner, W. and Pruss, A.,  
"The IAPWS Formulation 1995 for the Thermodynamic Properties of Ordinary Water Substance for General and Scientific Use,"  
J. Phys. Chem. Ref. Data, 31(2):387-535, 2002.

The uncertainty in density of the equation of state is 0.0001% at 1 atm in the liquid phase, and 0.001% at other liquid states at pressures up to 10 MPa and temperatures to 423 K. In the vapor phase, the uncertainty

Equation of State    Viscosity    Thermal Conductivity  
Surface tension    Melting Line    Sublimation Line

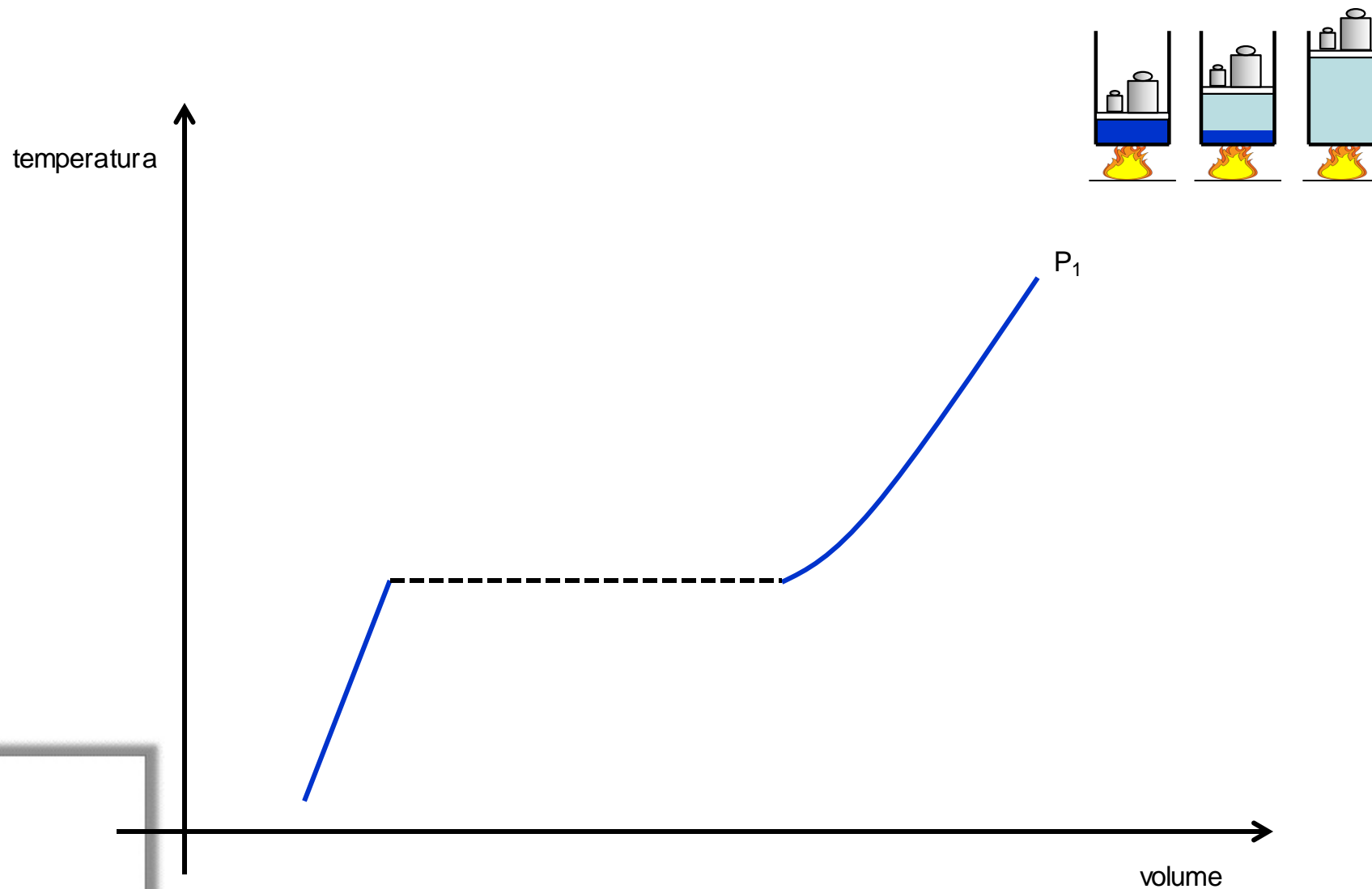
OK    Cancel    Print    Copy    Copy All

## Fases de uma substância pura: aquecimento a $P = \text{cte}$

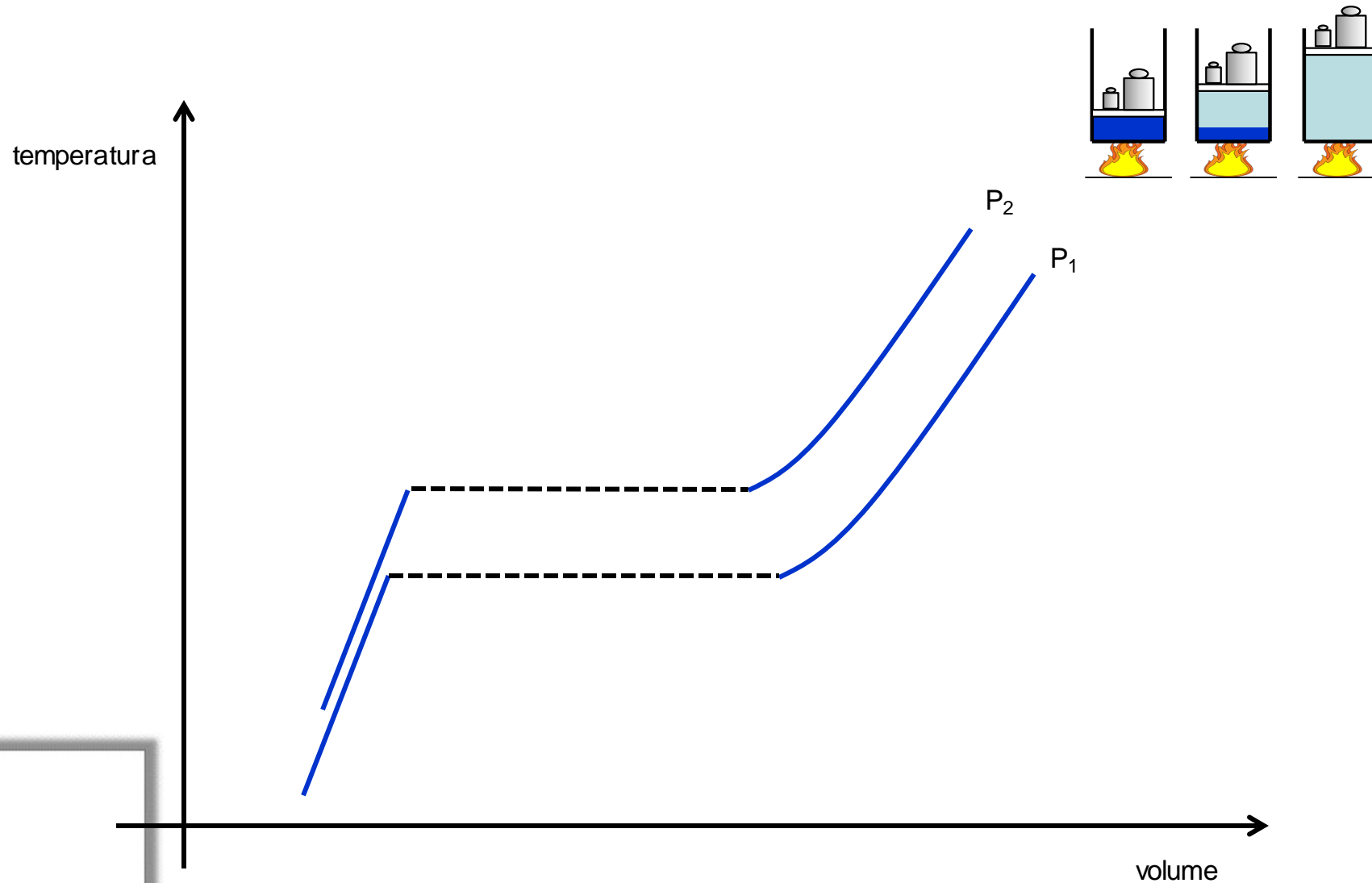


- ✓ Fase sólida: seu volume tem forma própria
- ✓ Fase líquida: ocupa parcialmente o volume do recipiente
- ✓ Fase gasosa: ocupa totalmente o volume do recipiente

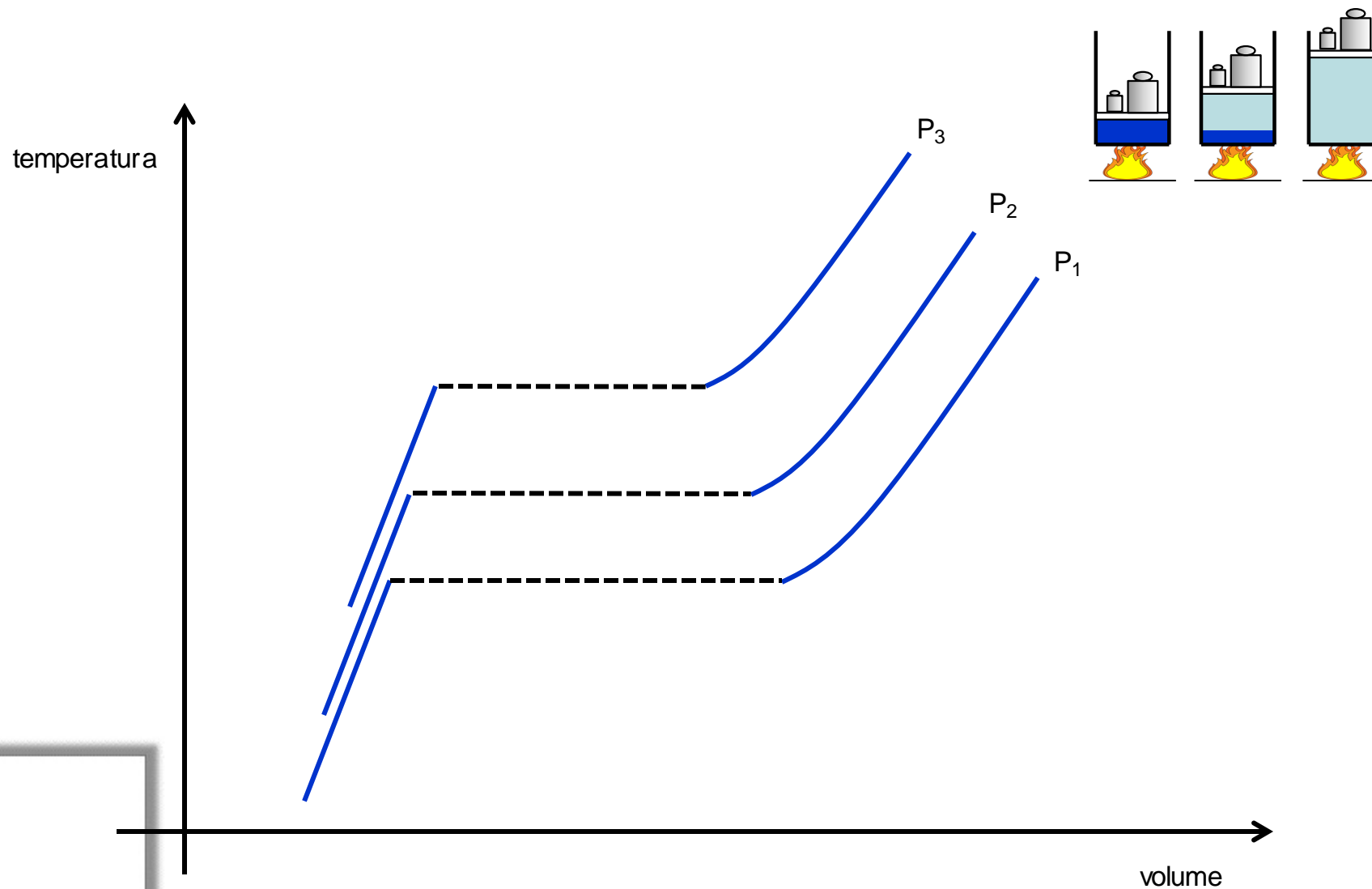
# Construção empírica do diagrama de equilíbrio



# Construção empírica do diagrama de equilíbrio

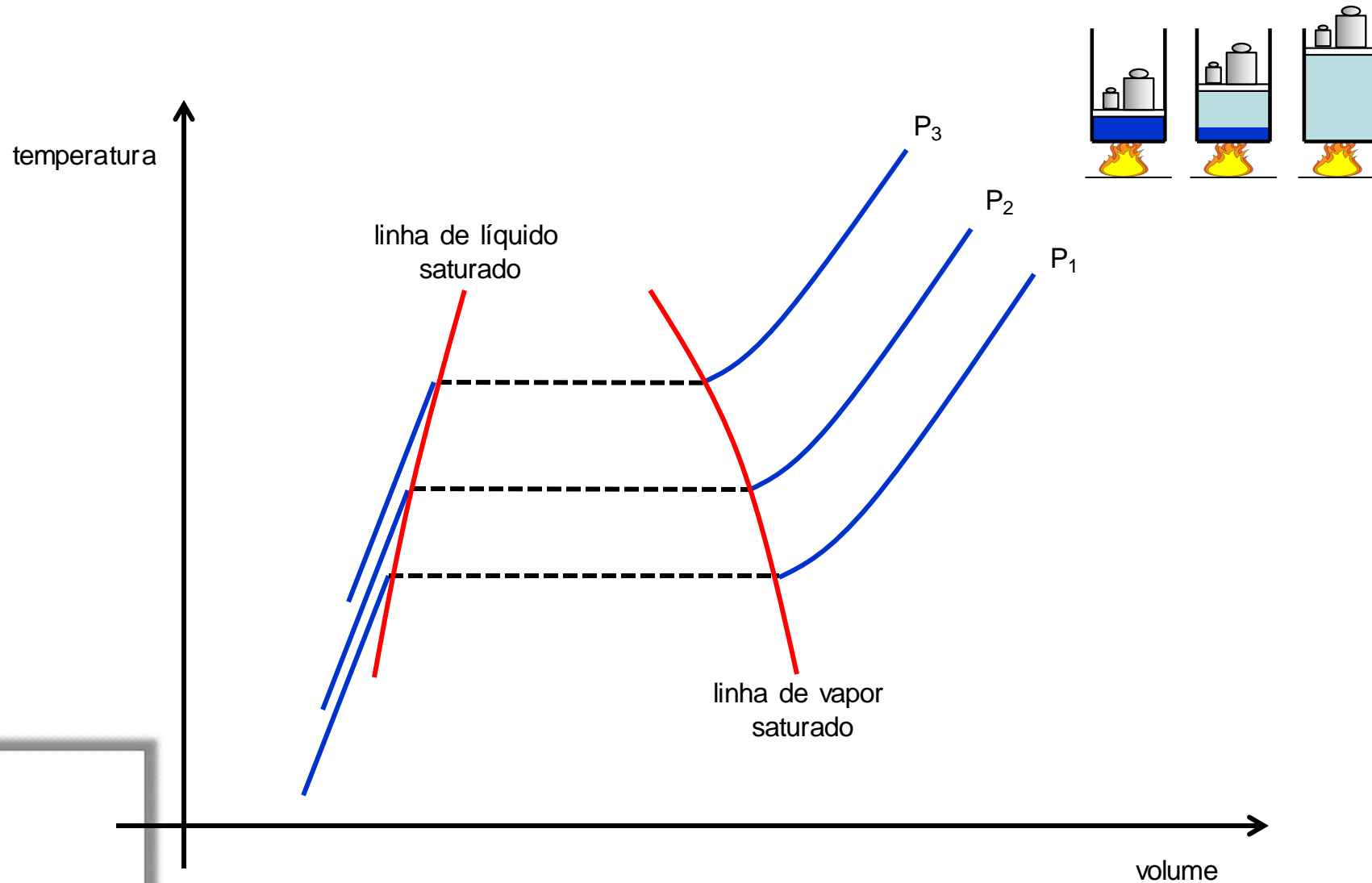


# Construção empírica do diagrama de equilíbrio

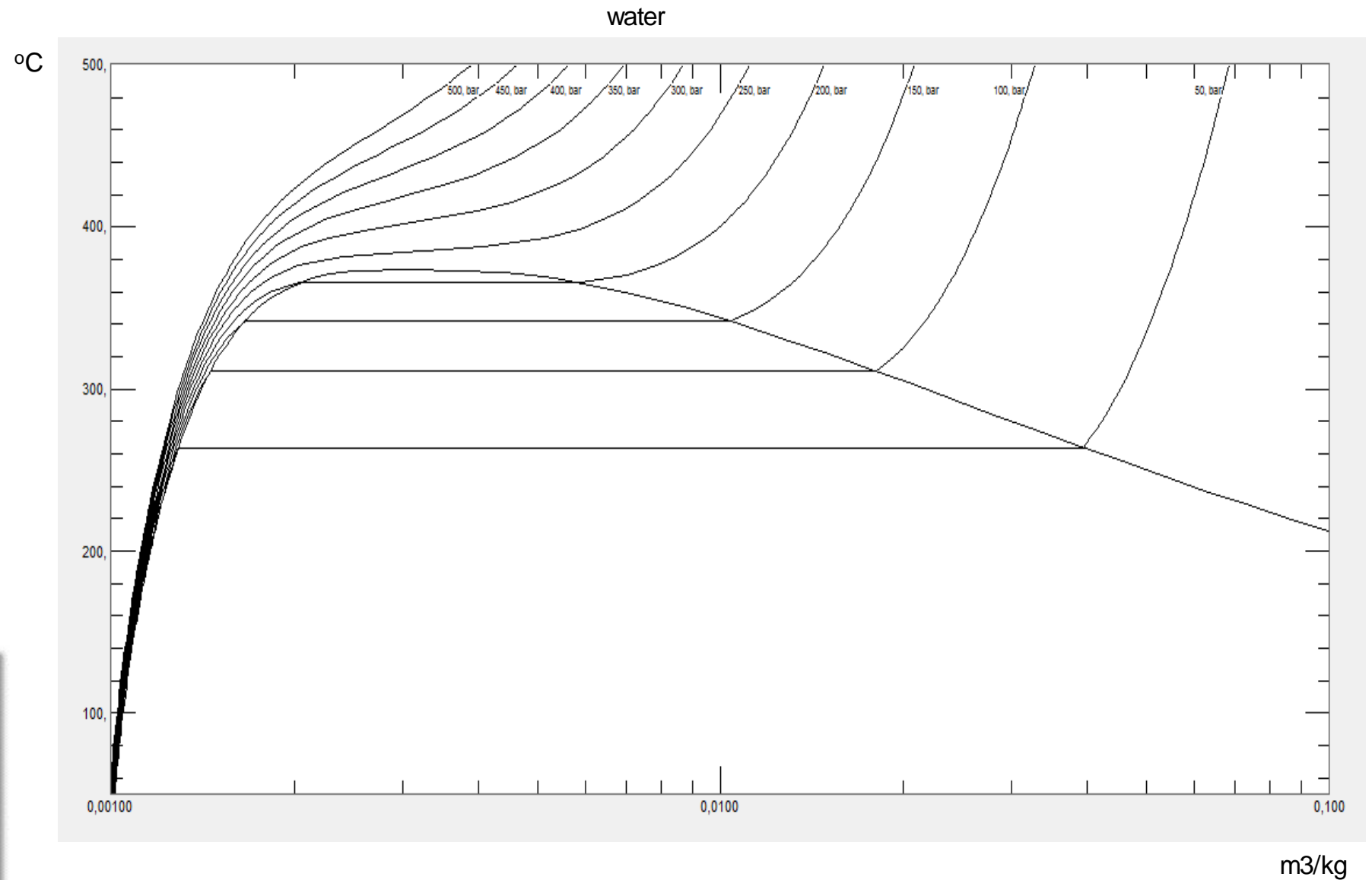




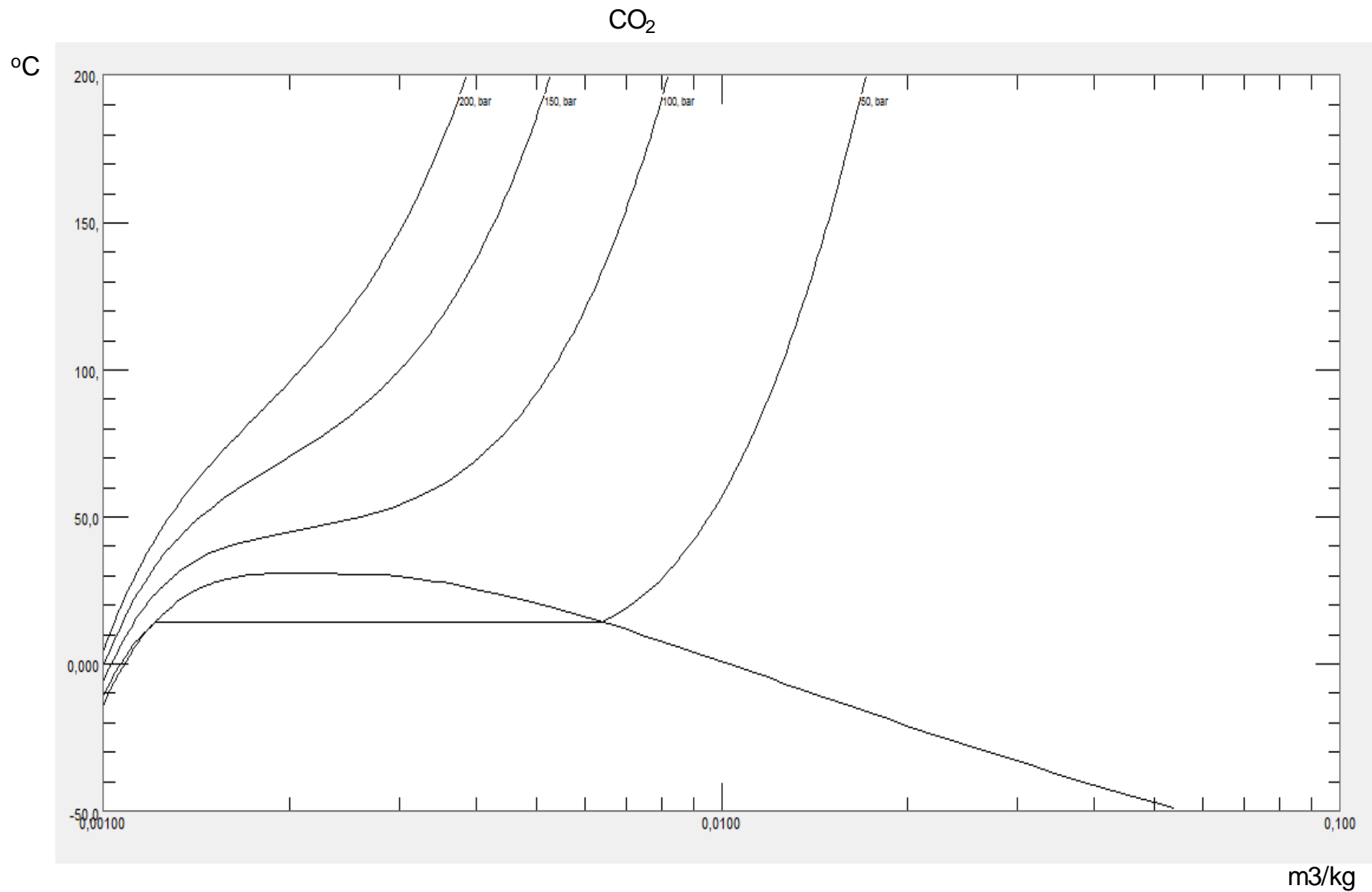
# Construção empírica do diagrama de equilíbrio

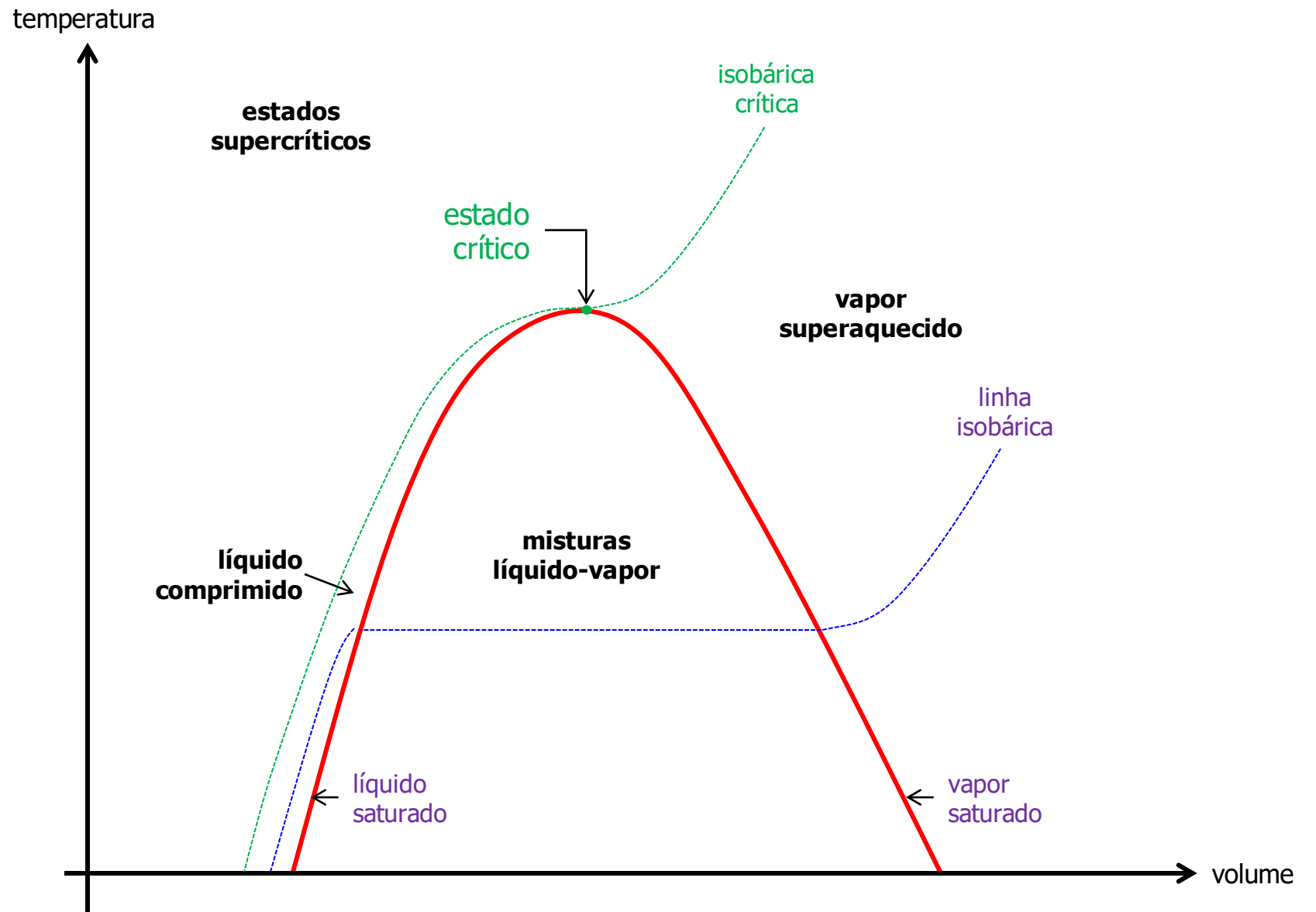


# Diagrama de equilíbrio da água (Refprop)

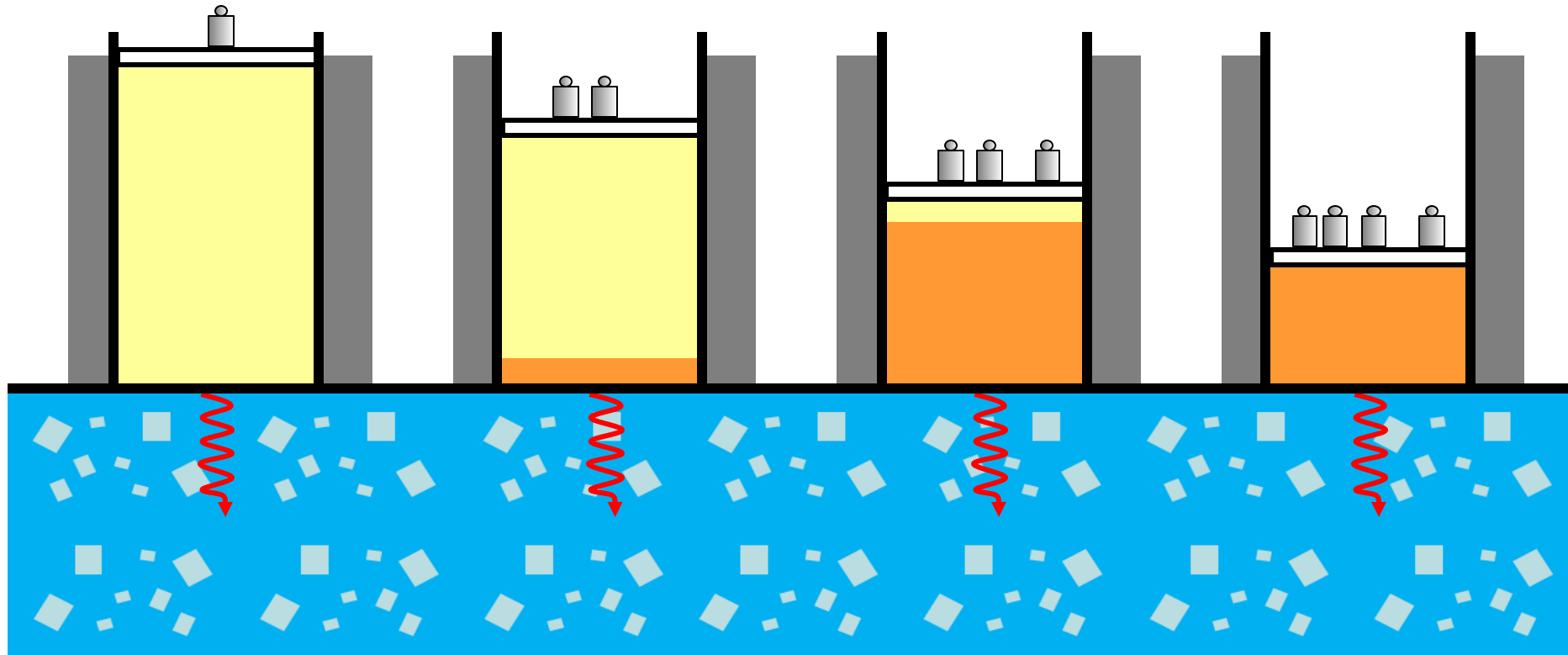


# Diagrama de equilíbrio do CO<sub>2</sub> (Refprop)

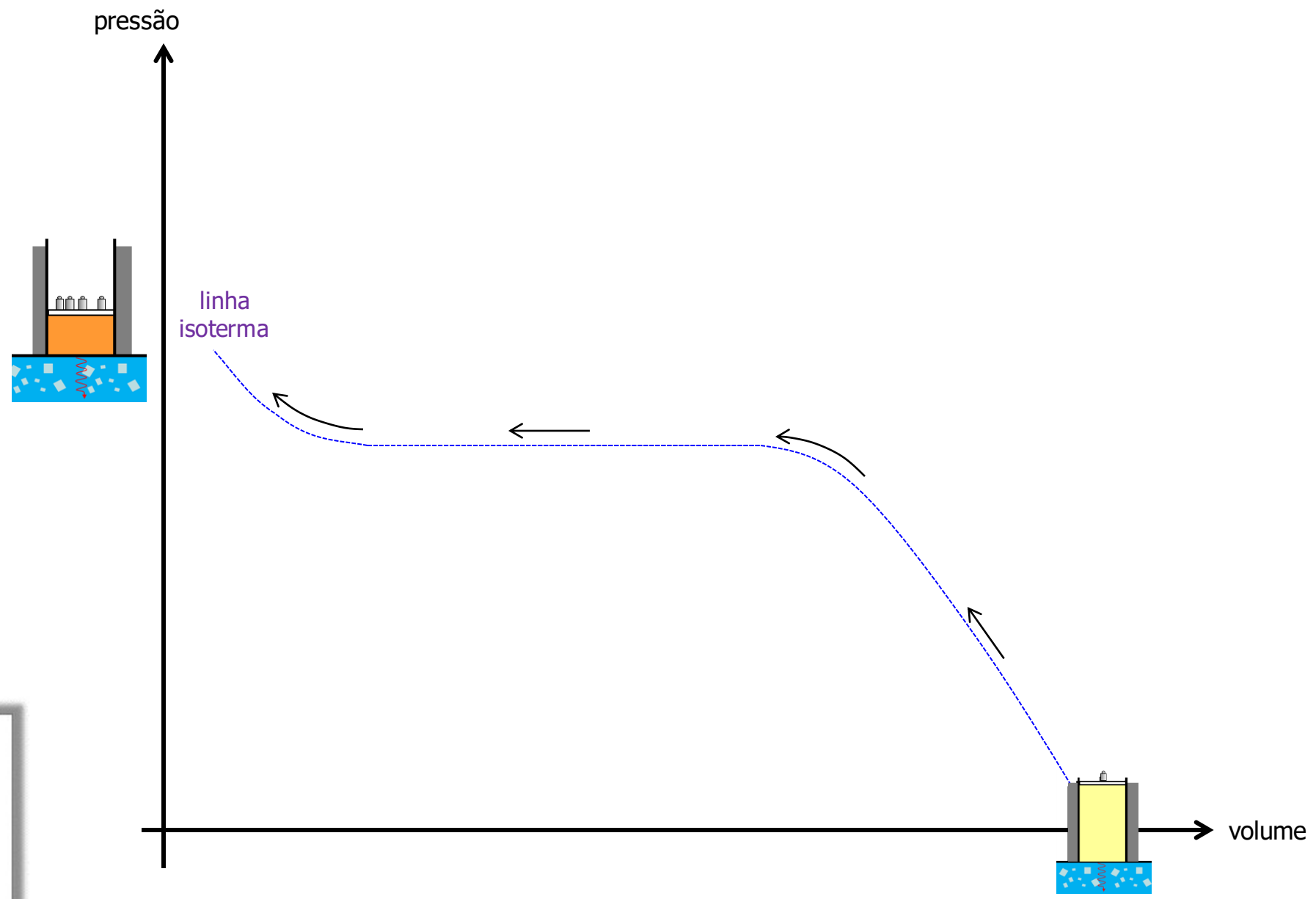


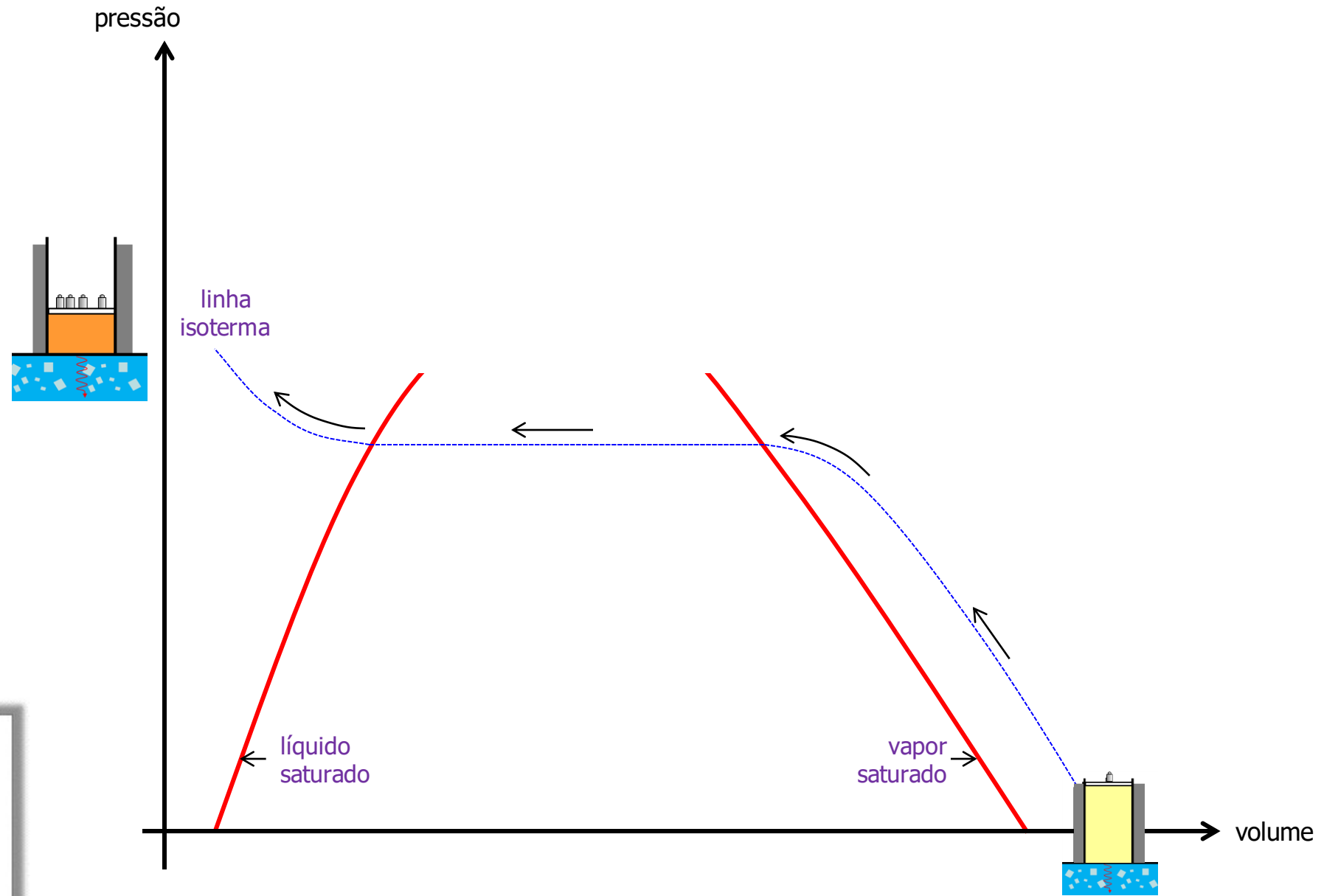


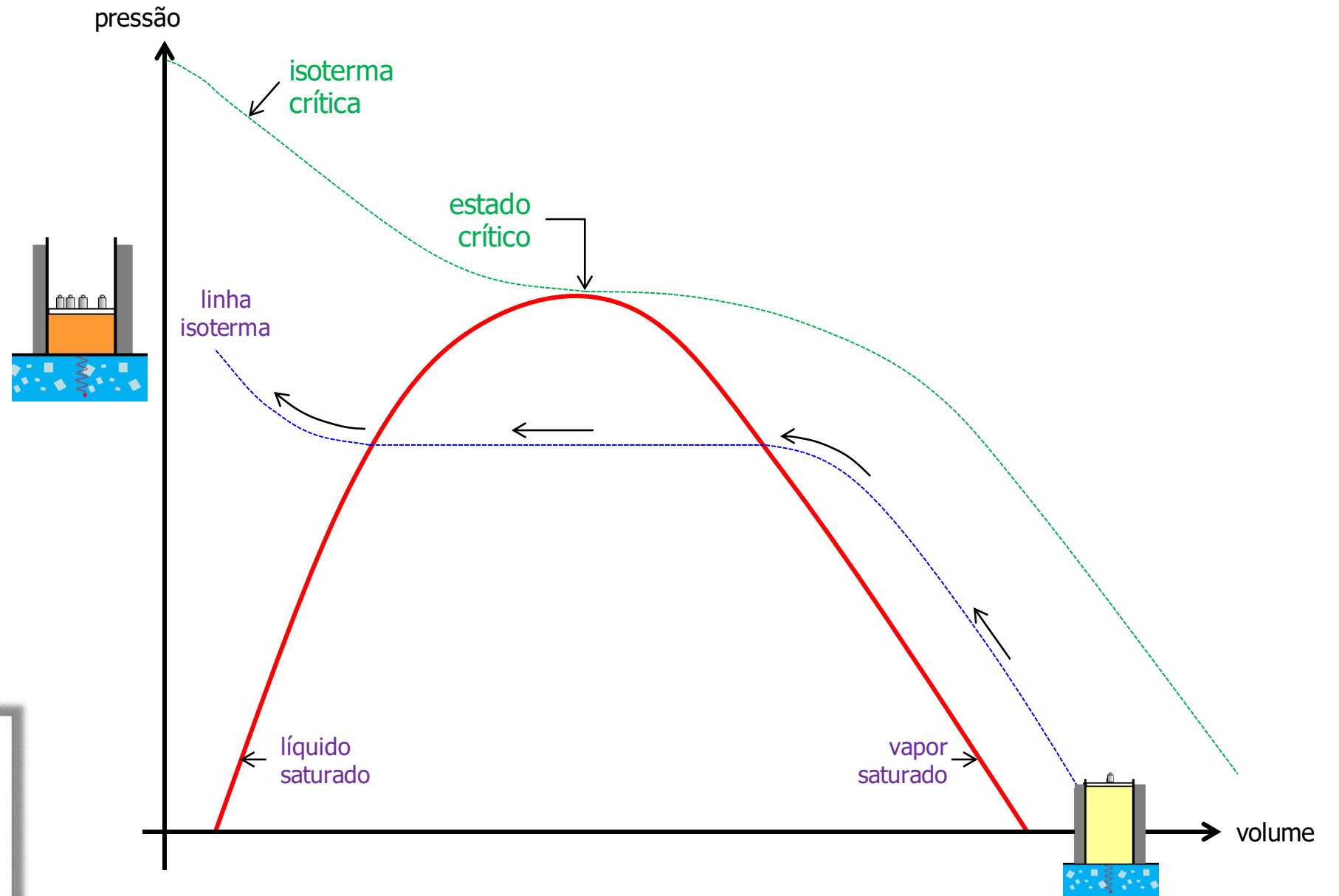
# Fases de uma substância pura, pressurização a $T = cte$



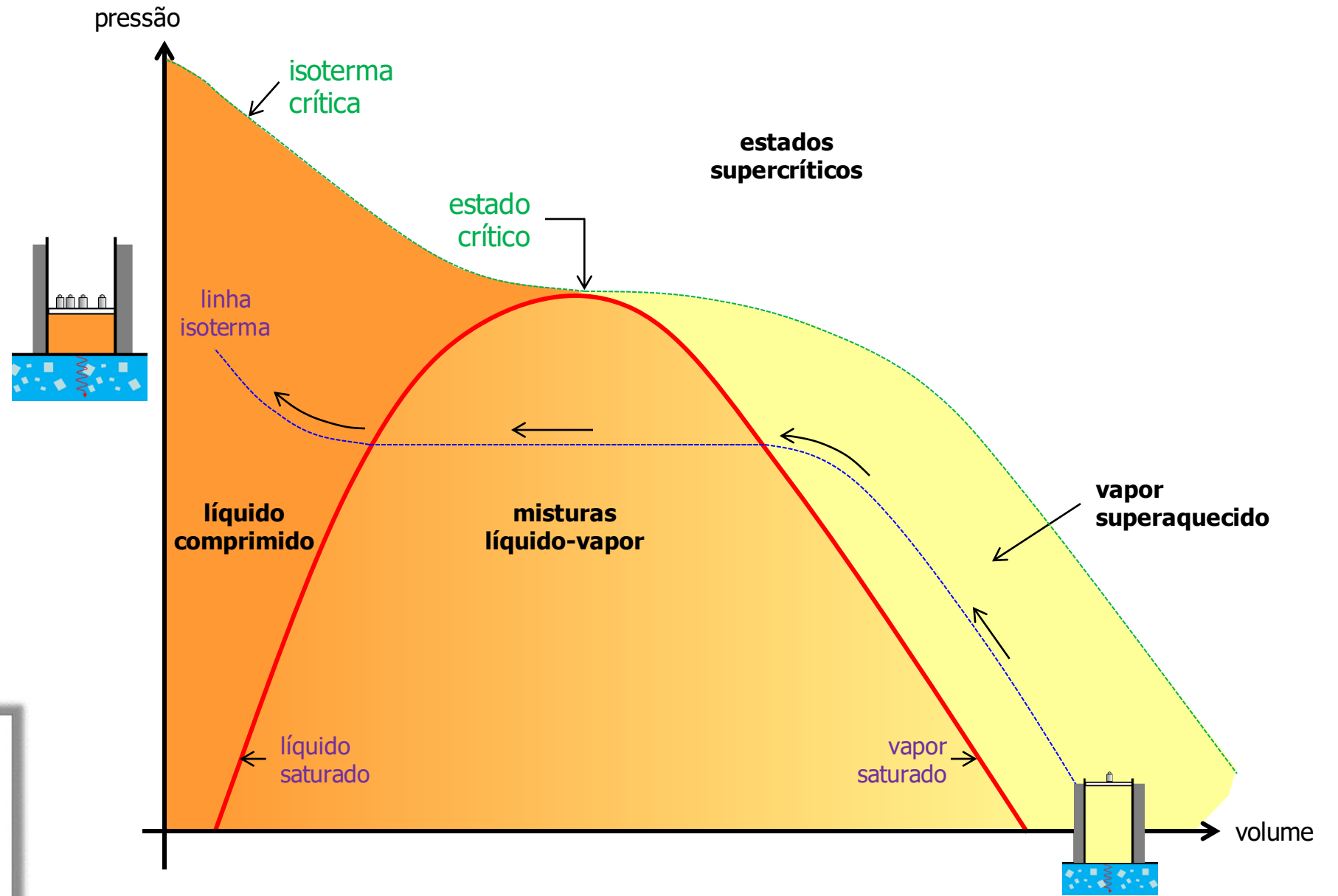
Meio com capacidade infinita de absorver de calor, i.e absorve calor sem alterar sua temperatura.





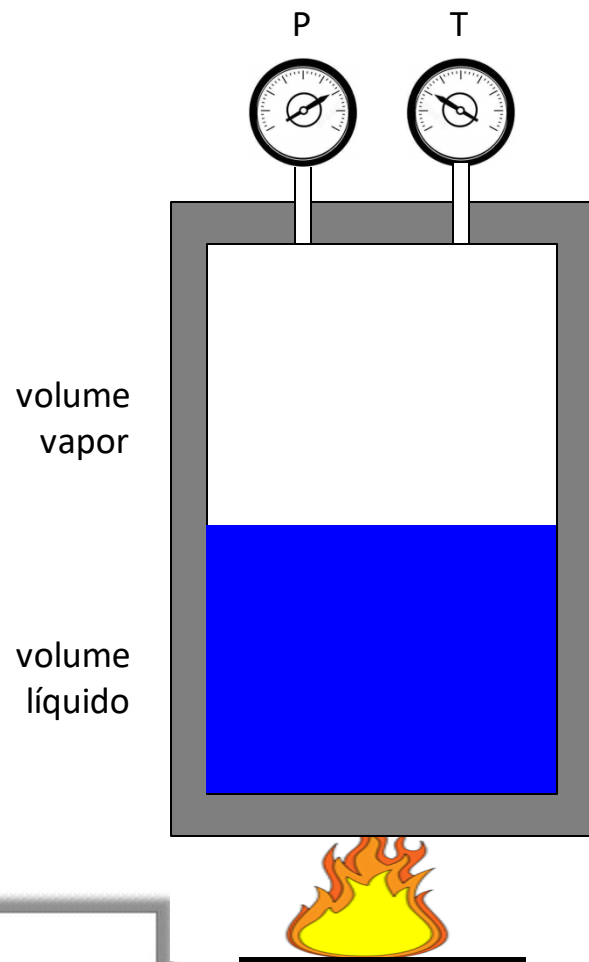






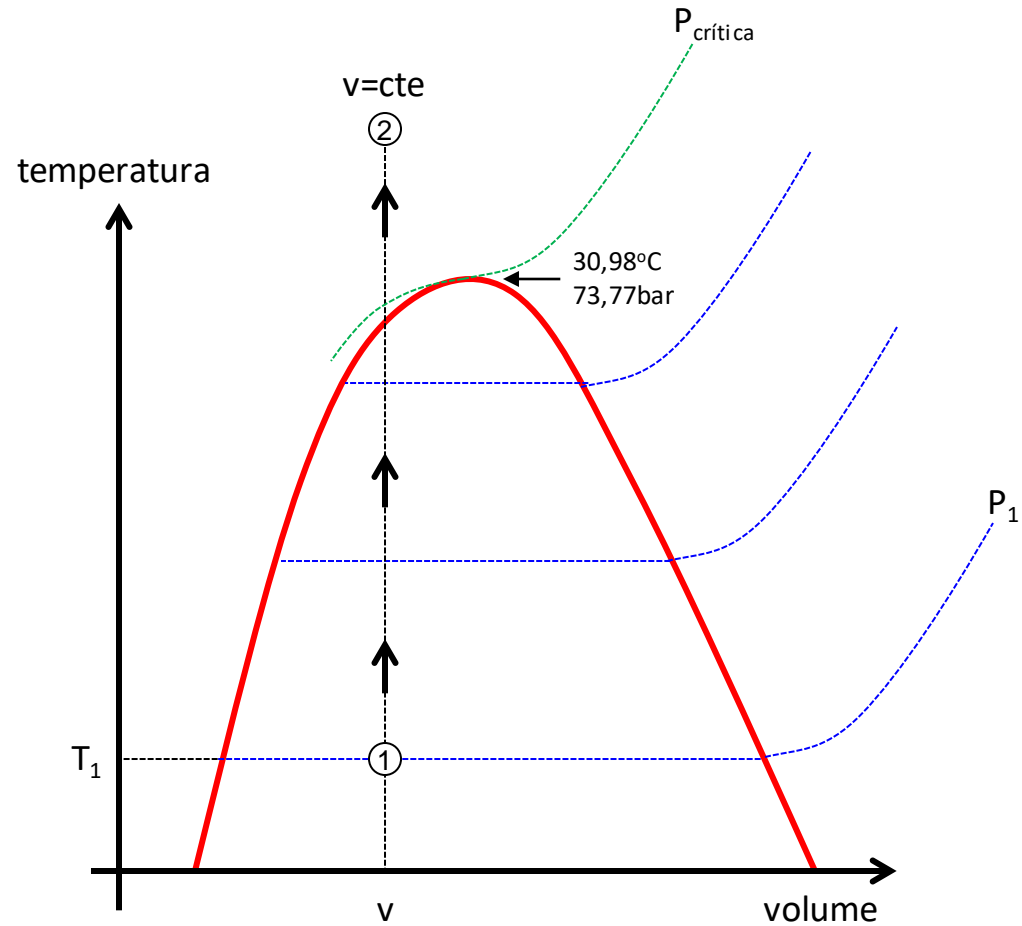
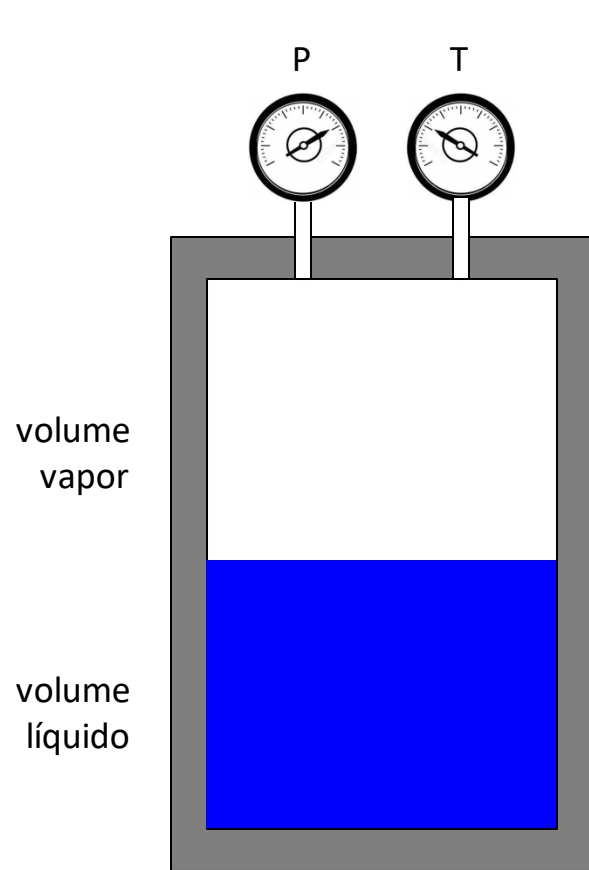
**Aplicação:**  
sistema de extração com  
CO<sub>2</sub> supercrítico

# Transformação isocórica ( $v = \text{cte}$ )



$$X \stackrel{\text{def}}{=} \frac{m_{\text{vap}}}{m_{\text{liq}} + m_{\text{vap}}}$$

# Transformação isocórica (v=cte)



$$x \stackrel{\text{def}}{=} \frac{m_{vap}}{m_{liq} + m_{vap}}$$



$$\left\{ \begin{array}{l} v = x \cdot v_{vap} + (1 - x) \cdot v_{liq} \\ \rho = x \cdot \rho_{vap} + (1 - x) \cdot \rho_{liq} \end{array} \right.$$

# Variação de $\rho_{\text{liq}}$ e $\rho_{\text{vap}}$ com a pressão e a temperatura...

REFPROP (carbon dioxide) - NIST Reference Fluid Properties

File Edit Options Substance Calculate Plot Window Help Cautions

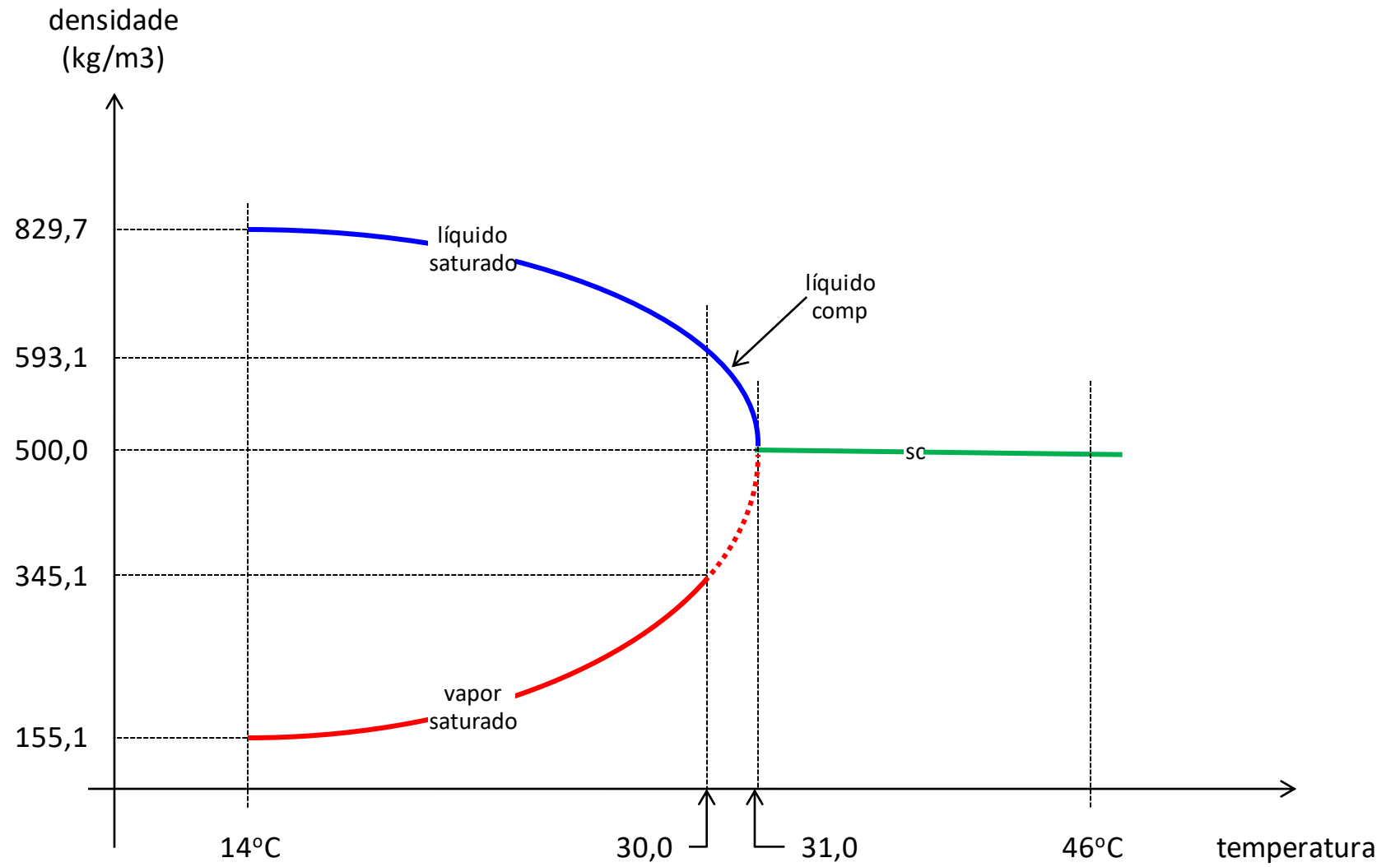
11: carbon dioxide rho = 500, kg/m<sup>3</sup>

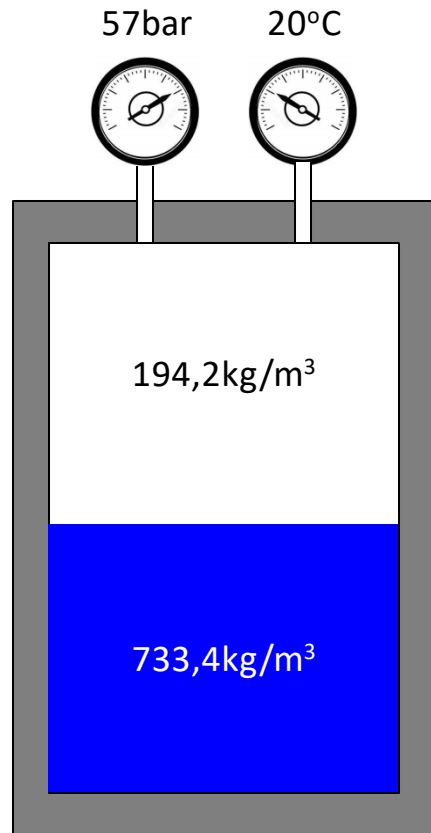
	Temperature (°C)	Pressure (bar)	Density (kg/m <sup>3</sup> )	Liquid Density (kg/m <sup>3</sup> )	Vapor Density (kg/m <sup>3</sup> )	Volume (m <sup>3</sup> /kg)	Liquid Volume (m <sup>3</sup> /kg)	Vapor Volume (m <sup>3</sup> /kg)
1	14,000	49,658	500,00	829,70	155,11	0,0020000	0,0012053	0,0064472
2	15,000	50,871	500,00	821,21	160,73	0,0020000	0,0012177	0,0062216
3	16,000	52,108	500,00	812,41	166,66	0,0020000	0,0012309	0,0060003
4	17,000	53,368	500,00	803,27	172,93	0,0020000	0,0012449	0,0057828
5	18,000	54,651	500,00	793,76	179,57	0,0020000	0,0012598	0,0055688
6	19,000	55,958	500,00	783,81	186,64	0,0020000	0,0012758	0,0053578
7	20,000	57,291	500,00	773,39	194,20	0,0020000	0,0012930	0,0051493
8	21,000	58,648	500,00	762,40	202,32	0,0020000	0,0013116	0,0049427
9	22,000	60,031	500,00	750,77	211,08	0,0020000	0,0013320	0,0047375
10	23,000	61,440	500,00	738,36	220,62	0,0020000	0,0013543	0,0045326
11	24,000	62,877	500,00	725,02	231,10	0,0020000	0,0013793	0,0043272
12	25,000	64,342	500,00	710,50	242,73	0,0020000	0,0014075	0,0041198
13	26,000	65,837	500,00	694,46	255,86	0,0020000	0,0014400	0,0039083
14	27,000	67,361	500,00	676,36	271,01	0,0020000	0,0014785	0,0036898
15	28,000	68,918	500,00	655,28	289,11	0,0020000	0,0015261	0,0034589
16	29,000	70,509	500,00	629,36	312,03	0,0020000	0,0015889	0,0032048
17	30,000	72,137	500,00	593,31	345,10	0,0020000	0,0016855	0,0028977
18	30,963	73,748	500,00	500,00	437,72	0,0020000	0,0020000	0,0022846
19	31,000	73,812	500,00	500,00	Undefined	0,0020000	0,0020000	Undefined
20	32,000	75,609	500,00	500,00	Undefined	0,0020000	0,0020000	Undefined

**Variação de  $\rho_{\text{liq}}$  e  $\rho_{\text{vap}}$  com a pressão e a temperatura...**

**REFPROP...**

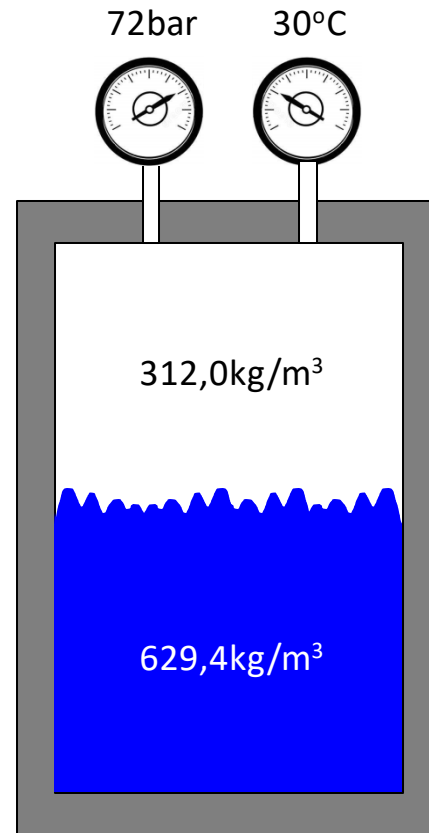
# Varição de $\rho_{liq}$ e $\rho_{vap}$ com a pressão e a temperatura...





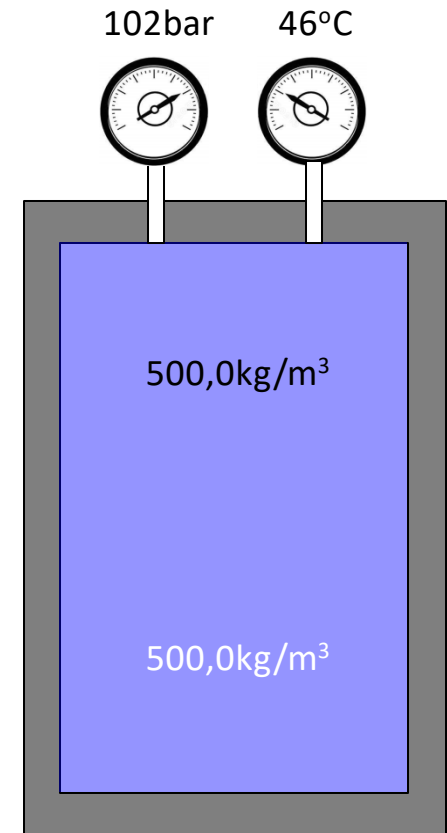
$$x = \frac{500,0 - 733,4}{194,2 - 733,4}$$

$$x = 0,433$$



$$x = \frac{500,0 - 629,4}{312,0 - 629,4}$$

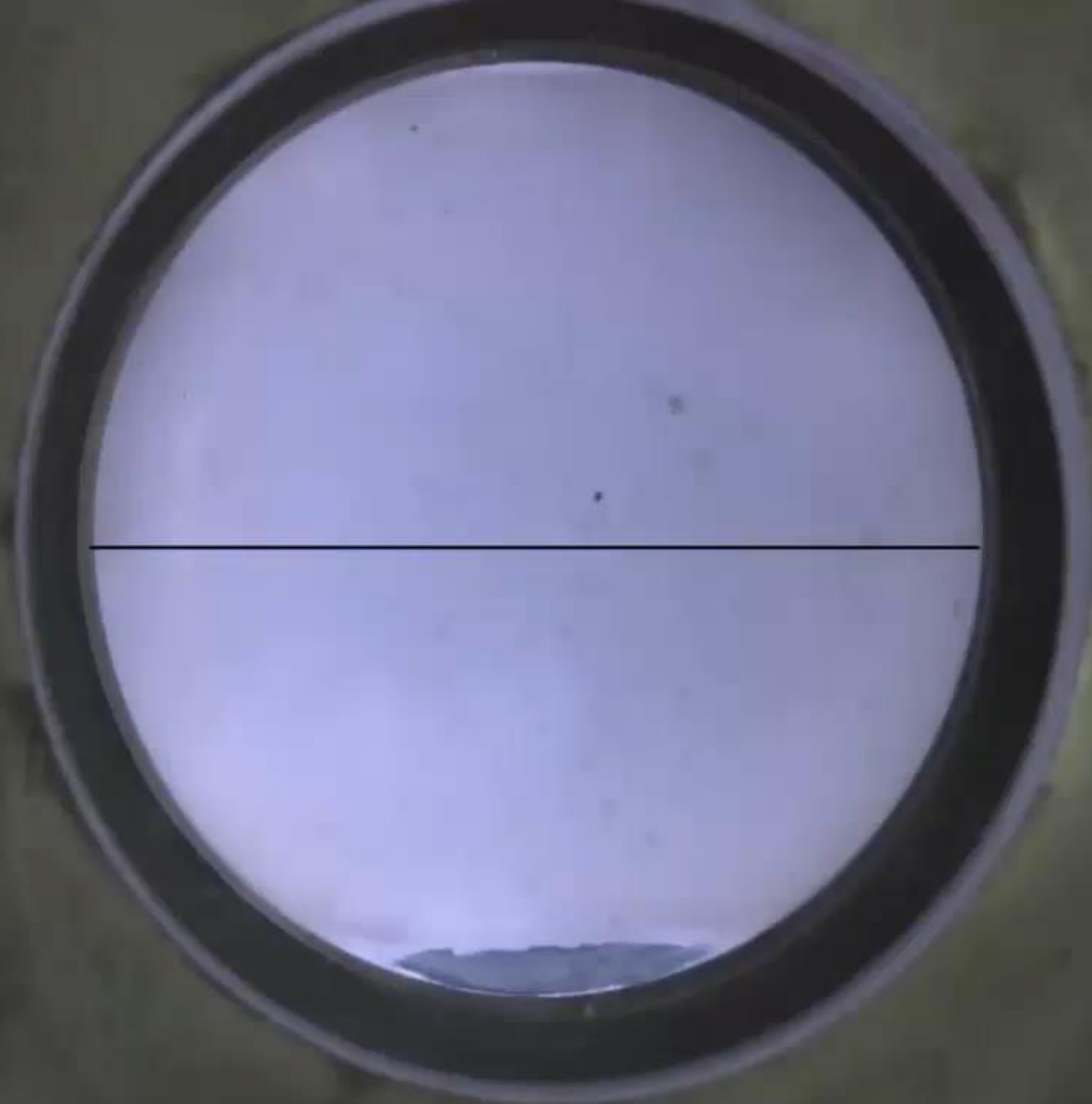
$$x = 0,408$$



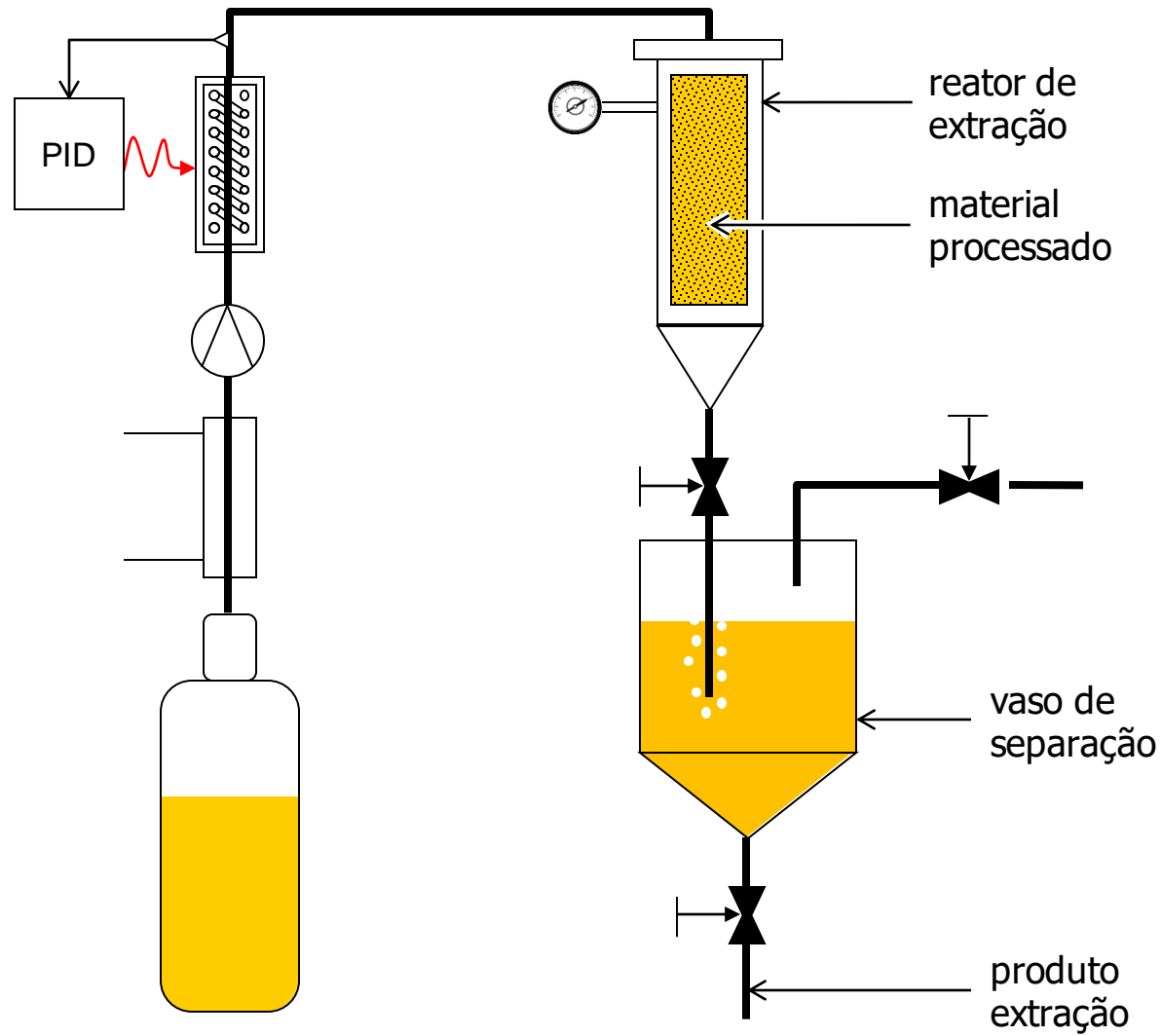
$$x = \frac{500,0 - 500,0}{500,0 - 500,0}$$

$$x \stackrel{H}{=} 0,408$$





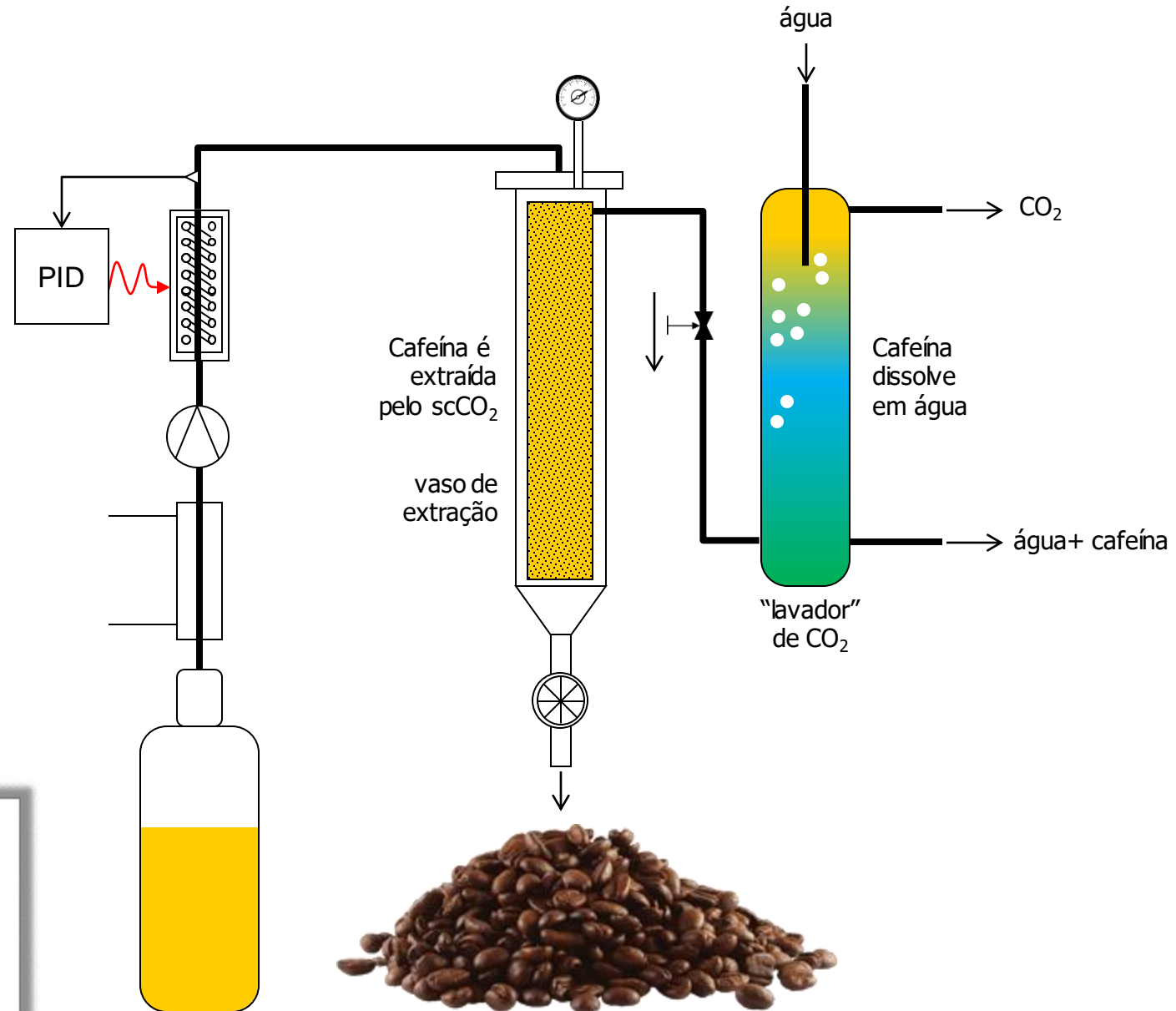
# Sistema de extração com scCO<sub>2</sub>



# Produção de óleos essenciais

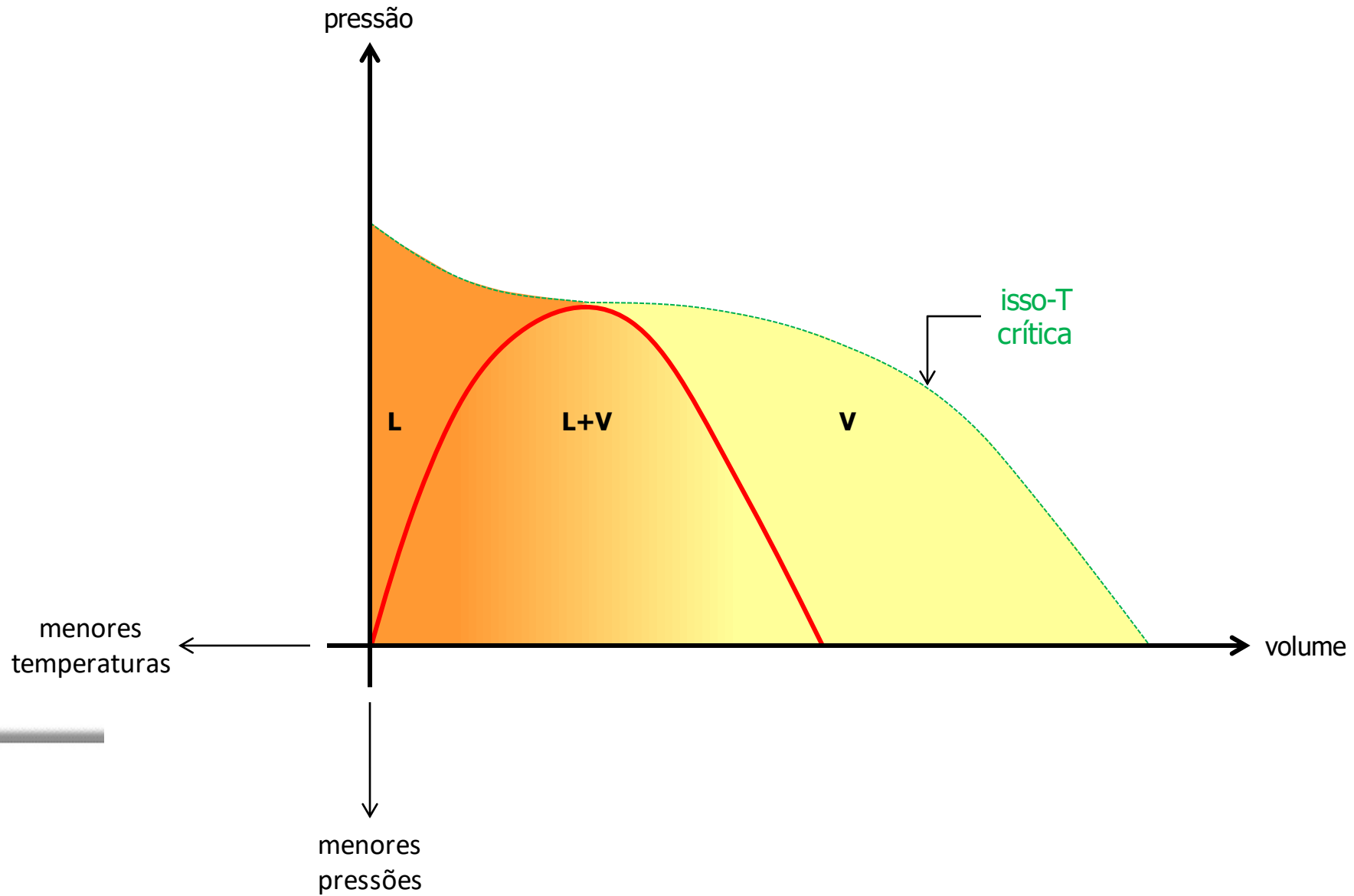


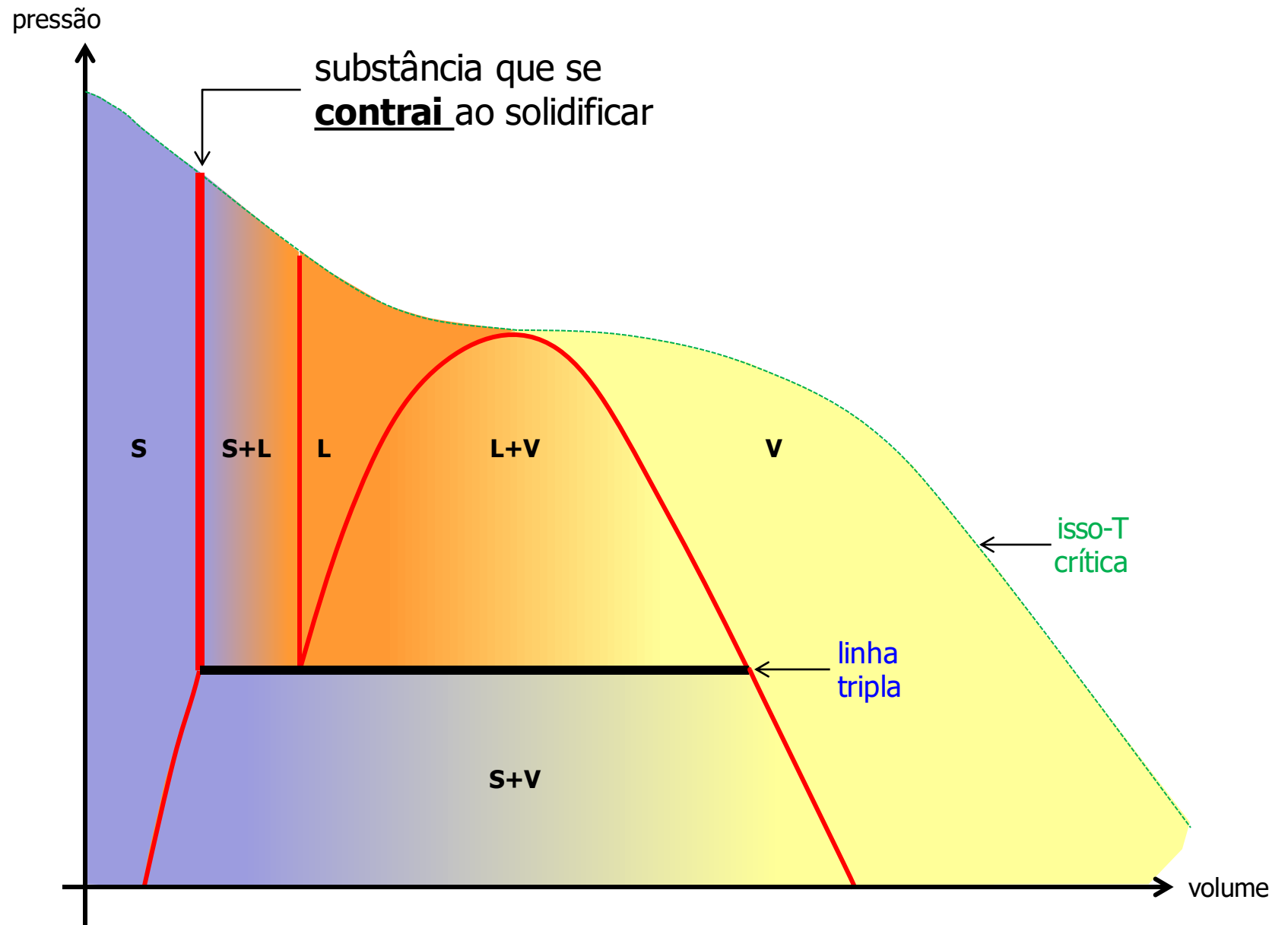
# Grãos de café descafeinado

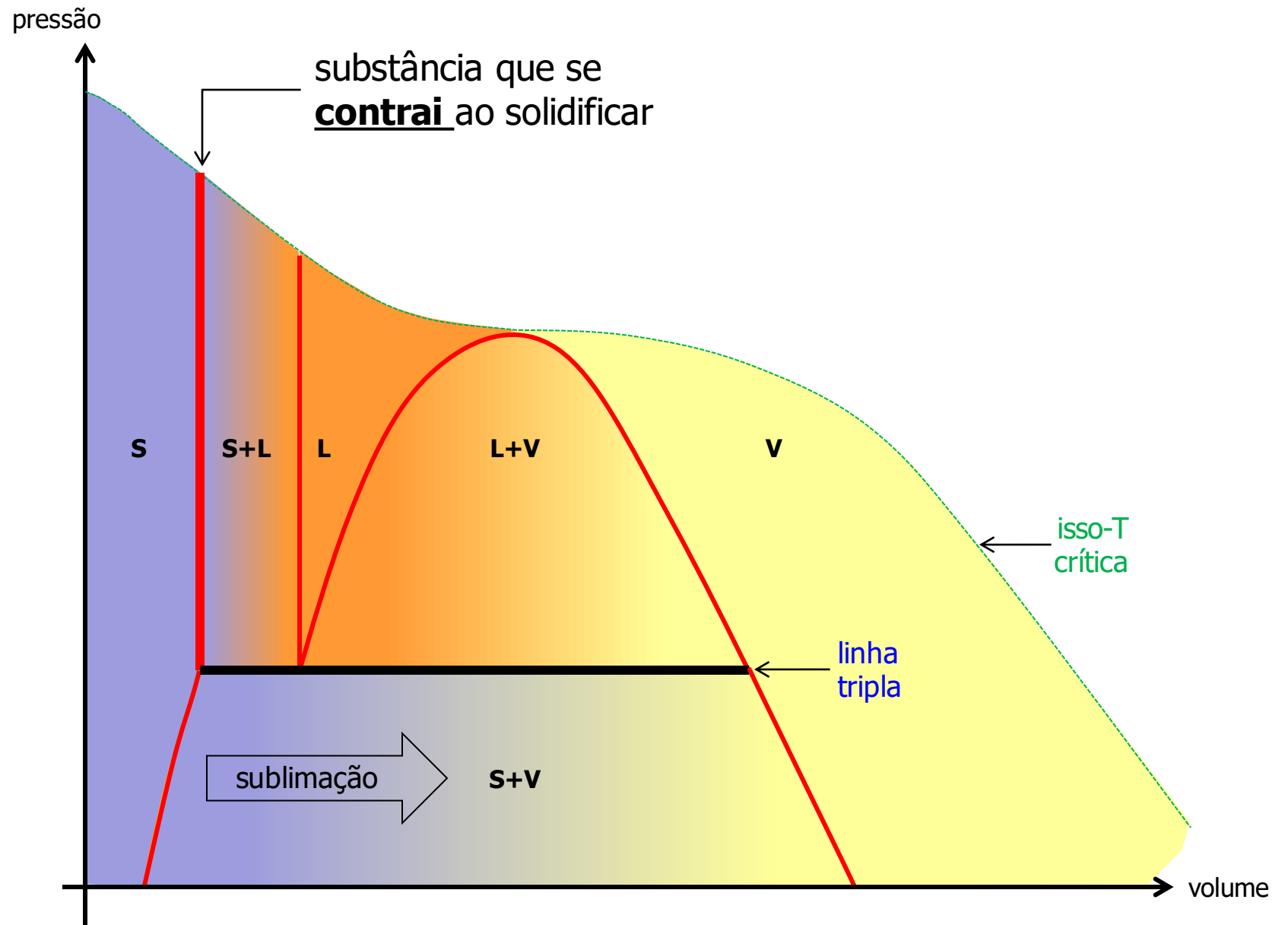


# Diagramas de equilibrio sólido-líquido-vapor

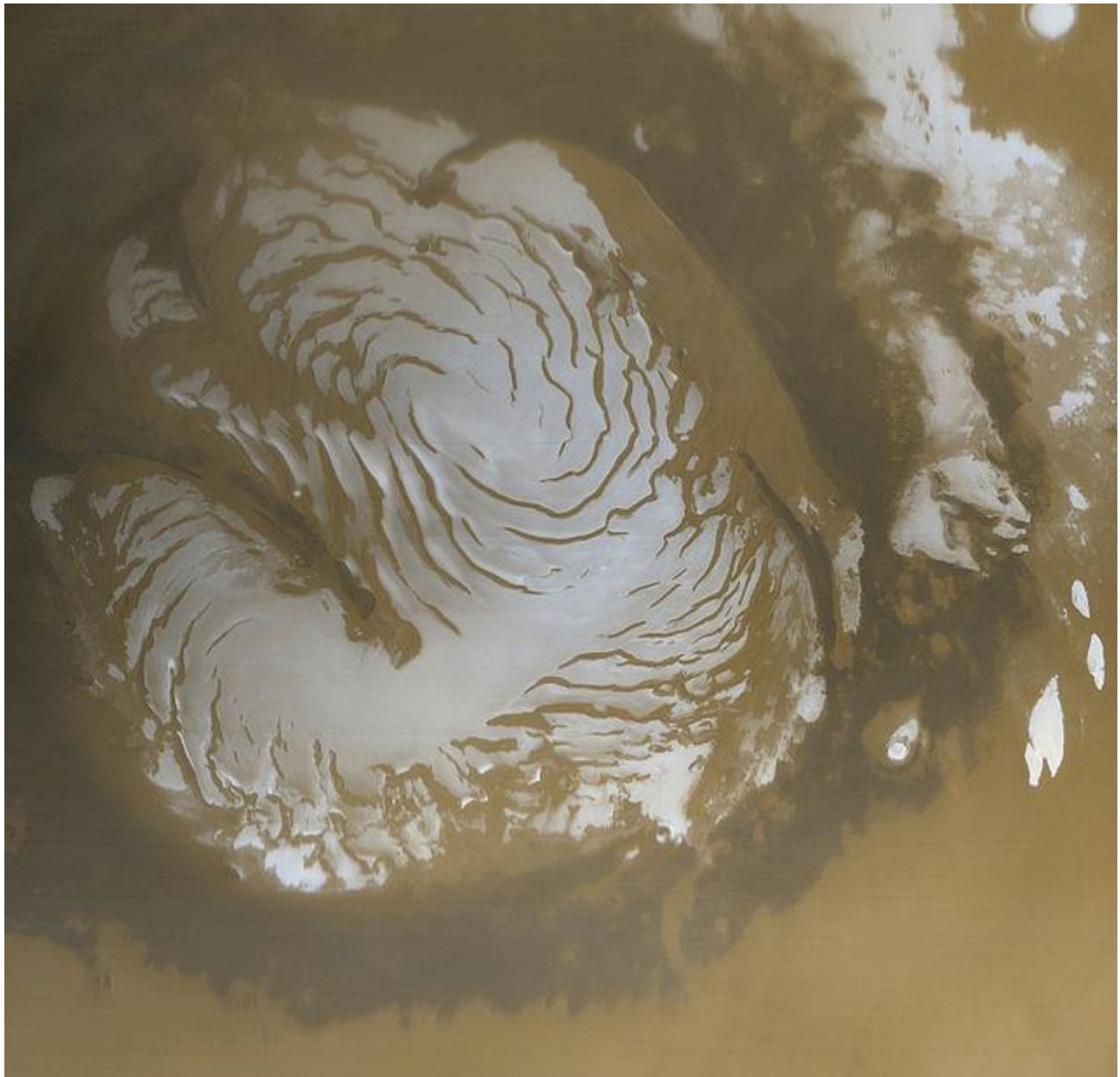




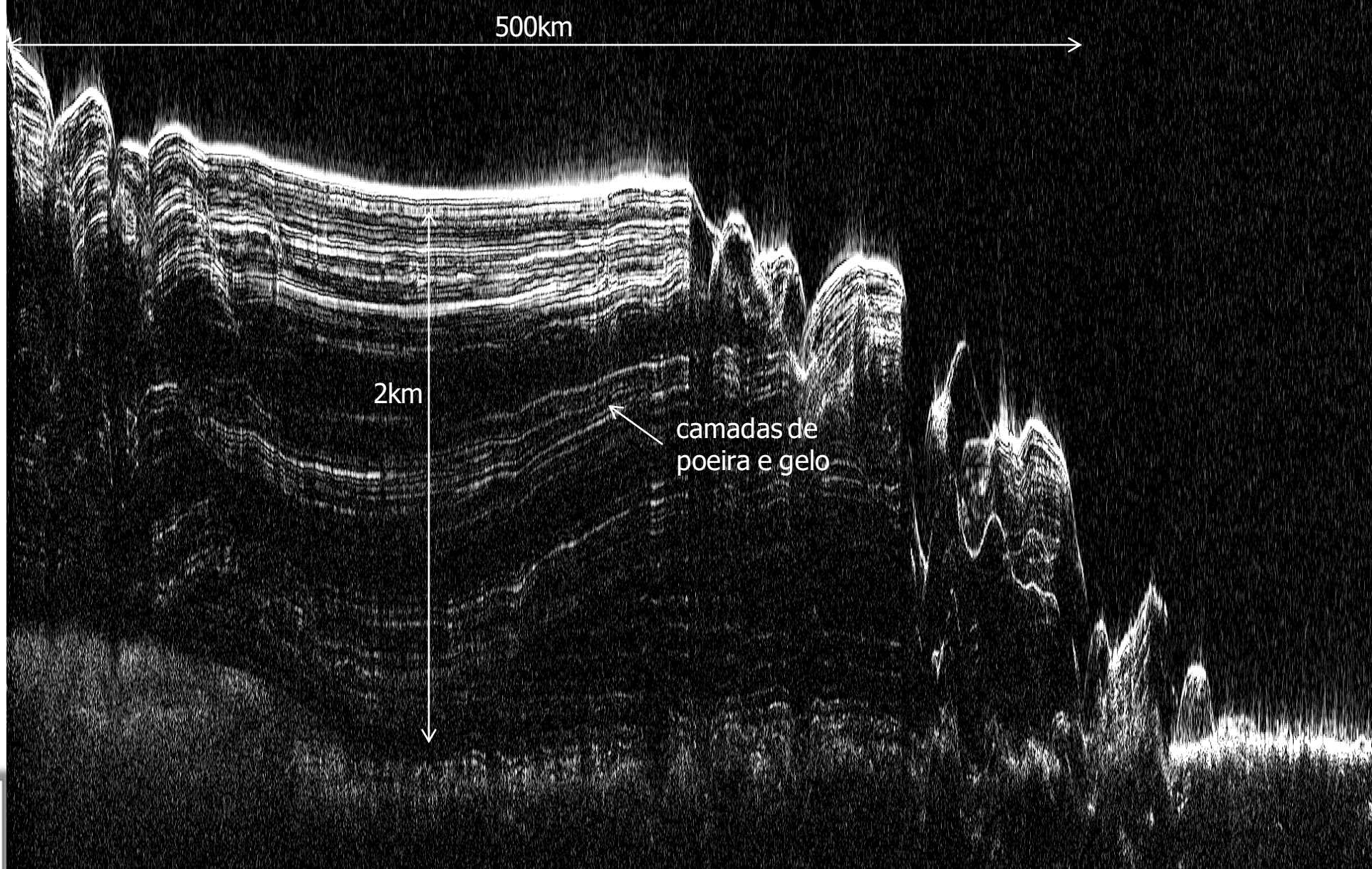








Mars Global Surveyor  
March, 1999



Camada superficial de CO<sub>2</sub> forma-se no inverno e sublima “explosivamente” no verão. Isto gera ventos de ~400km/h que transportam partículas do solo, transportando-as por todo o planeta. (Mars Reconnaissance Orbiter)

Target Name:	Mars
Is a satellite of:	Sol (our sun)
Mission:	Mars Reconnaissance Orbiter (MRO)
Spacecraft:	Mars Reconnaissance Orbiter (MRO)
Instrument:	Shallow Subsurface Radar (SHARAD)
Product Size:	1936 x 939 pixels (w x h)
Produced By:	Italian Space Agency
Other Information:	JPL News Release 2010-180



Geleira do Lago Grey,  
Pq Nacional de Torres del Paine, 03/2013

## Retração das Geleiras



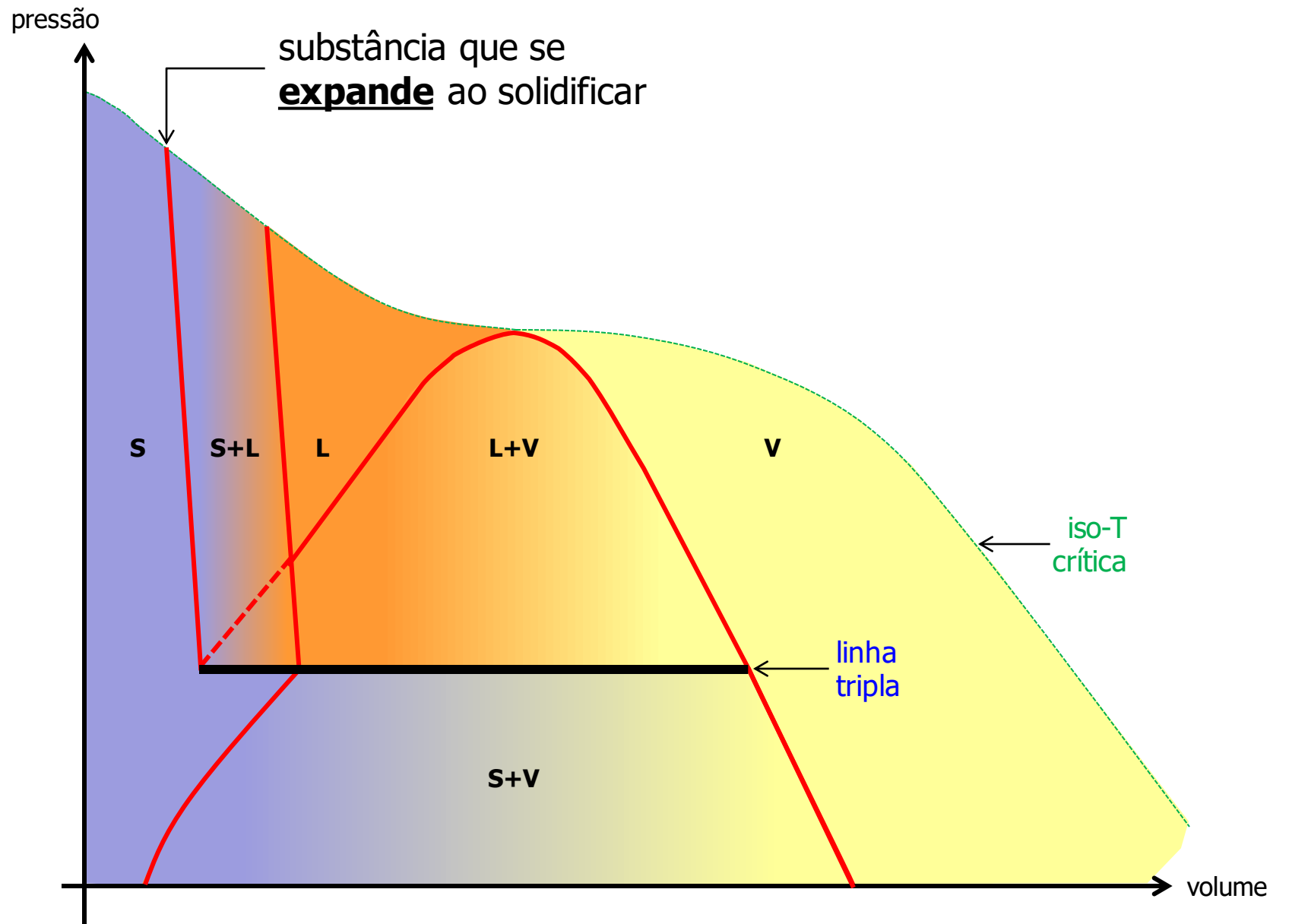
Glaciar Grey, Campo de Gelo Patagônico Sul

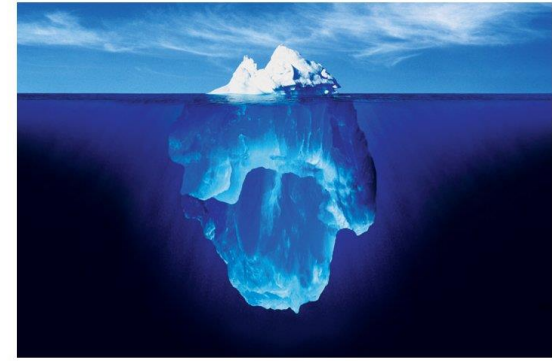
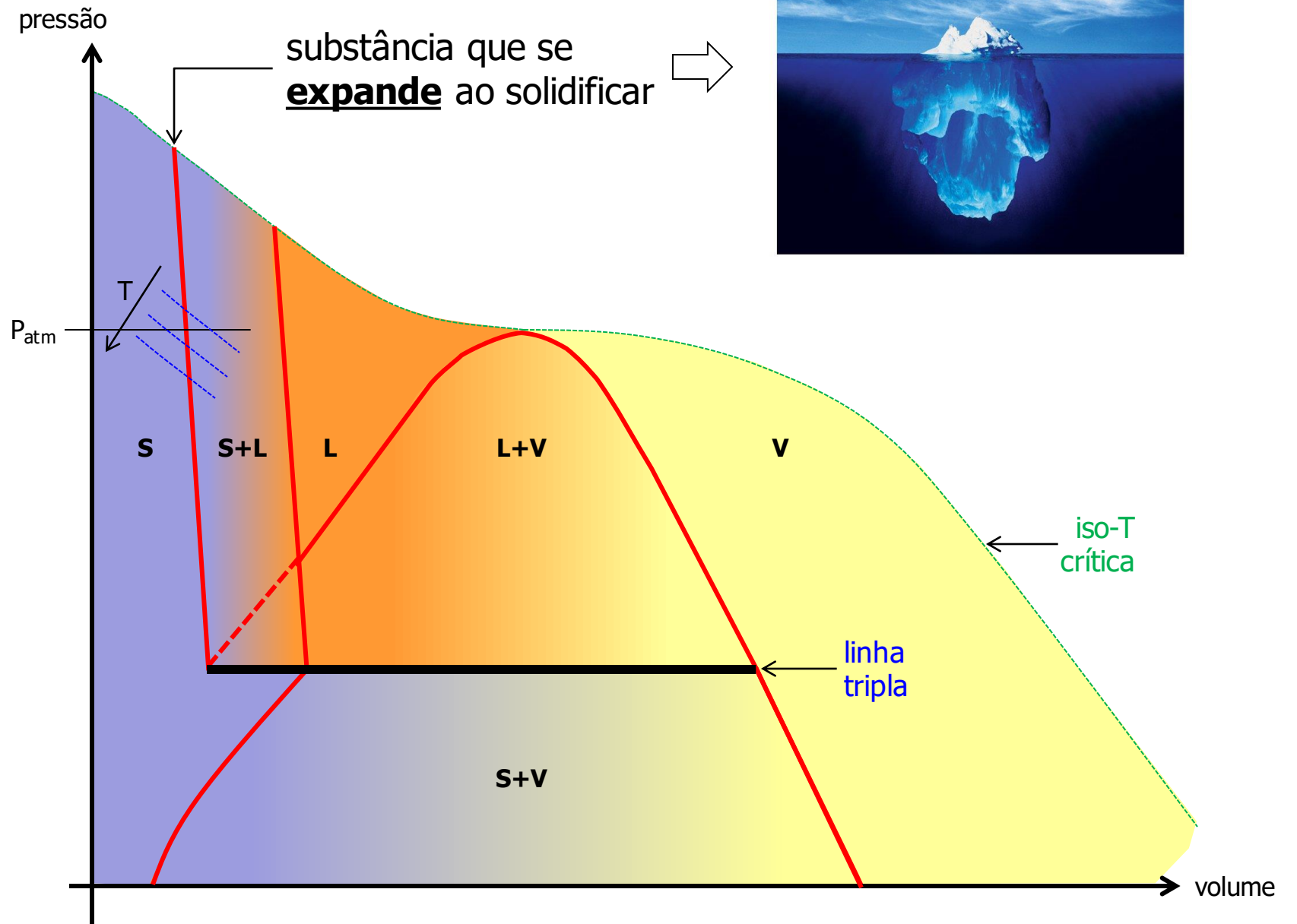
## Retração das Geleiras



Glaciar Grey, Campo de Gelo Patagônico Sul

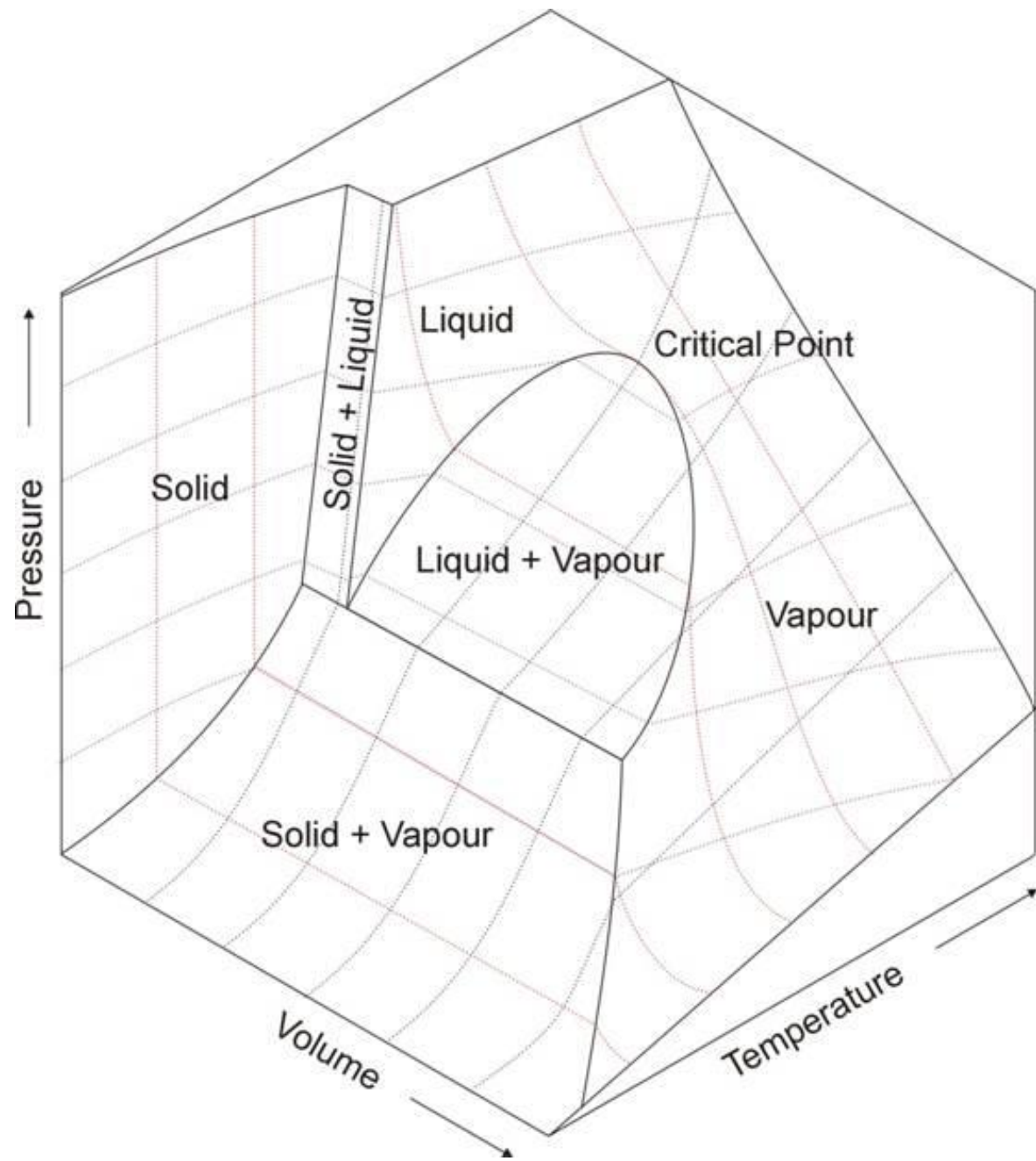


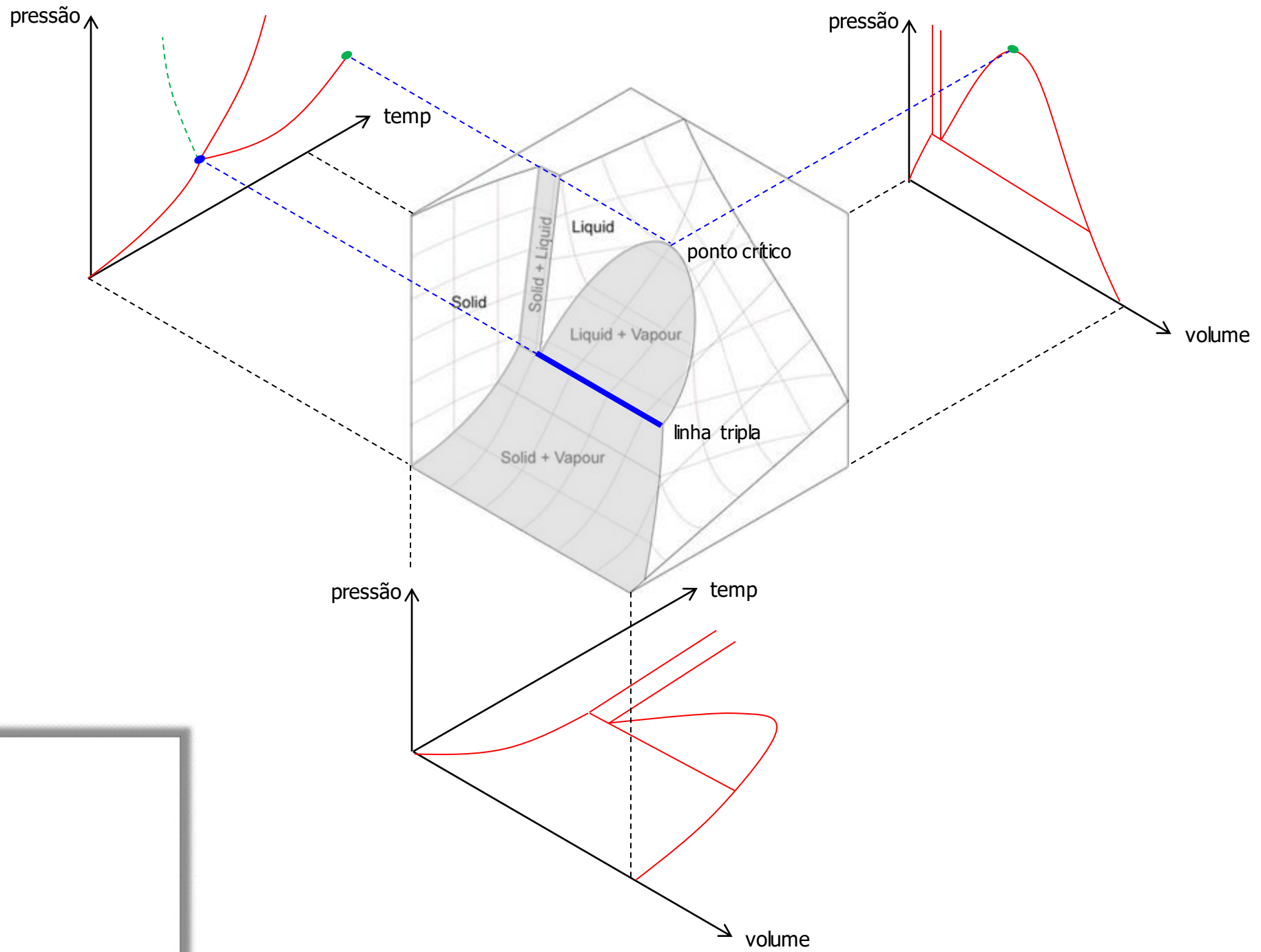




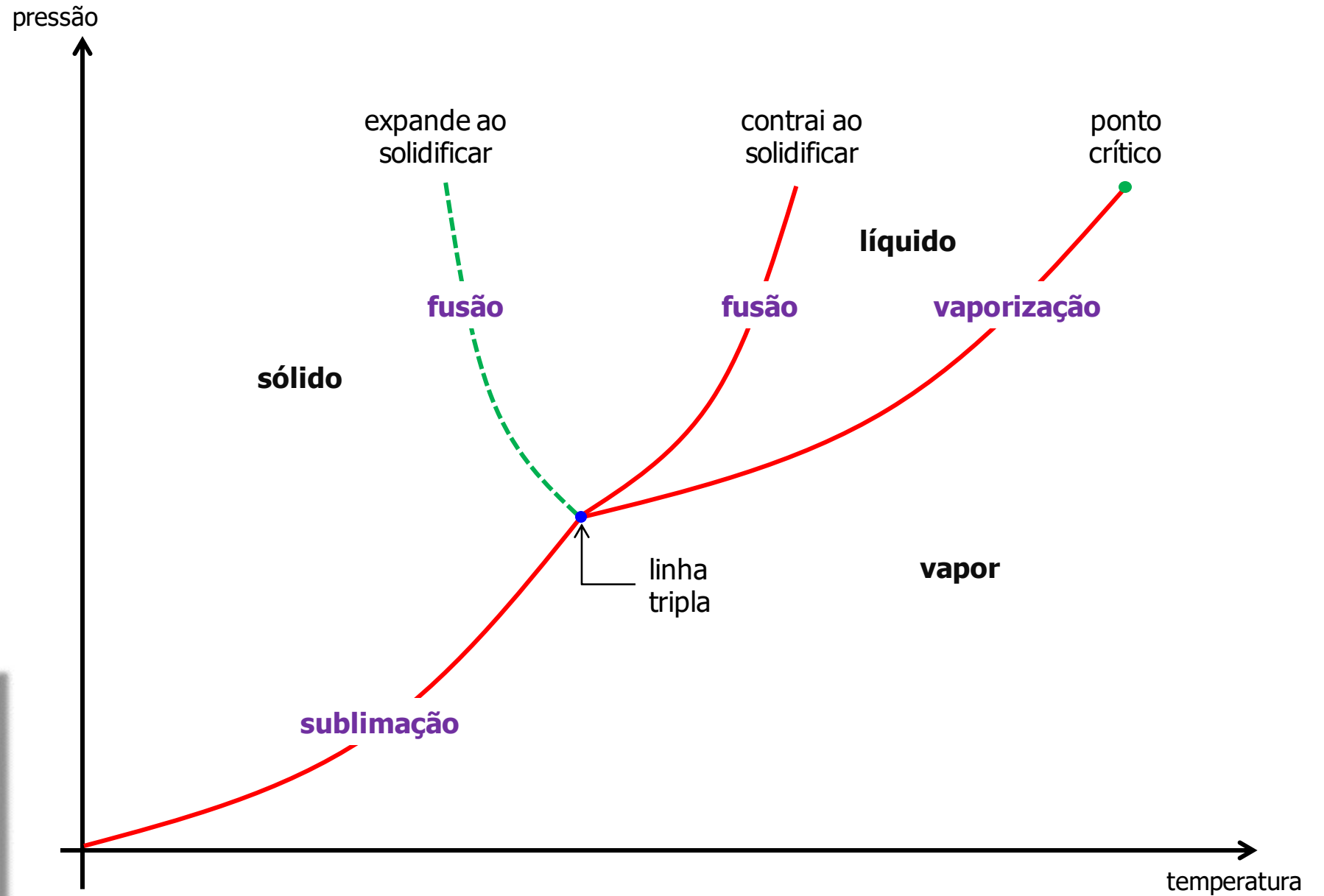


Superfície  $P \times v \times T$

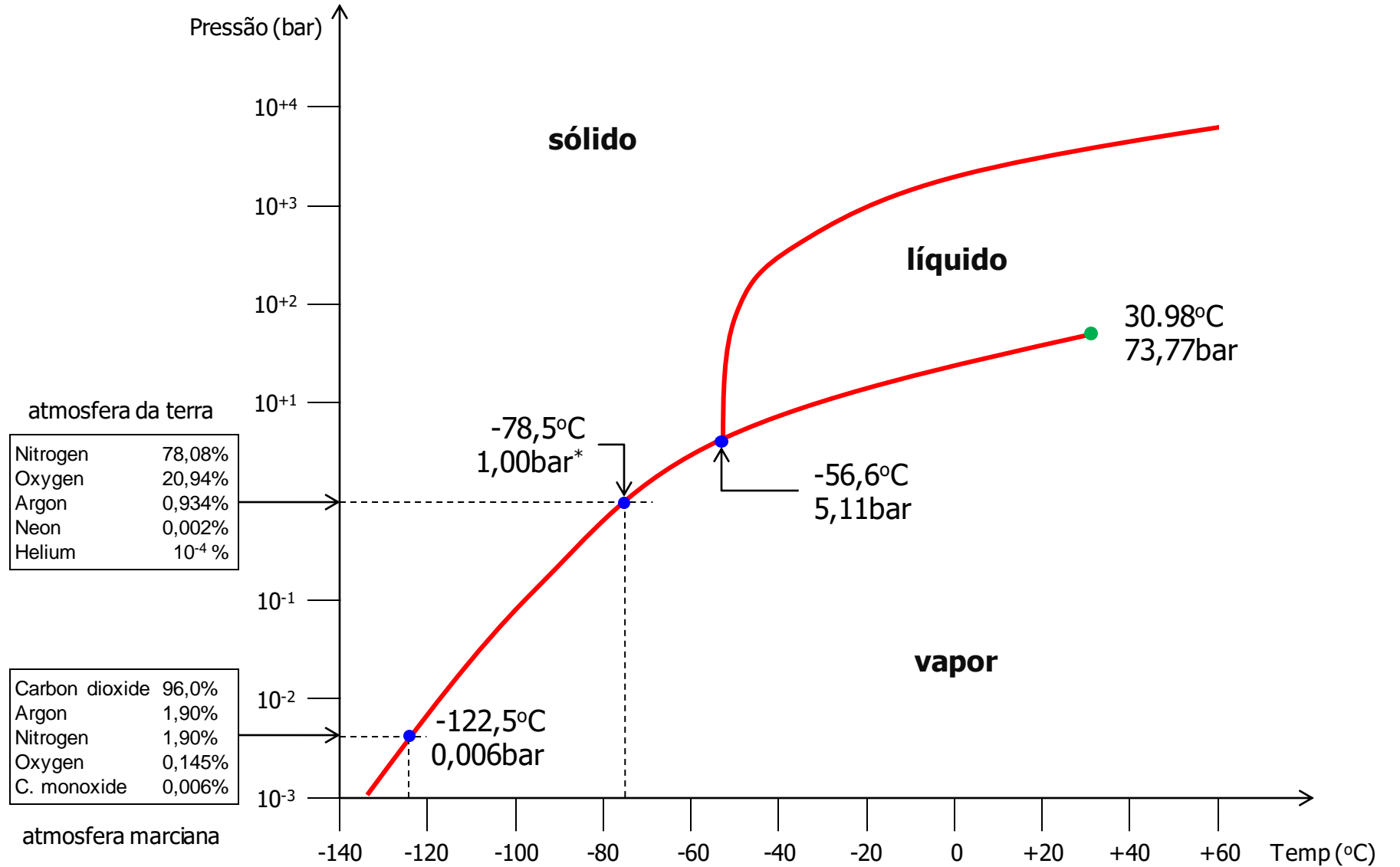




# Diagrama P × T



# Diagrama P × T: dióxido de carbono

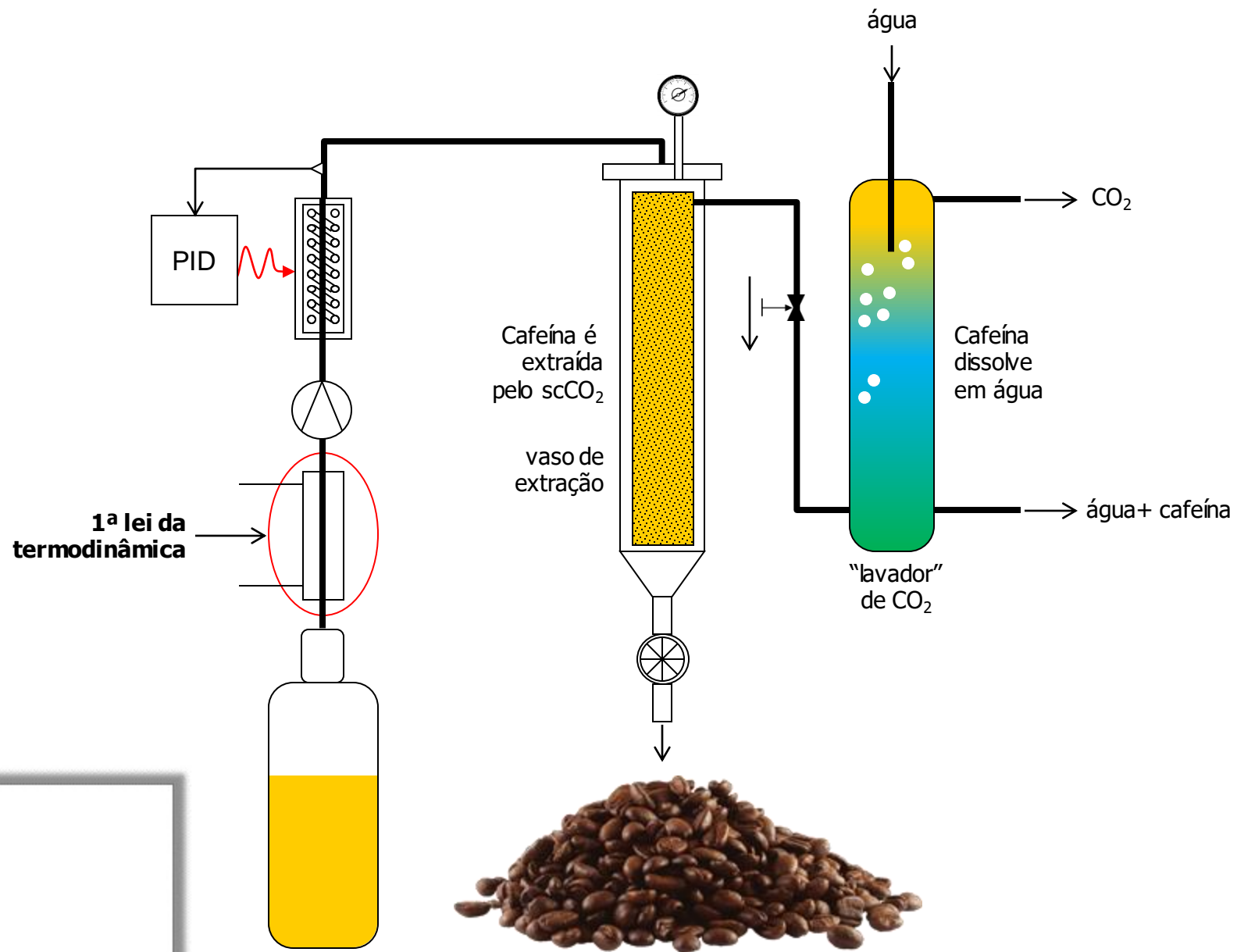


## Formação de neve de dióxido de carbono em Marte

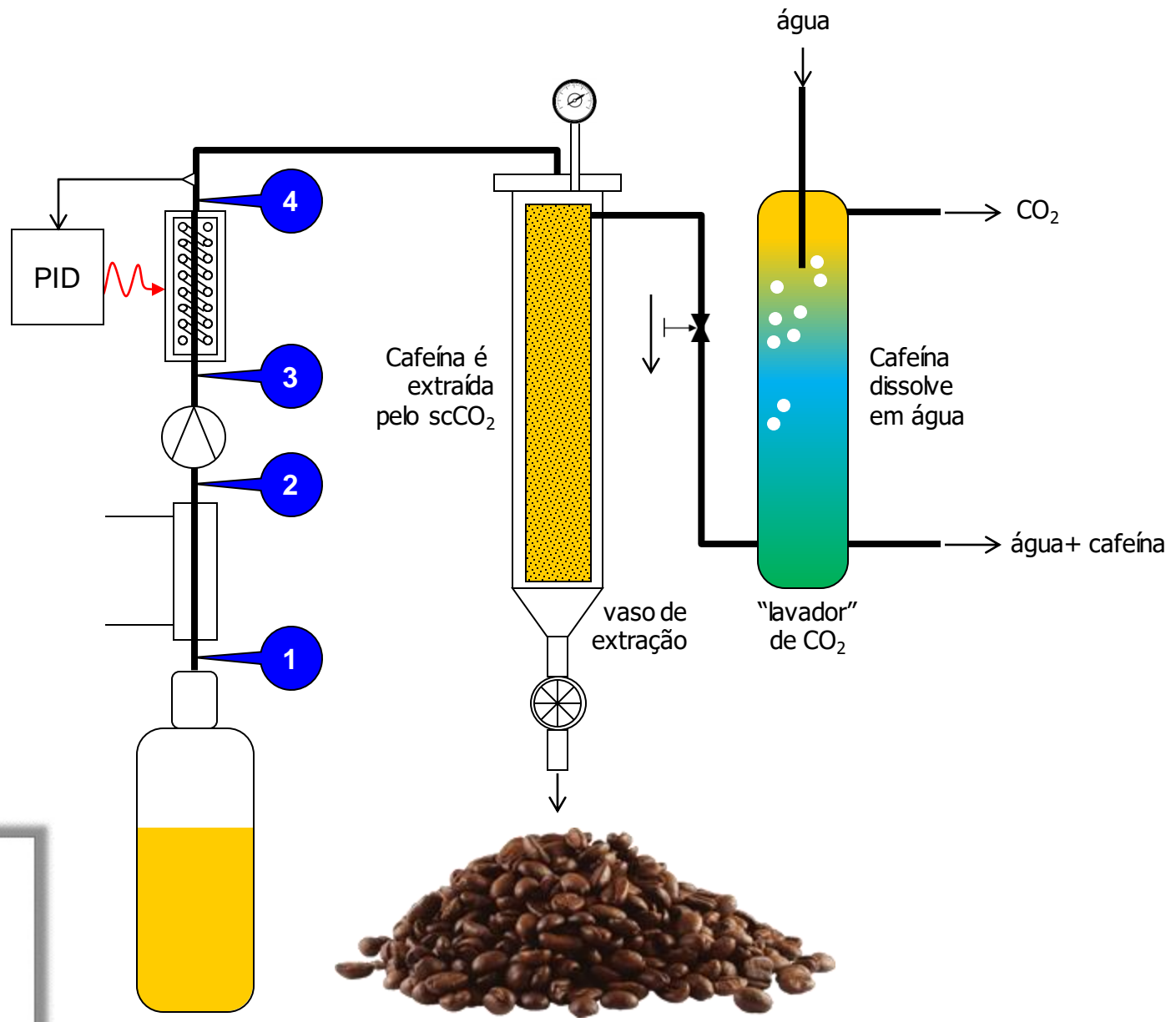


Heavy Frost, or Snow, Deposit at Viking Lander 2 Site (Viking Lander Image 21I093)

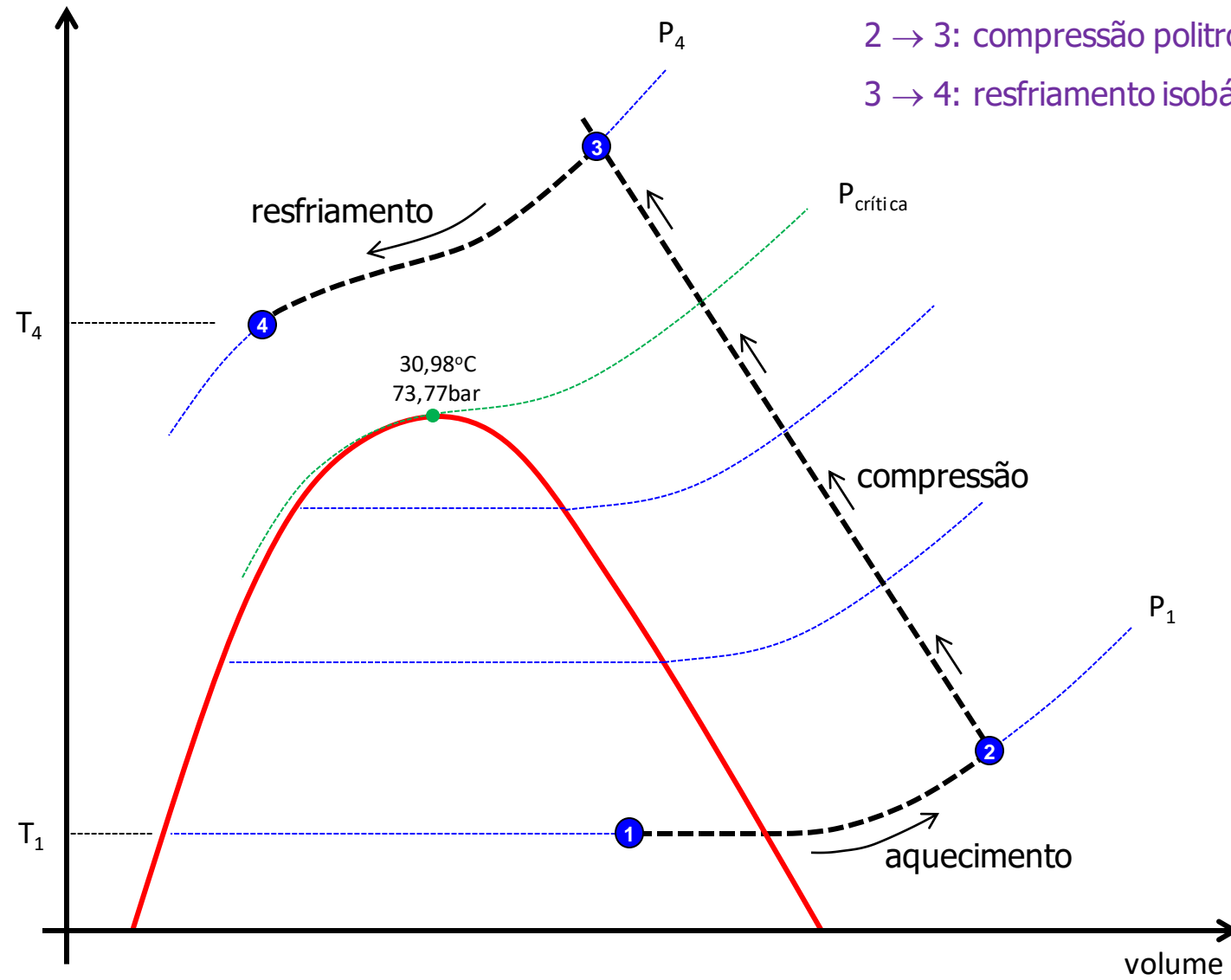
**Aplicação:**  
transferência de calor a  
pressão constante – entalpia





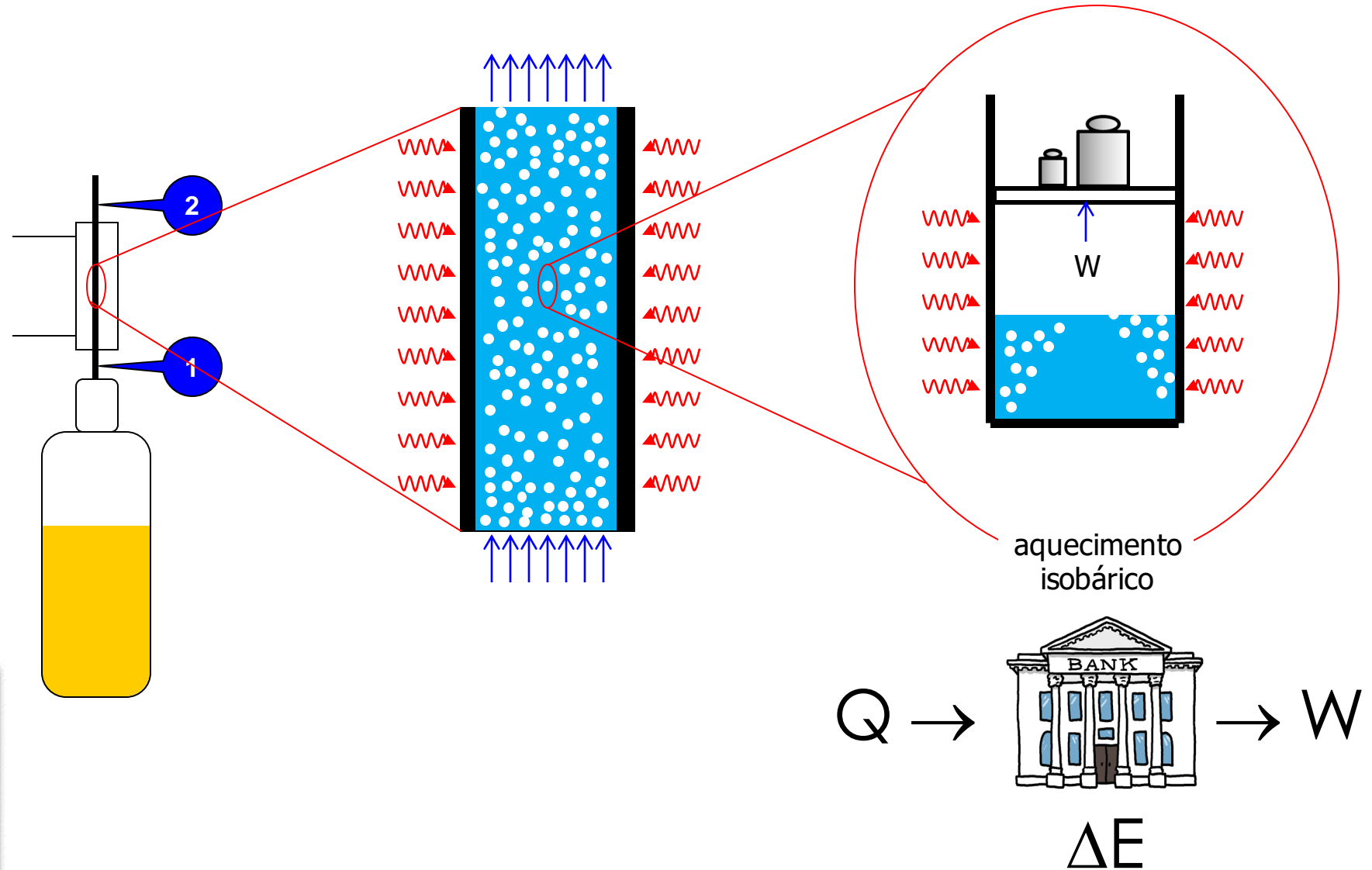


temperatura

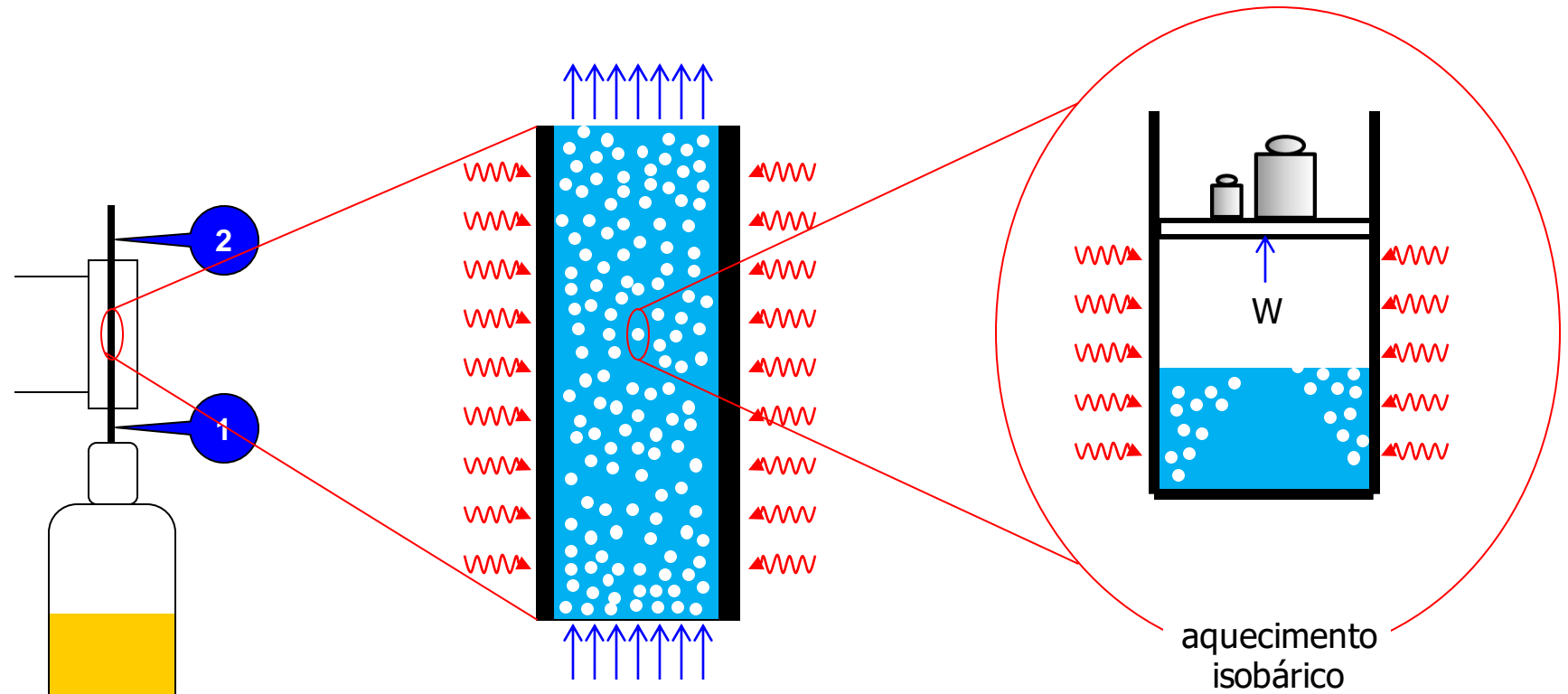


- 1 → 2: aquecimento isobárico ( $P=\text{cte}$ )
- 2 → 3: compressão politrópica ( $P \cdot v^n = \text{cte}$ )
- 3 → 4: resfriamento isobárico ( $P=\text{cte}$ )

# Aplicação da 1ª lei da termodinâmica



# Aplicação da 1ª lei da termodinâmica



$$\Delta E = Q - W$$

$$U_2 - U_1 = Q_{12} - W_{12}$$

## Aplicação da 1ª lei da termodinâmica

$$W = F \cdot \Delta x$$

$$U_2 - U_1 = Q_{12} - W_{12}$$

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$$U_2 - U_1 = Q_{12} - \int_1^2 P \cdot dV = Q_{12} - P \cdot \int_1^2 dV$$

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$$U_2 - U_1 = Q_{12} - P \cdot (V_2 - V_1)$$

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$$U_2 - U_1 = Q_{12} - W_{12}$$

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$$U_2 - U_1 = Q_{12} - P_2 V_2 + P_1 V_1$$



# Aplicação da 1ª lei da termodinâmica

$$W = F \cdot \Delta x$$

$$U_2 - U_1 = Q_{12} - W_{12}$$

$$U_2 - U_1 = Q_{12} - \int_1^2 P \cdot dV = Q_{12} - P \cdot \int_1^2 dV$$

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$$Q_{12} = (U_2 + P_2 V_2) - (U_1 + P_1 V_1)$$

# Aplicação da 1ª lei da termodinâmica

$$W = F \cdot \Delta x$$

$$U_2 - U_1 = Q_{12} - W_{12}$$

$$U_2 - U_1 = Q_{12} - \int_1^2 P \cdot dV = Q_{12} - P \cdot \int_1^2 dV$$

$$U_2 - U_1 = Q_{12} - P \cdot (V_2 - V_1)$$

$$U_2 - U_1 = Q_{12} - P_2 V_2 + P_1 V_1$$

$$Q_{12} = \underbrace{(U_2 + P_2 V_2)}_{\text{entalpia 2}} - \underbrace{(U_1 + P_1 V_1)}_{\text{entalpia 1}}$$

# Aplicação da 1ª lei da termodinâmica

$$H \stackrel{\text{def}}{=} U + PV$$

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# Aplicação da 1ª lei da termodinâmica

$$H \stackrel{\text{def}}{=} U + PV$$

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$$Q_{12} = (U_2 + P_2 V_2) - (U_1 + P_1 V_1)$$

$$Q_{12} = H_2 - H_1$$

# Aplicação da 1ª lei da termodinâmica

$$H \stackrel{\text{def}}{=} U + PV$$

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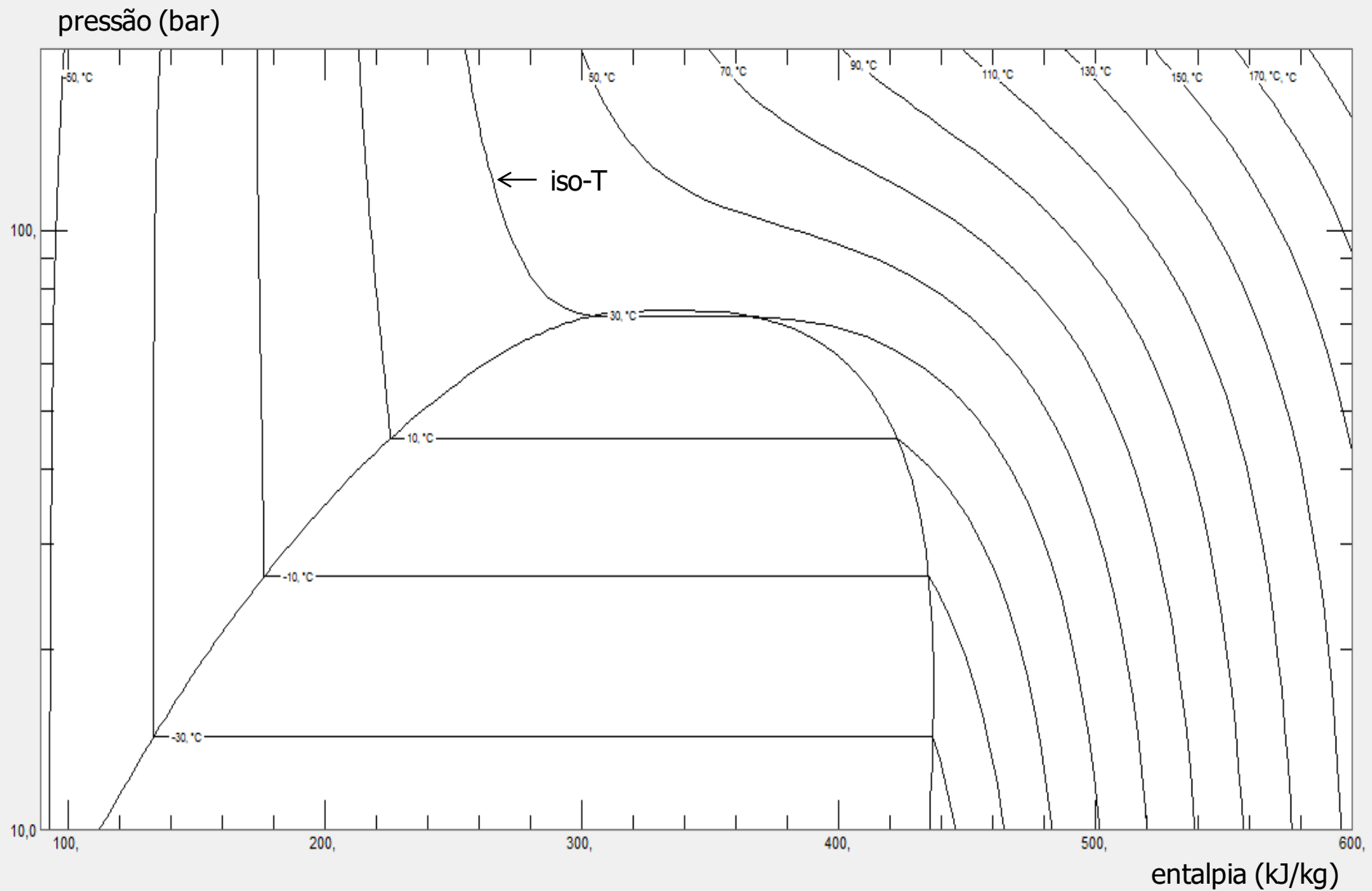
$$Q_{12} = (U_2 + P_2 V_2) - (U_1 + P_1 V_1)$$

$$Q_{12} = H_2 - H_1$$

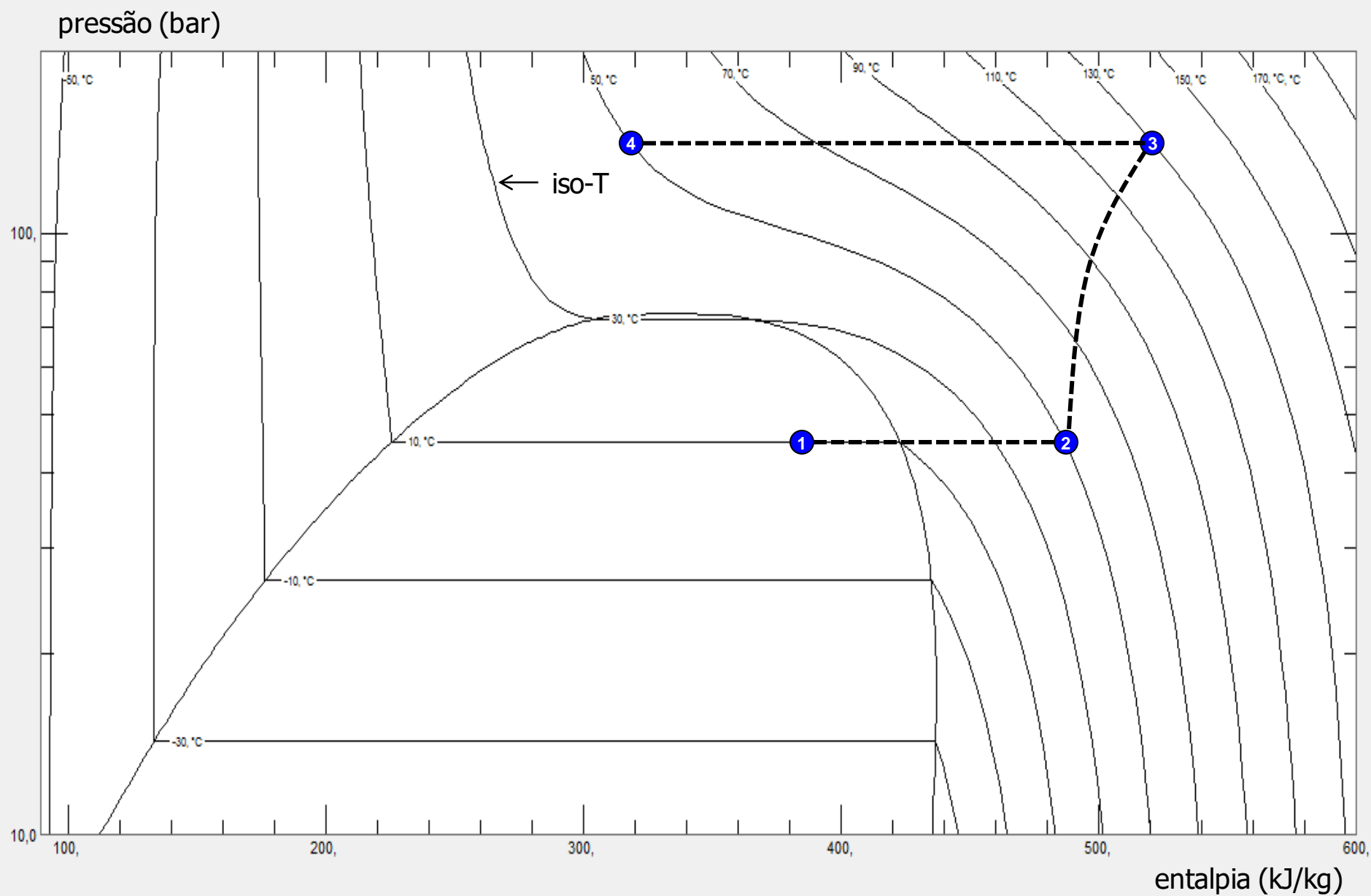
$$Q_{12} = m \cdot (h_2 - h_1)$$

A entalpia pode ser interpretada como a quantidade de calor transferido a pressão constante

# Diagrama P × h do CO<sub>2</sub>

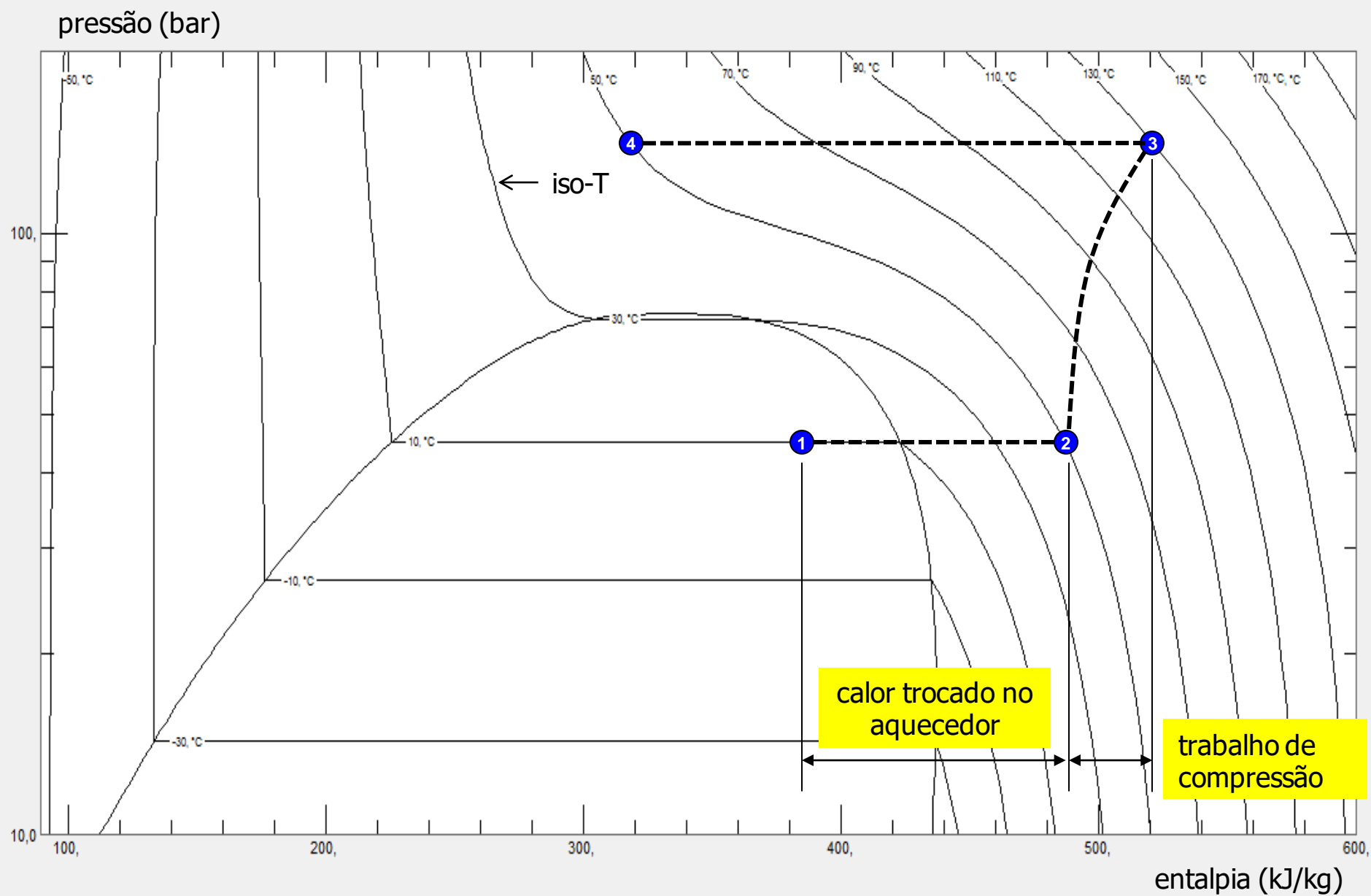


# Diagrama P × h do CO<sub>2</sub>



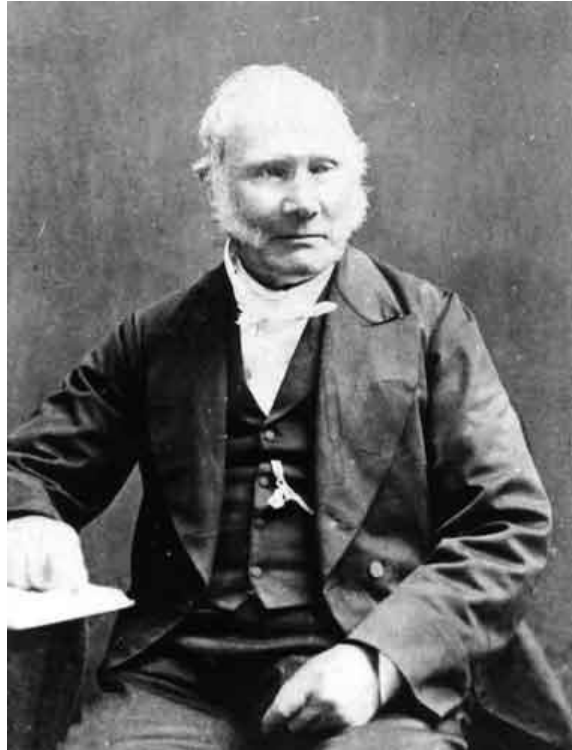


# Diagrama $P \times h$ do $\text{CO}_2$



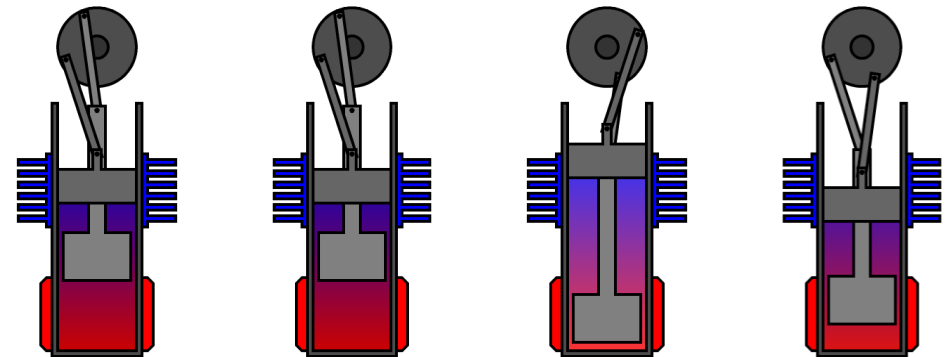
Voltando ao problema de  
converter calor em  
trabalho mecânico...

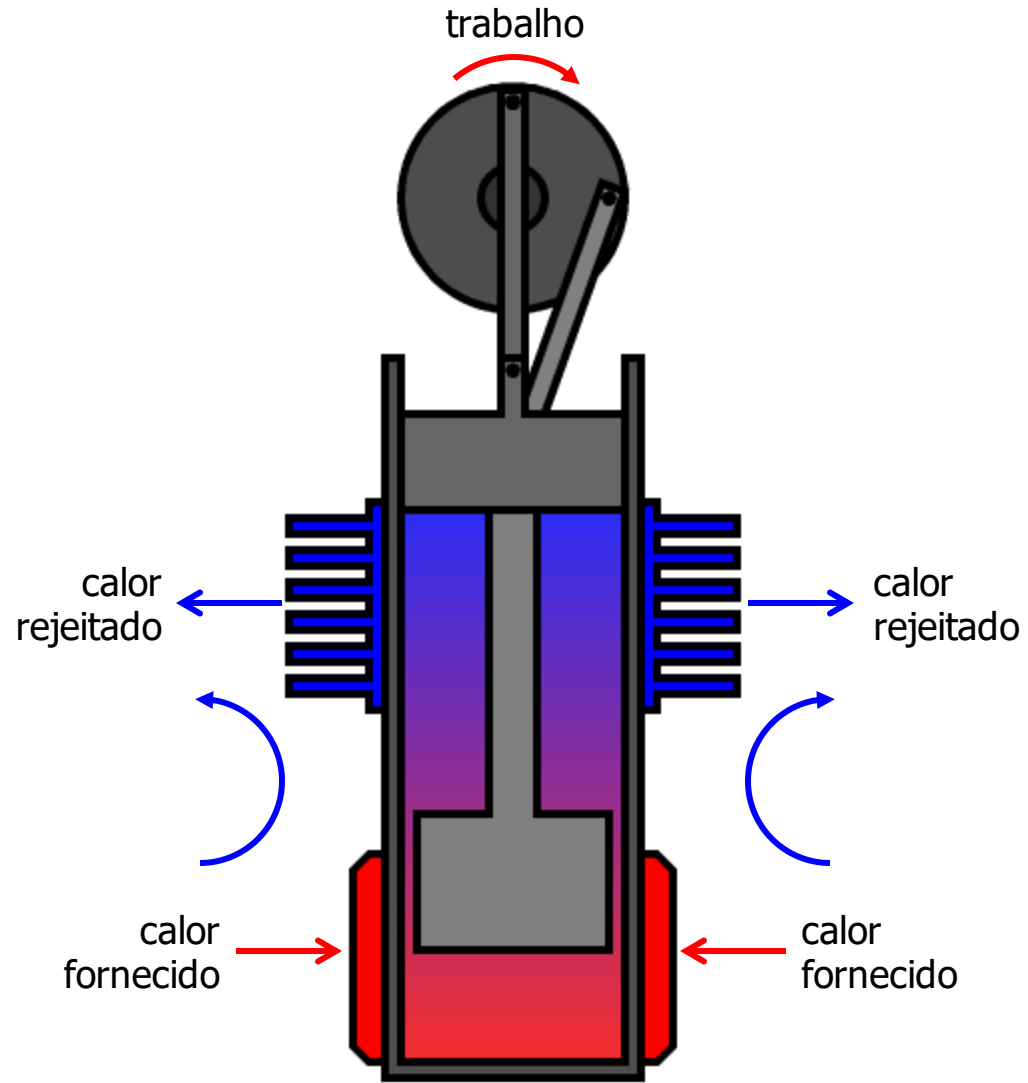
# Motor de Stirling – “combustão externa”



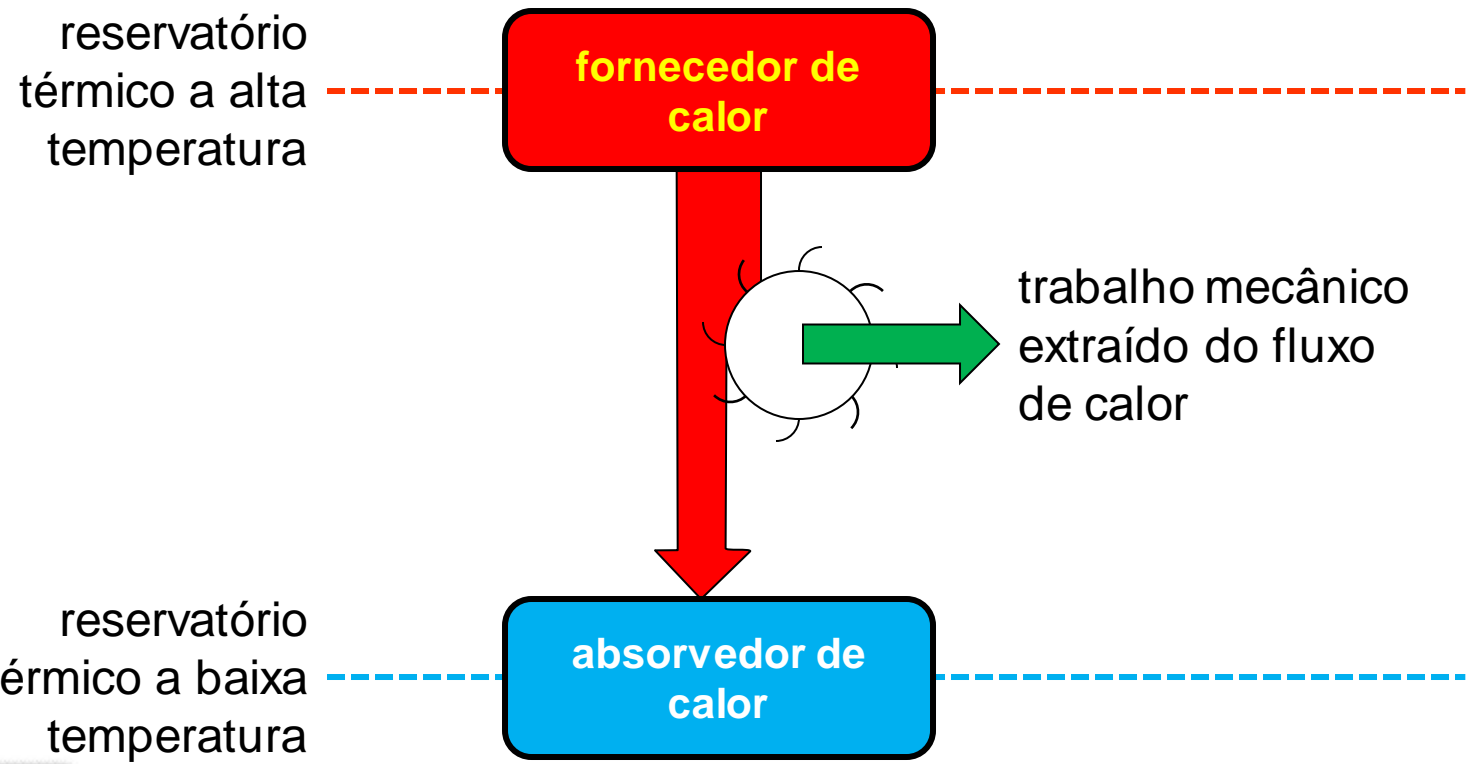
Reverendo Dr. Robert Stirling  
em 1816

- ✓ Mais eficiente que os motores a vapor
- ✓ Fontes de calor a baixa temperatura





Tipo Beta



... mas este é um assunto  
para as próximas aulas !

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