Autour de la thermodynamique

About « Thermodynamics »

Cours de méthodologie – Ecole d'été (ITC Phnom Penh)

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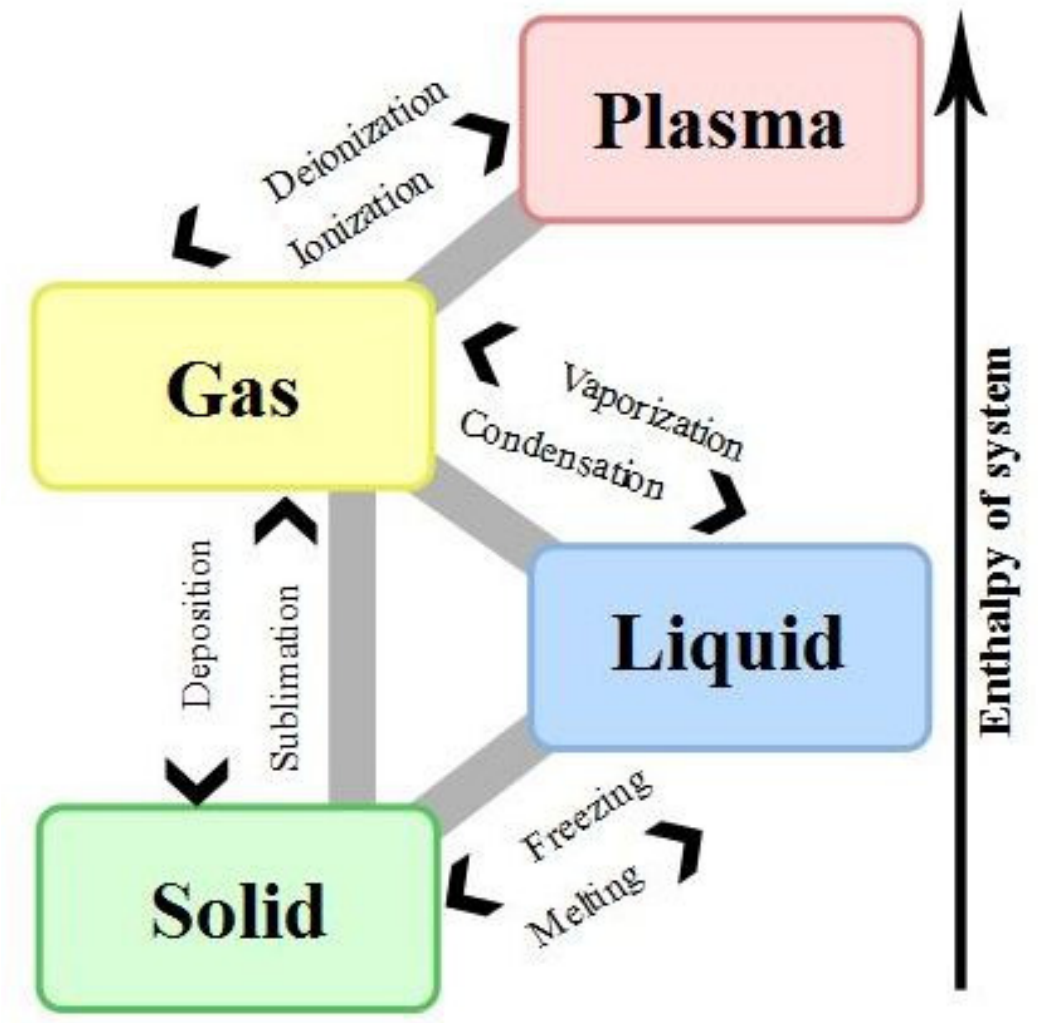
(Du lundi 20 au mercredi 29 août 2012)

1) Some experimental setups about phase transitions :



A **phase transition** is the transformation of a thermodynamic system from one phase or state of matter to another.

$$\Phi_1 \rightleftharpoons \Phi_2$$

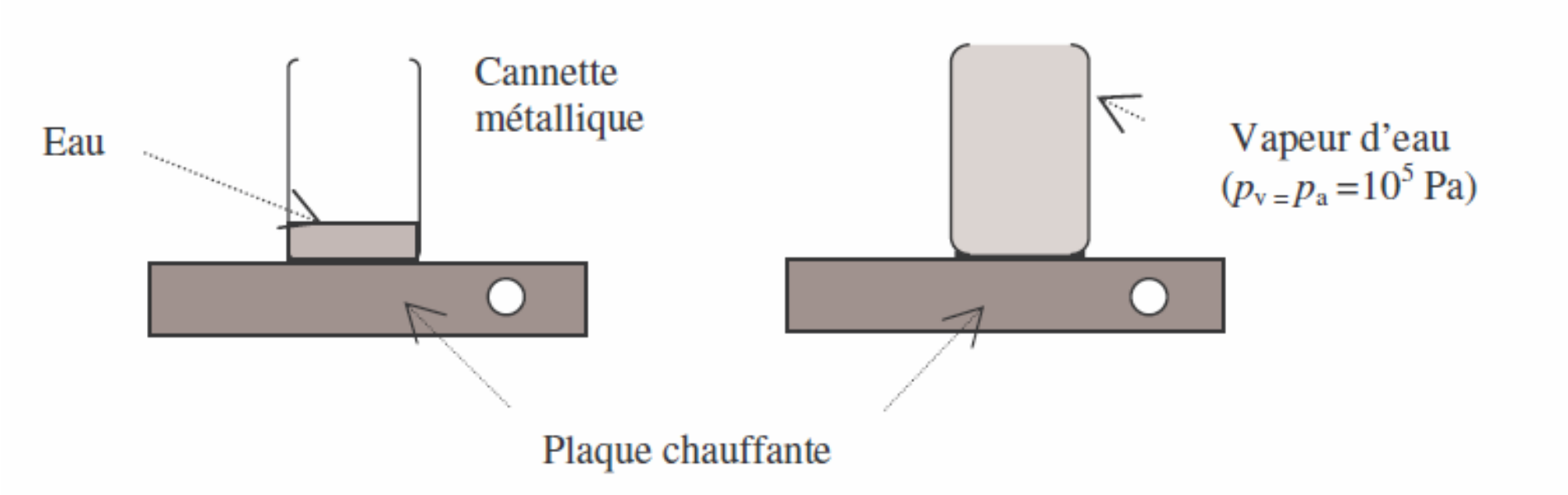
Latent heat of phase transition :

$$q_m = \ell_{1\to 2,m} = h_{2,m} - h_{1,m} = \Delta h_m$$

$$\Delta H = m\ell_{1\to 2,m} = Q$$

$$\Delta S = \frac{Q}{T} = \frac{m\ell_{1\to 2,m}}{T}$$

$$\Delta U = m\ell_{1\to 2,m} - Pm(v_{2,m} - v_{1,m})$$



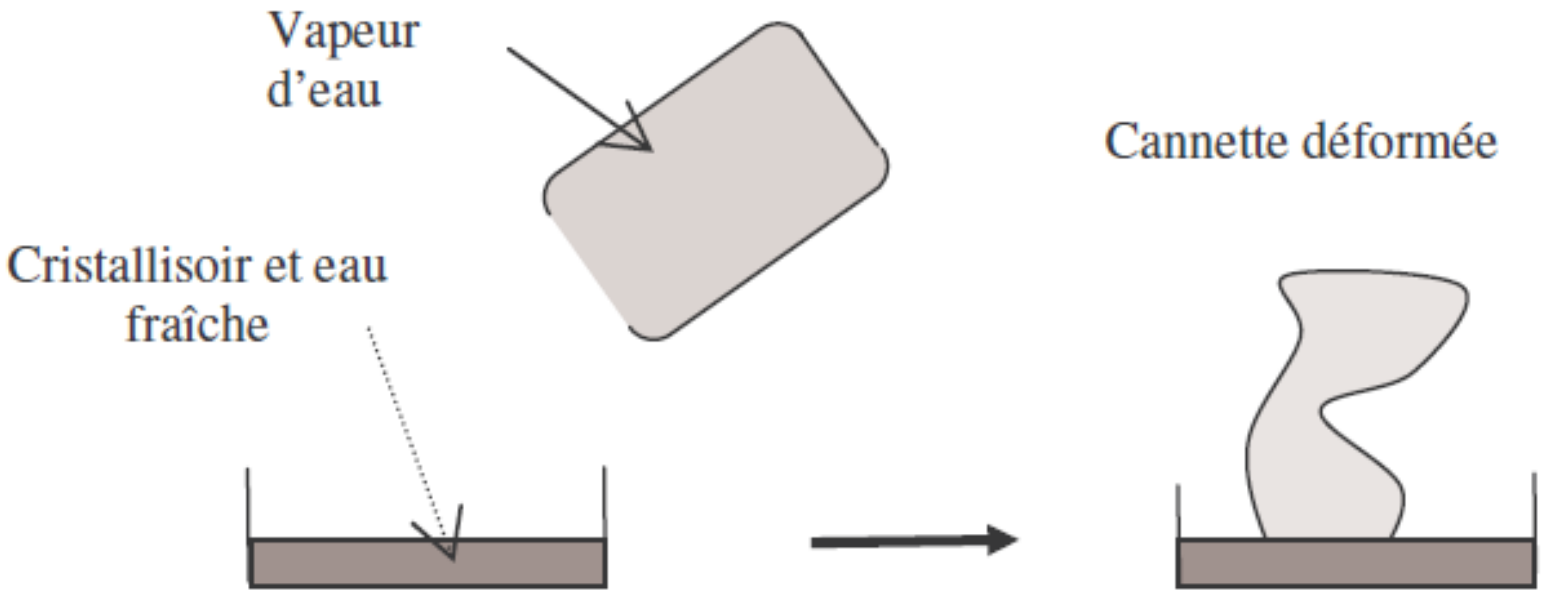
A few cubic centimeters of water is poured into a can (just enough to cover the bottom).

The can is held above a laboratory burner for about 30 seconds, the water can be brought to the boiling point where its vapor pressure is equal to atmospheric pressure.

The vapor will then push most of the air out of the can.

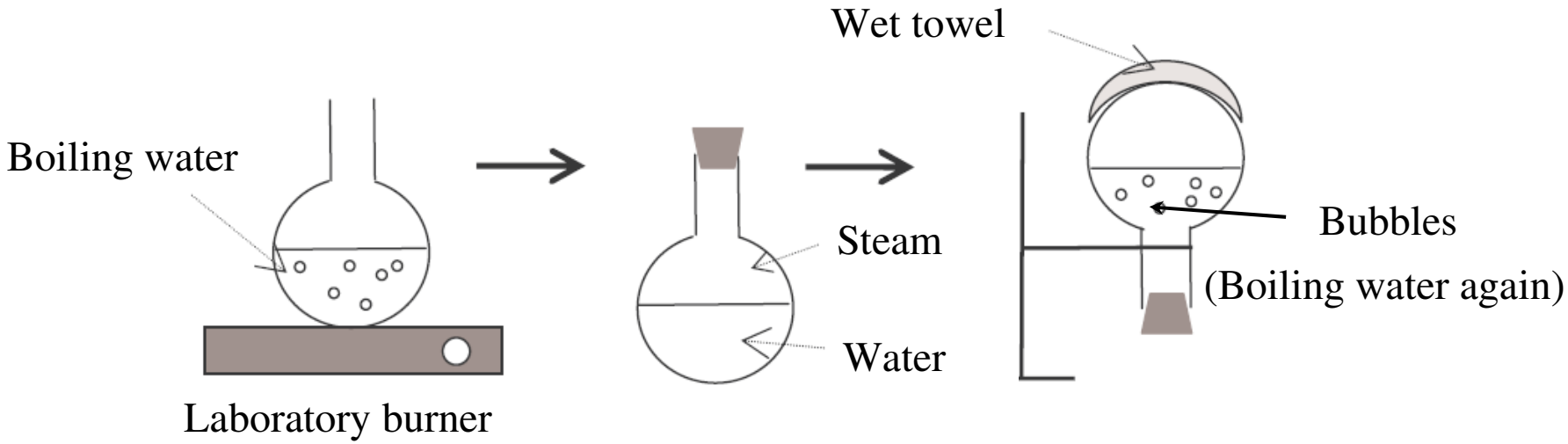
Videos : « Crushing of Steel Drum – DRUM4 »

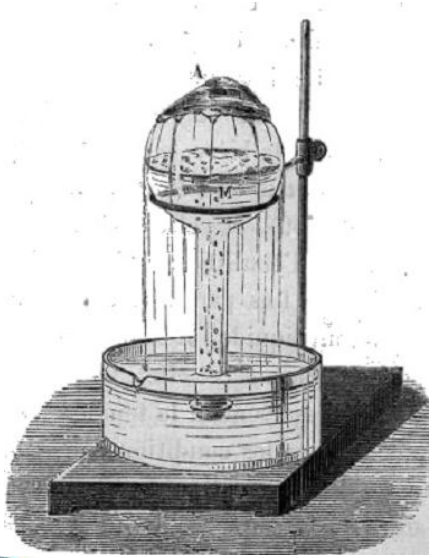
« Can-Crushing Experiment – CRUSHCAN »

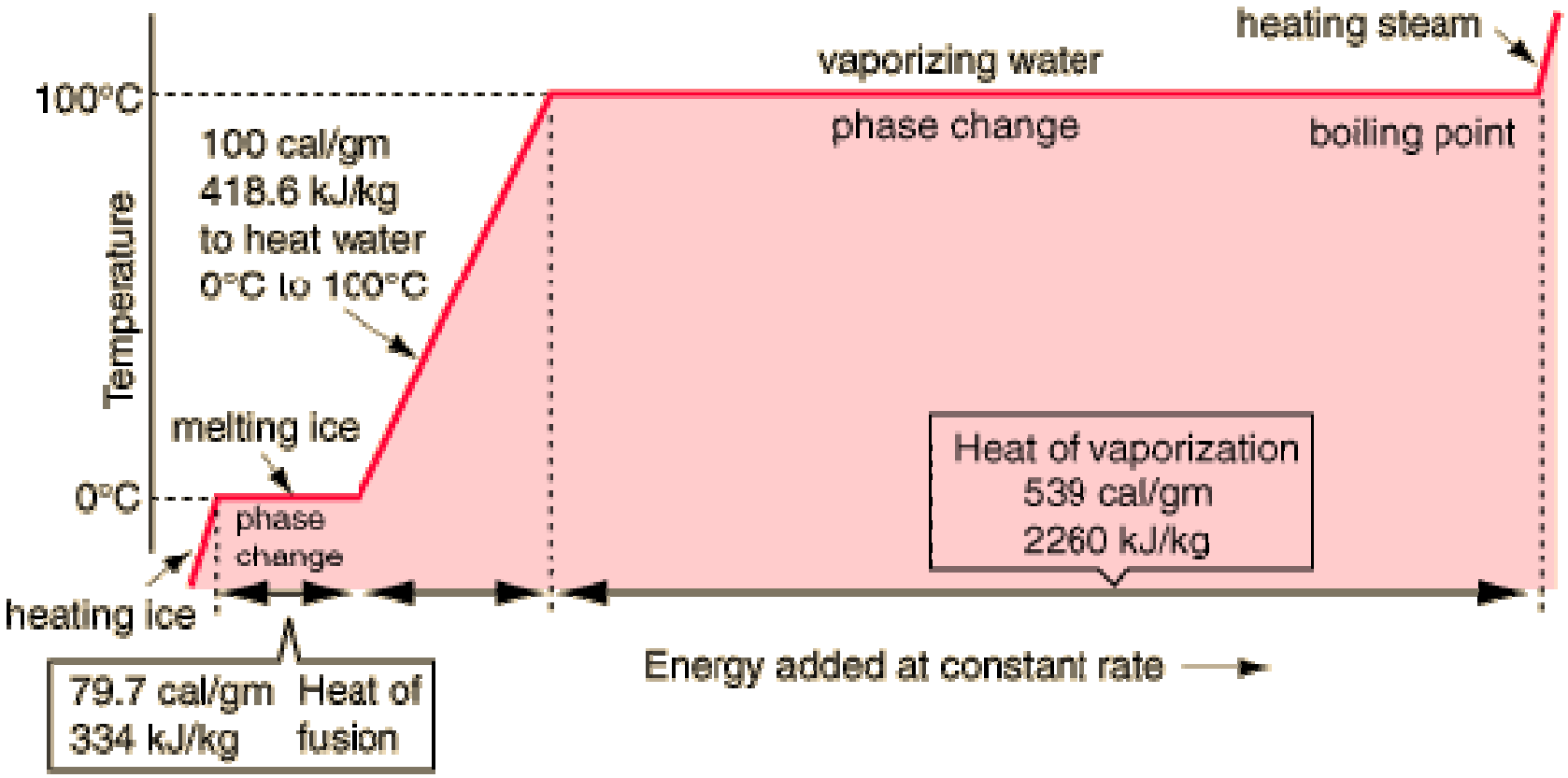


If the can is quickly inverted into a beaker of water, sealing off the opening, the sudden drop in vapor pressure will result in enough net inward pressure to quickly crush the can.

Vidéo : « Le bouillant de Franklin »



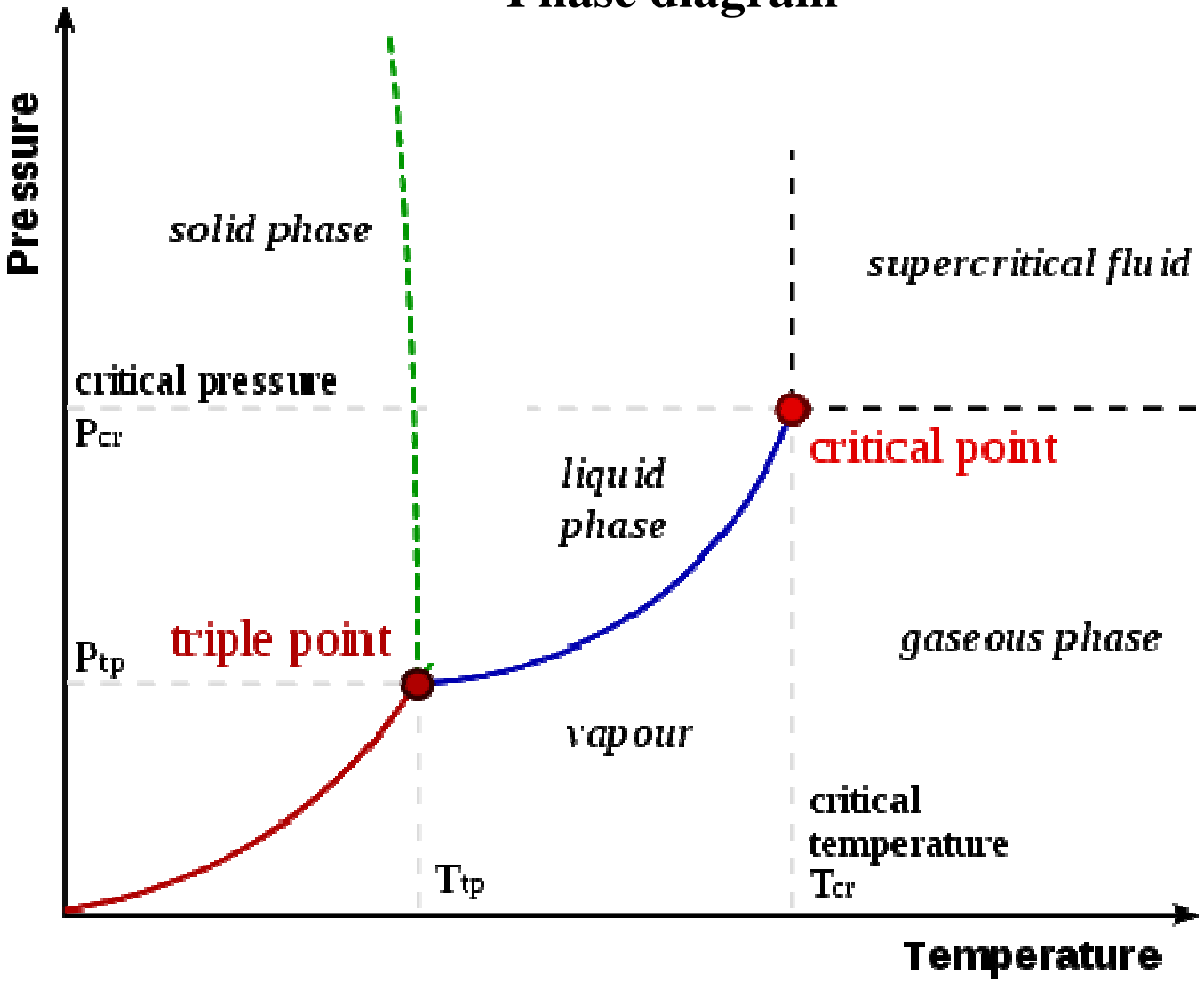




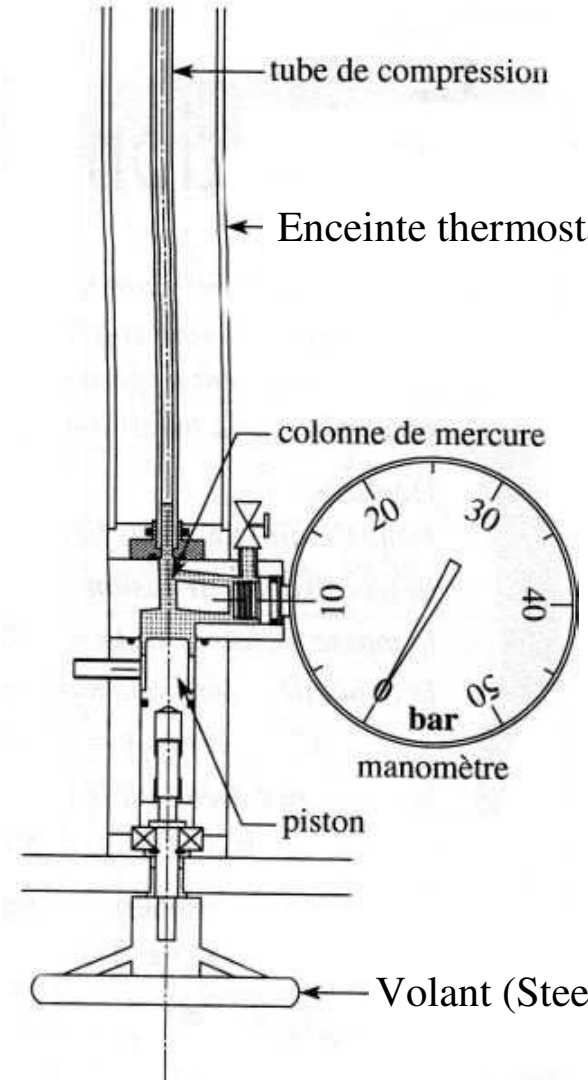
Phase changes (for water, under P = 1 bar) from ice to steam.

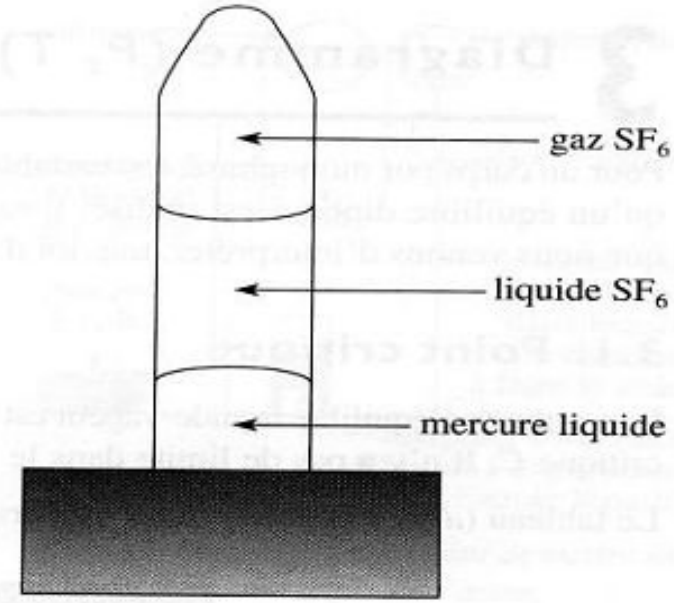
The energies required to accomplish the phase changes (called the latent heat of fusion and latent heat of vaporization) would lead to plateaus in the temperature vs time graph.

Phase diagram



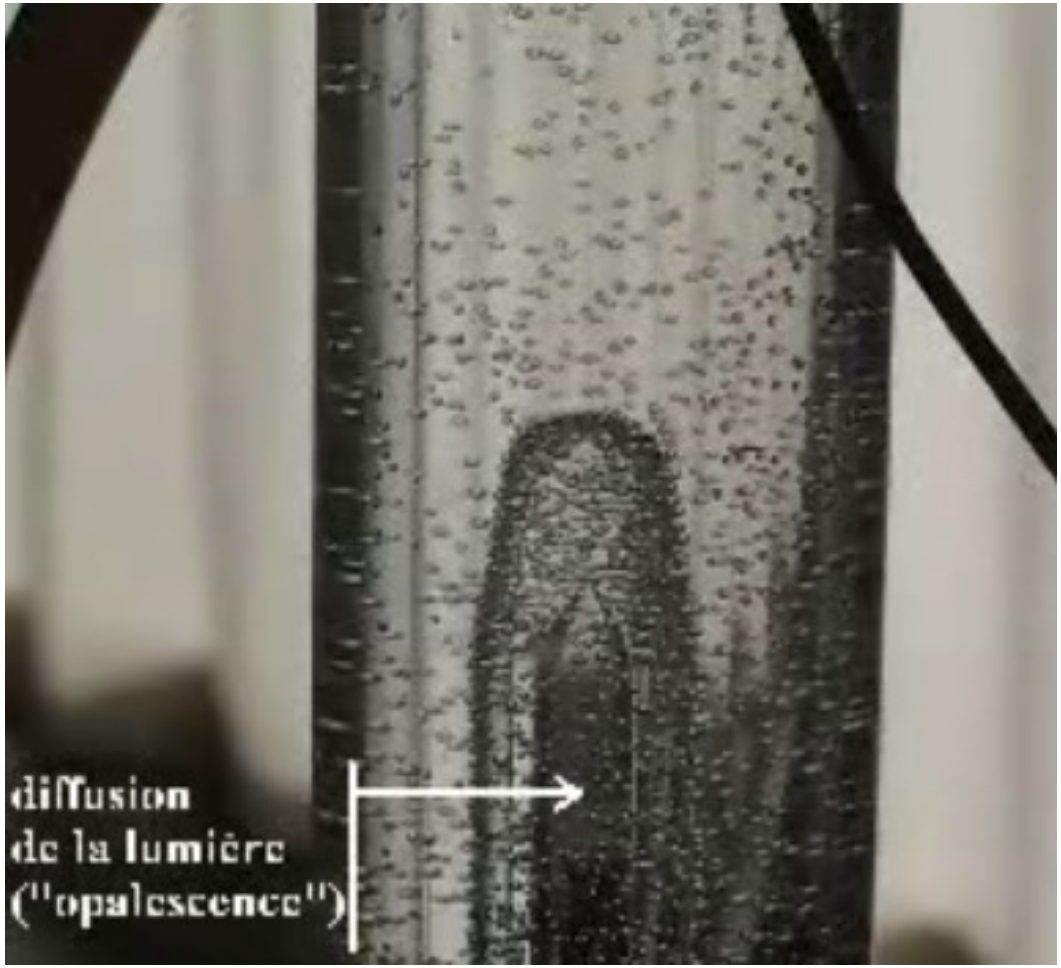
Vidéo : « Going around the critical point »





Aspect du tube de compression

Vidéo : « Going around the critical point »



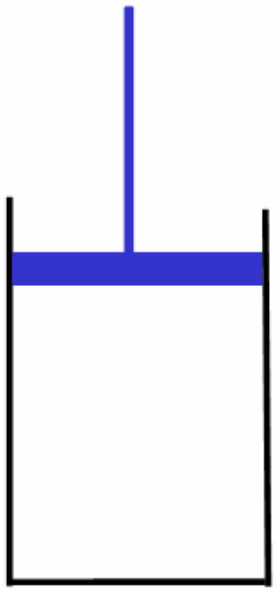
In any system containing liquid and gaseous phases, there exists a special combination of pressure and temperature, known as the **critical point**.

Near the critical point, the fluid is sufficiently hot and compressed that the distinction between the liquid and gaseous phases is almost non-existent.

This is associated with the phenomenon of **critical opalescence**, a milky appearance of the liquid due to density fluctuations at all possible wavelengths
(including those of visible light).

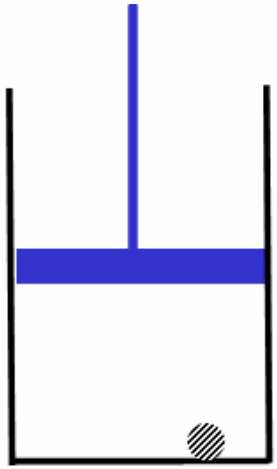
Thermostat at T

(Temperature being kept constant)



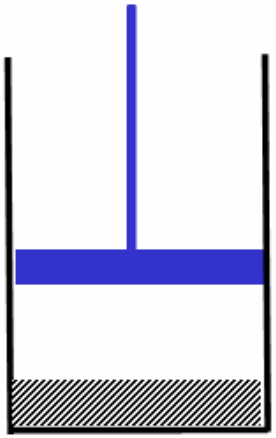
Steam water

Isothermal compression of steam



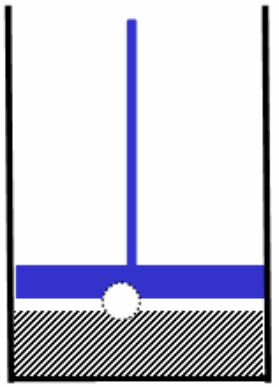
Seam water and a drop of water

Dew point



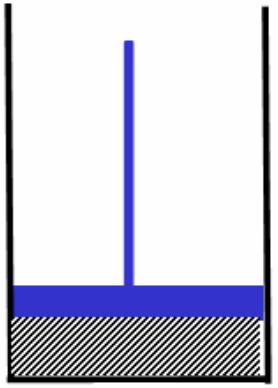
Saturated steam and water

Phase transition (Condensation)



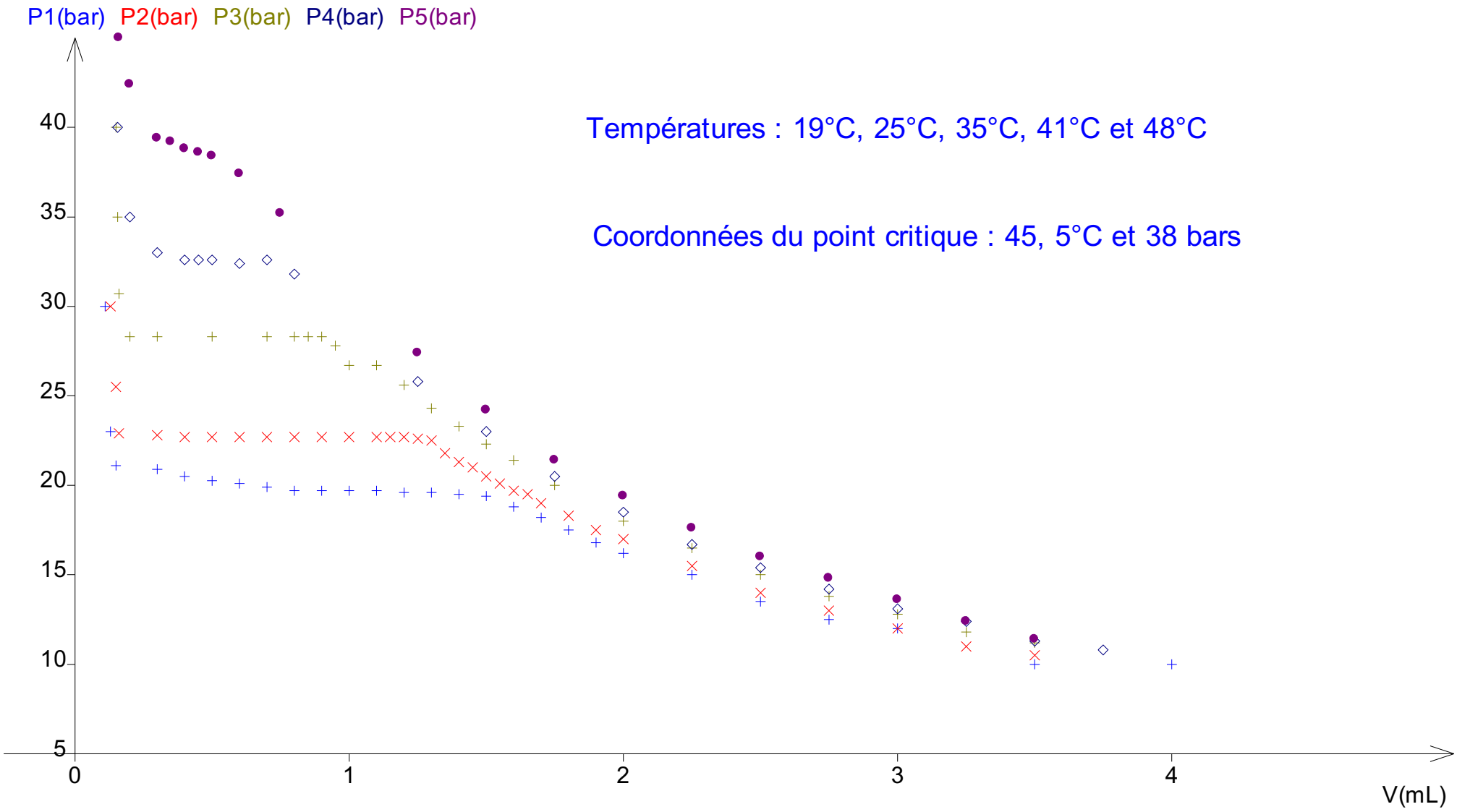
Water and a steam bubble

Boiling point



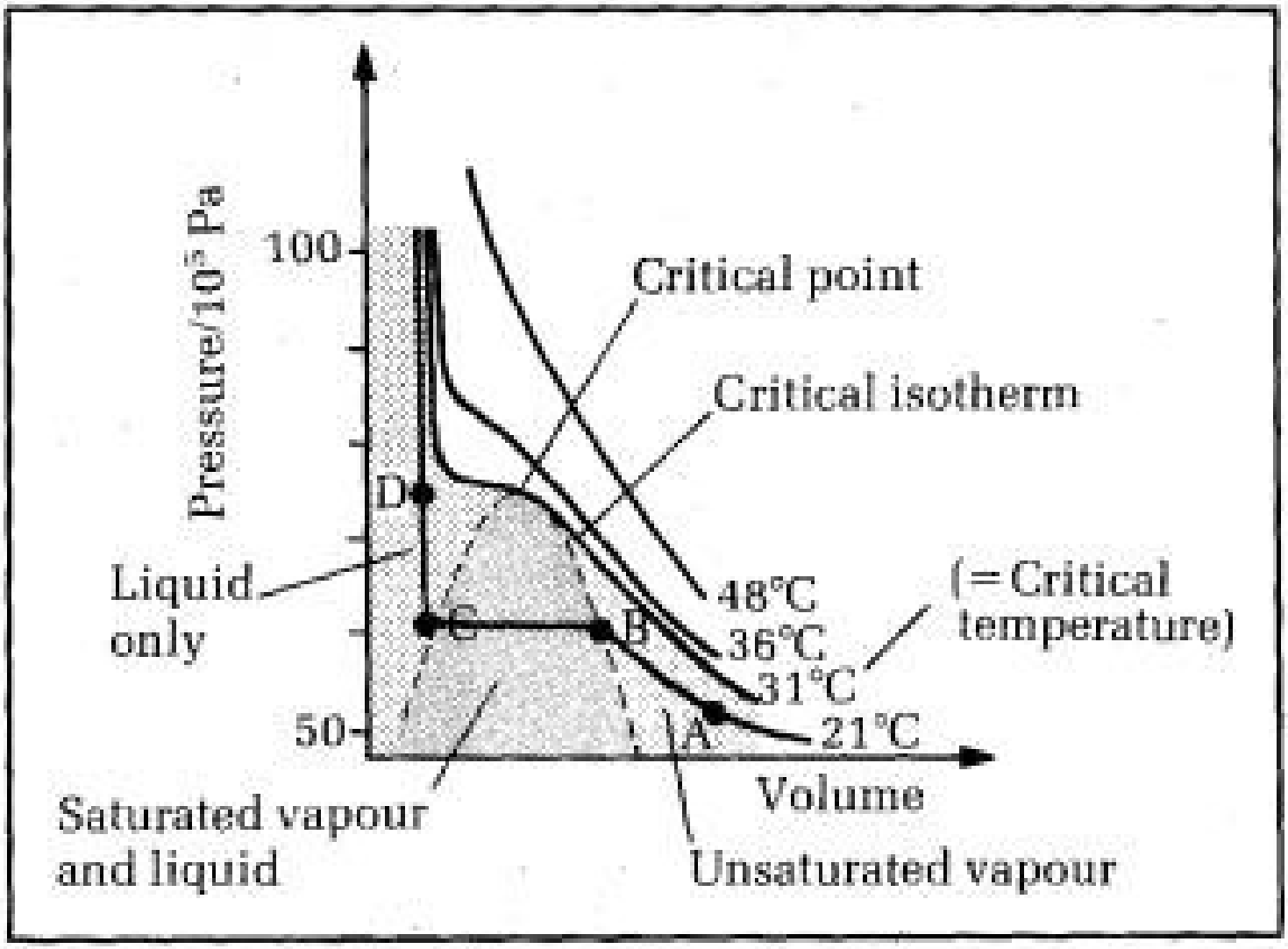
Water

Isothermal compression of water

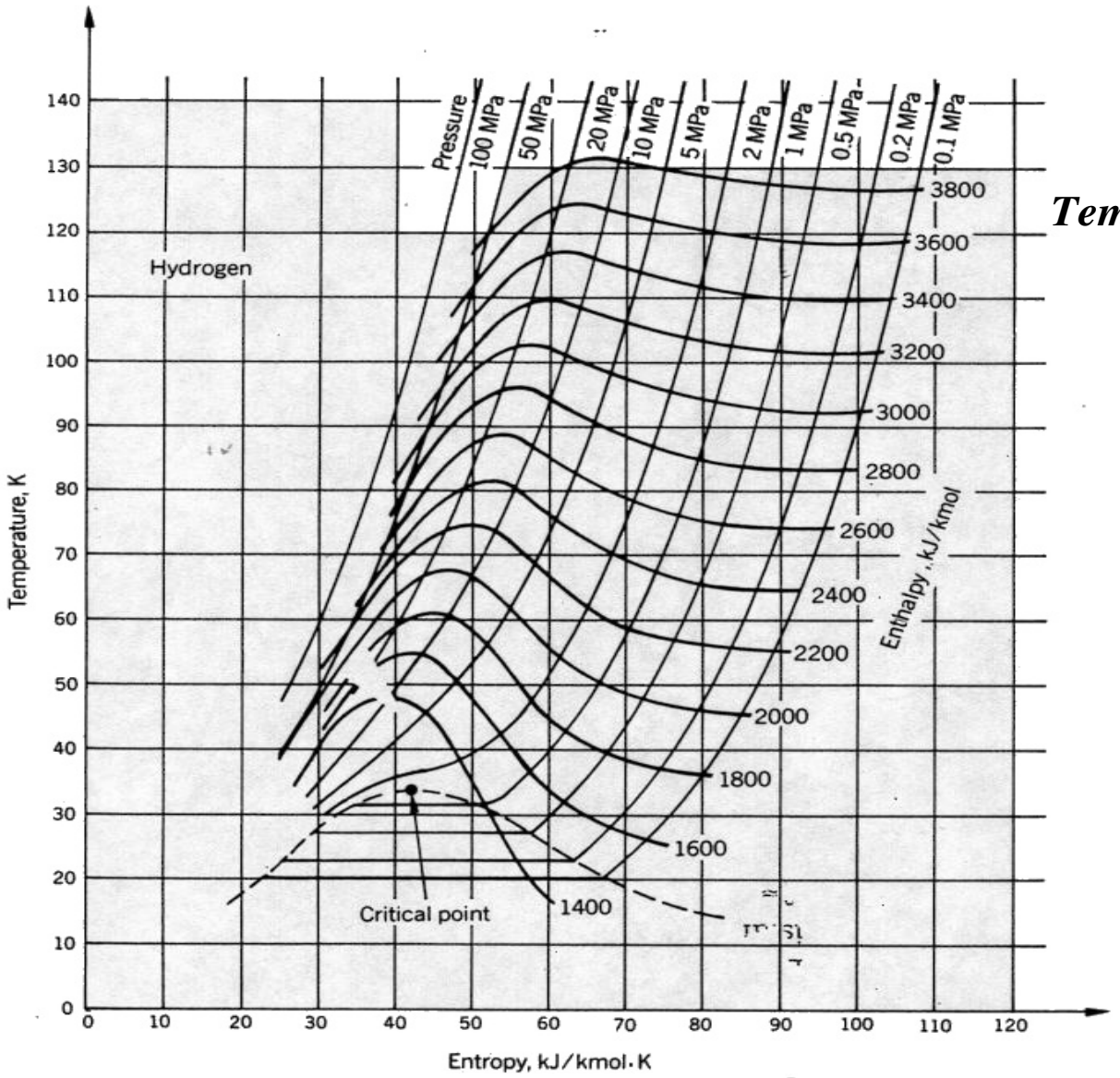


Températures : 19°C, 25°C, 35°C, 41°C et 48°C

Coordonnées du point critique : 45, 5°C et 38 bars



CO isotherms of p against V

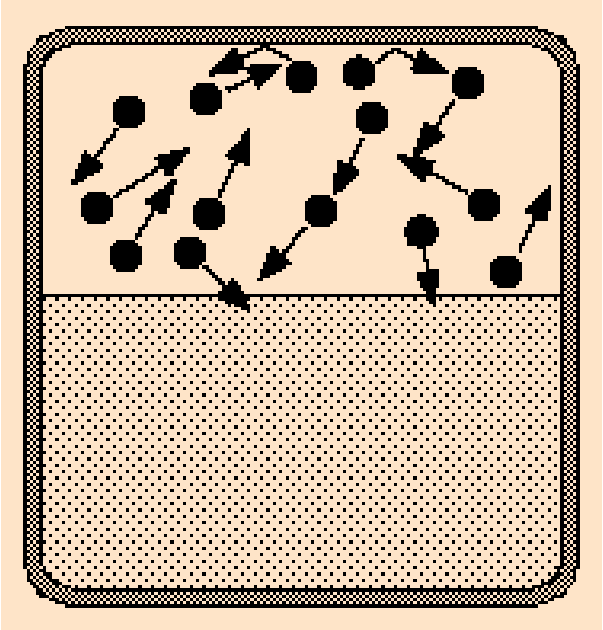


(T,S)
Temperature – Entropy diagram
(for Hydrogen)

Saturated vapor pressure :

The process of evaporation in a closed container will proceed until there are as many molecules returning to the liquid as there are escaping.

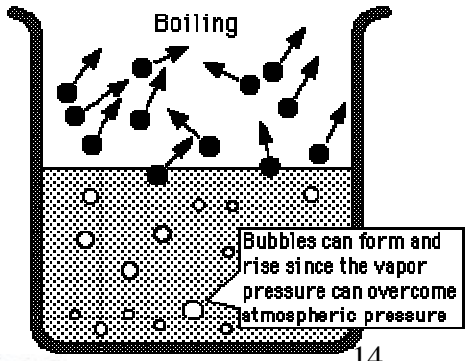
At this point, the vapor is said to be saturated and the pressure of that vapor is called the ***saturated vapor pressure***.



The temperature higher, the saturated vapor pressure higher too (kinetic energy is greater at higher temperature)

The temperature at which the vapor pressure is equal to the atmospheric pressure is called **the boiling point**.

Bubbles form and the vaporization becomes a volume phenomena.



$$\ell_v(T) = T\left(u_g - u_l\right)\left(\frac{dP}{dT}\right)_{vap}$$ (Clapeyron's relationship)

* $\left(\frac{dP}{dT}\right)_{vap}$: slope of the curve $P_V(T)$ (saturated vapor pressure) vs the temperature T

* T : temperature during the phase transition (vapour – liquid), in Kelvin (K)

* u_g and u_ℓ : specific volume (for the gas and the liquid)

* $\ell_v(T)$: latent heat of vaporization

With $u_\ell << u_g \approx \frac{RT}{PM}$:

$$\ell_v \approx \frac{RT^2}{PM}\left(\frac{dP}{dT}\right)_{vap}$$

Equilibrium relationship for (T,P) and (T + dT,P + dP) :

$$g_\ell(T,P) = g_g(T,P) \qquad and \qquad g_\ell(T+dT,P+dP) = g_g(T+dT,P+dP)$$

g(T,P) is the ***molar Gibbs energy*** (or Gibbs function; also known as free enthalpy) :

$$g(T,P) = u + Pu - Ts = h - Ts$$

So :

$$dg_\ell = dg_g$$

Or :

$$dg_\ell = -s_\ell dT + u_\ell dP = dg_g = -s_g dT + u_g dP$$

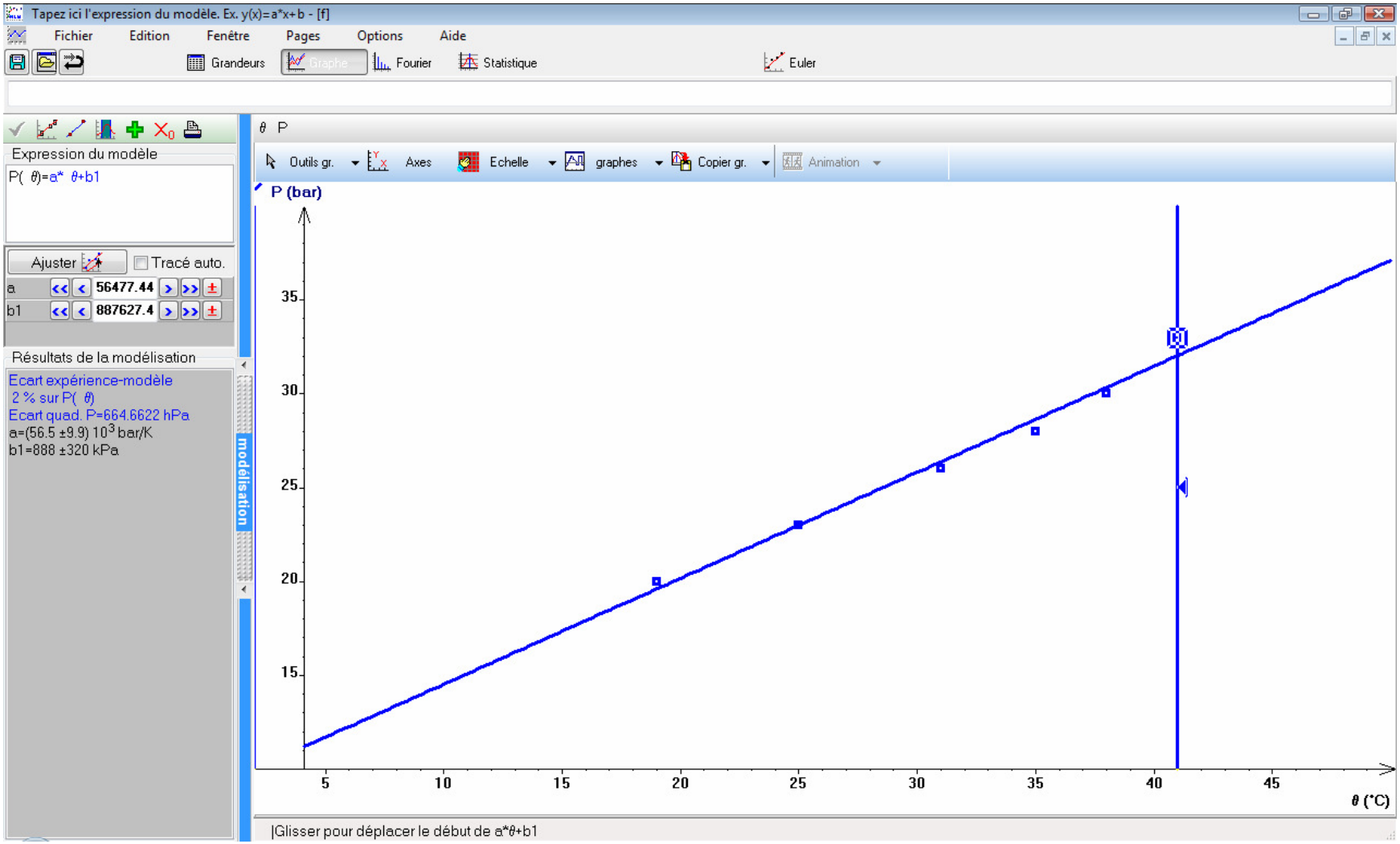
With :

$$s_g - s_\ell = \frac{\ell_v}{T}$$

Finally :

$$\boxed{\ell_v(T) = T\left(u_g - u_l\right)\left(\frac{dP}{dT}\right)_{vap}}$$

(Clapeyron's relationship)



Regressi software file : « chaleur-latente-sf6-2 »

Développement du viriel (a viriel series expansion) :

- Product PV as a function of 1 / V.
- Amagat's plot : product PV as a function of P.

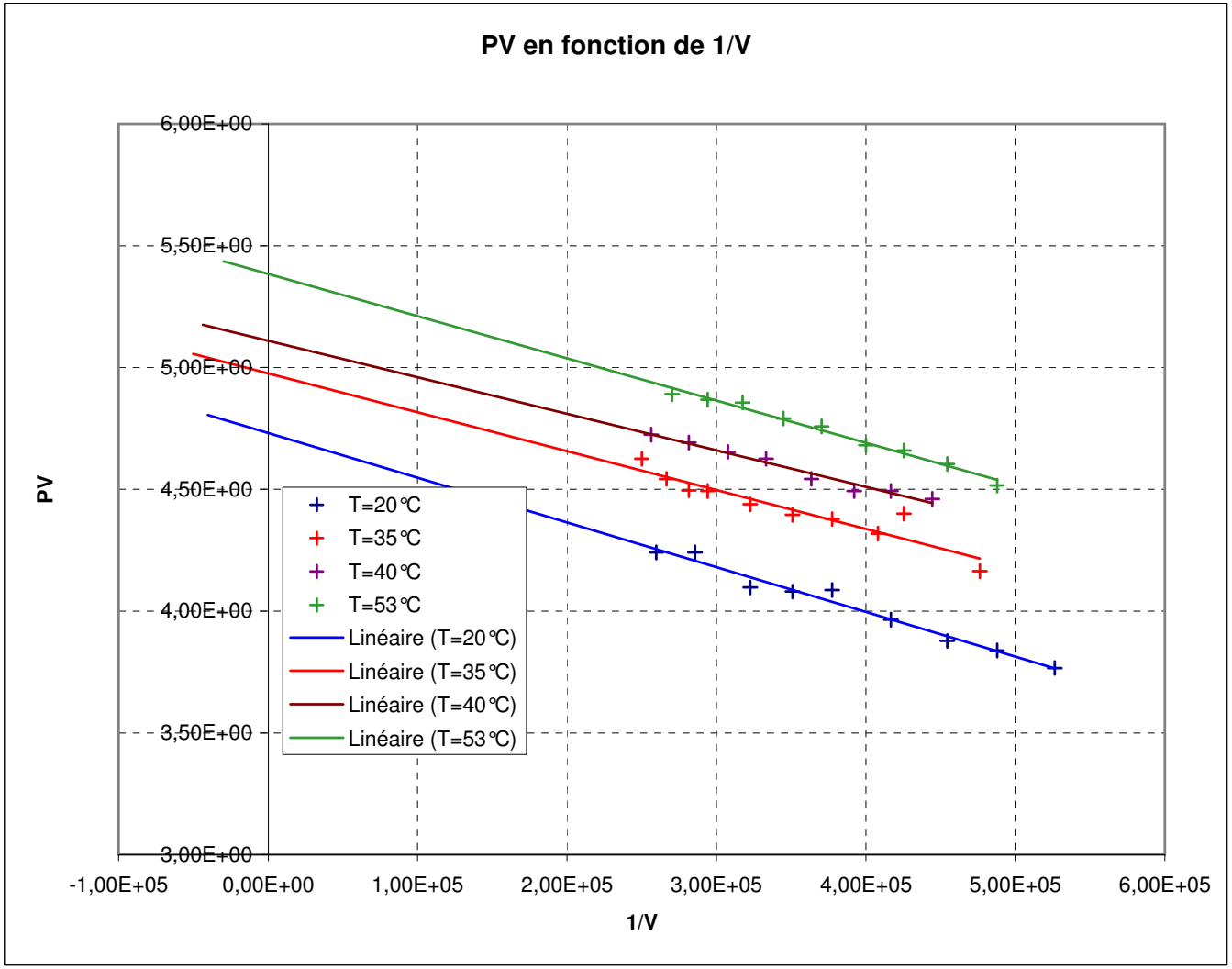
The equation of state for the SF_6 gaz can be written as (a viriel series expansion) :

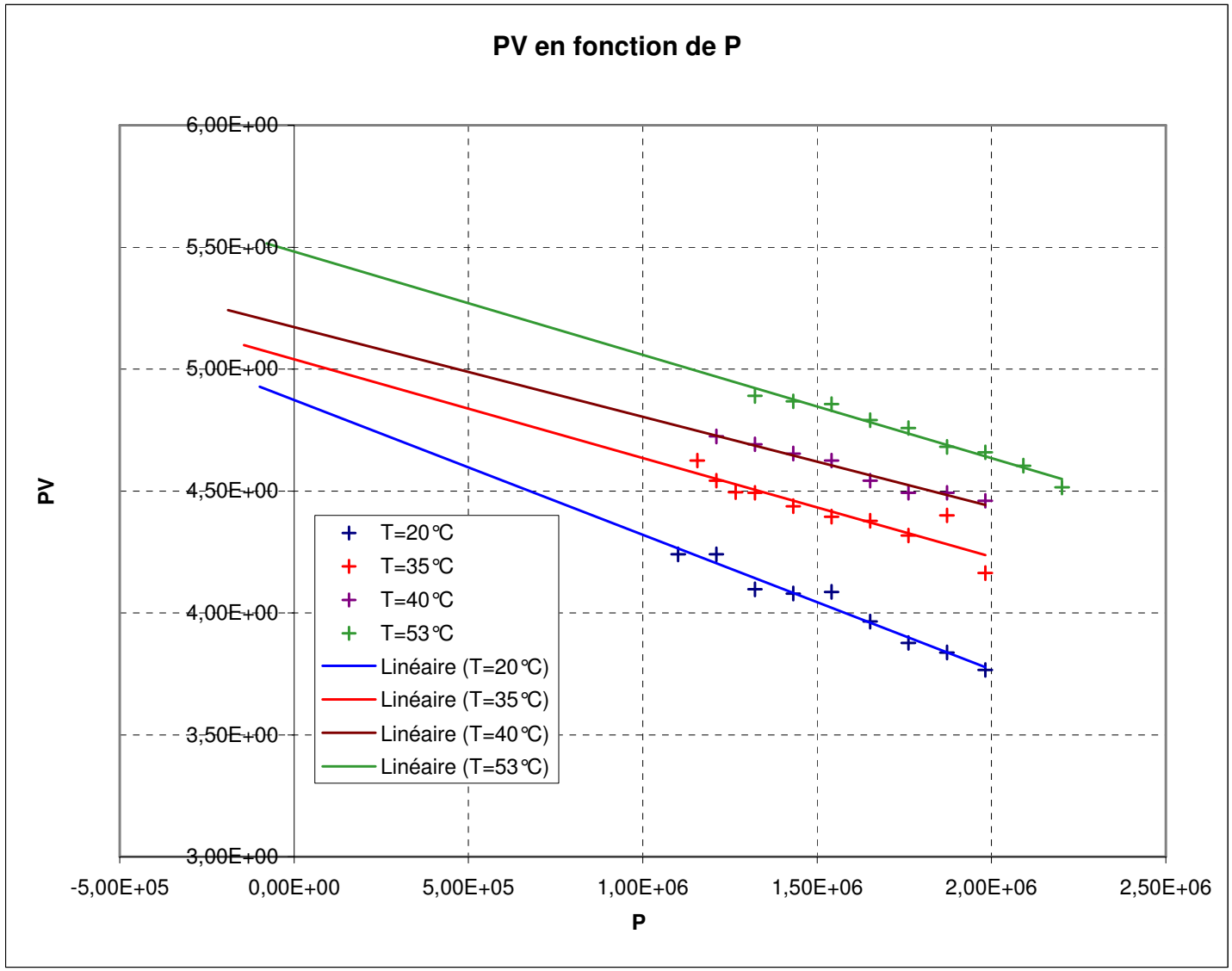
* As a function of 1/V : $PV = nRT(1 + A / V)$
* As a function of P : $PV = nRT(1 + BP)$

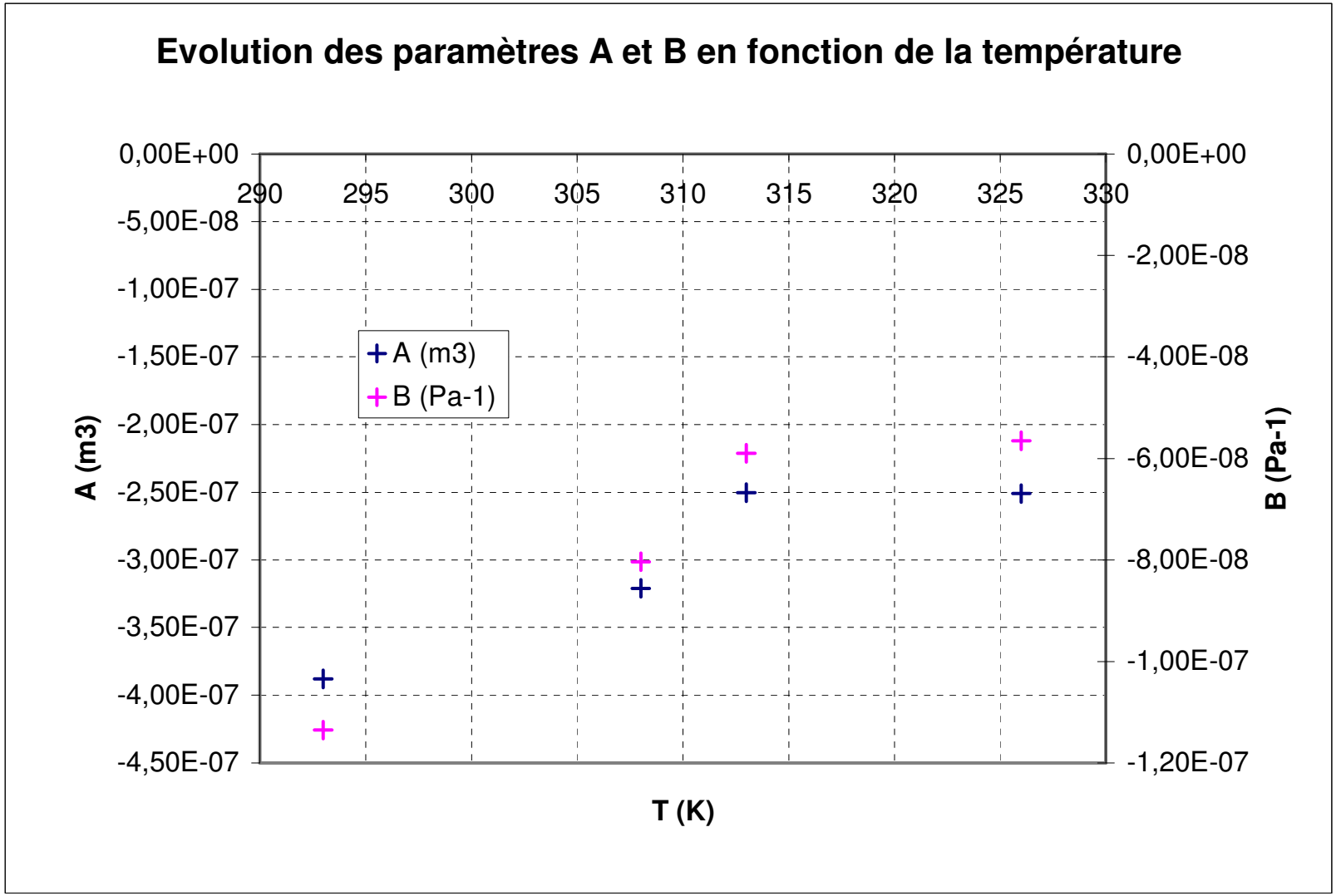
* We plot, for different temperatures, $PV = g(1 / V)$.
  The slope is nRTA
  The y-intercept is nRT

* We plot, for different temperatures, $PV = f(P)$.
  The slope is nRTB
  The y-intercept is nRT

Développement du viriel (a viriel series expansion) :




PV en fonction de P
6,00E+00
5,50E+00
5,00E+00
4,50E+00
4,00E+00
3,50E+00
3,00E+00
PV
-5,00E+05
0,00E+00
5,00E+05
1,00E+06
1,50E+06
2,00E+06
2,50E+06
P
T=20°C
T=35°C
T=40°C
T=53°C
Linéaire (T=20°C)
Linéaire (T=35°C)
Linéaire (T=40°C)
Linéaire (T=53°C)


Evolution des paramètres A et B en fonction de la température
0,00E+00
-5,00E-08
-1,00E-07
-1,50E-07
-2,00E-07
-2,50E-07
-3,00E-07
-3,50E-07
-4,00E-07
-4,50E-07
290
295
300
305
310
315
320
325
330
A (m3)
B (Pa-1)
0,00E+00
-2,00E-08
-4,00E-08
-6,00E-08
-8,00E-08
-1,00E-07
-1,20E-07
A (m3)
B (Pa-1)
T (K)

Viriel series expansion for a Van der Waals gaz :

The equation of state for a Van der Waals gaz is (for one mol) :

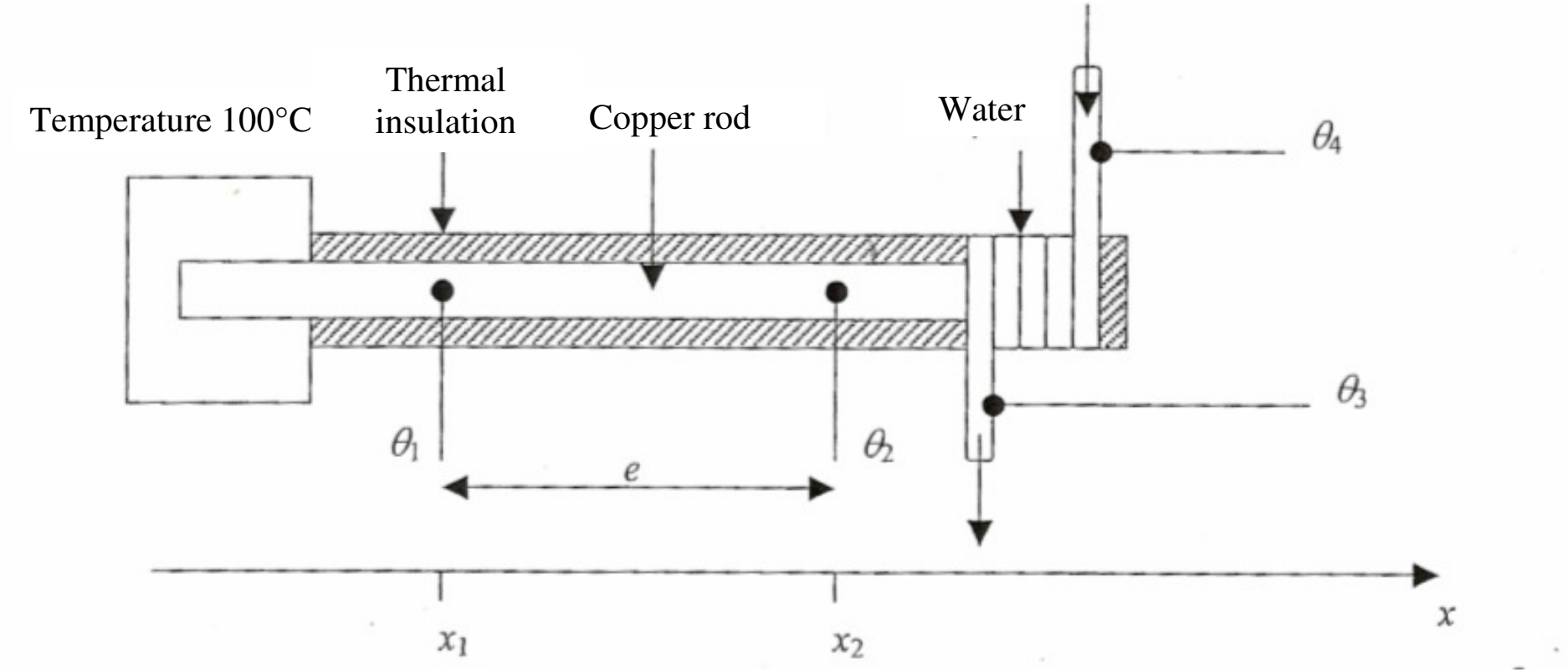
$$\left(P + \frac{a}{V^2}\right)(V - b) = RT$$

For the dioxygen gas O_2 :

$$a = 1{,}36\ atm.L^2.mol^{-2} \quad ; \quad b = 0{,}0318\ L.mol^{-1} \quad ; \quad 1\ atm = 1{,}013.10^5\ Pa$$

- Interpretation of the a and b coefficients
- viriel series expansion (PV as a function of 1 / V)

2 – An experimental setup : how to measure the thermal conductivity of the copper ?



On réalise le montage suivant afin de mesurer la conductivité thermique K du cuivre. L'extrémité gauche de la barre cylindrique de cuivre, de section S = 11,5 cm^2, est placée dans une étuve maintenue à 100°C.

- L'autre extrémité est en contact avec un serpentin dans lequel circule de l'eau (de capacité thermique massique $c = 4{,}18\ kJ{\cdot}K^{-1}{\cdot}kg^{-1}$) avec un débit massique $D_m = 0{,}80\ g{\cdot}s^{-1}$. L'échangeur thermique ainsi constitué permet de réchauffer l'eau de θ_4 à θ_3.
- La barre est calorifugée latéralement à l'aide d'enveloppes isolantes.
- On mesure les températures θ_1 et θ_2 de la barre en deux points de celle-ci distants de $e = 10$ cm ainsi que les températures θ_4 et θ_3 de l'eau juste avant et après la zone d'échange thermique.
- Le problème est unidimensionnel, le matériau homogène et on négligera tout phénomène de rayonnement et de convection au niveau de la barre.

1) Pourquoi calorifuge-t-on la surface latérale de la barre ? Citer un exemple de matériau isolant thermique pouvant être utilisé dans ce montage.

2) On attend que le régime stationnaire soit établi. En appliquant l'équation de la conduction thermique, exprimer la température $T(x)$ le long de la barre en fonction de la variable x et des constantes x_1, e, T_1 et T_2 ($T(K) = \theta(°C) + 273.$).

3) Déterminer la puissance thermique traversant la section S de la barre. Celle-ci dépend-elle de x ? justifier.

4) Déterminer la puissance thermique reçue par l'eau circulant dans le serpentin en fonction de θ_3 et θ_4 (on pourra d'abord réaliser un bilan sur la masse dm d'eau traversant le serpentin pendant la durée dt).

5) En déduire l'expression de la conductivité thermique K du cuivre.
Avec les valeurs suivantes: $\theta_1 = 81{,}5°C$, $\theta_2 = 57{,}0°C$, $\theta_3 = 48{,}5°C$, $\theta_4 = 17{,}0°C$ on obtient $K = 374$. Donner l'unité de K.

6) La valeur donnée dans les tables est $K = 390$. Comment expliquer cette différence.

An experimental setup : how to measure the thermal conductivity of the copper ?

Conduction is heat transfer by means of molecular agitation within a material without any motion of the material as a whole.

If one end of a metal rod is at a higher temperature, then energy will be transferred down the rod toward the colder end because the higher speed particles will collide with the slower ones with a net transfer of energy to the slower ones.

Conduction is due to a temperature gradient.

The law of heat conduction (Fourier's law) states that the time rate of heat transfer through a material is proportional to the negative gradient in the temperature and to the area, through which the heat is flowing.

$$\vec{j}_{th} = -K\,\overrightarrow{grad T} = -K\frac{\partial T(x,t)}{\partial x}\vec{u}_x$$

(Local heat flux vector, $W.m^{-2}$)

(K is the thermal conductivity of the material)

Steady state conduction is the form of conduction that happens when the temperature difference is constant, so that (after a relaxation time), the spatial distribution of temperatures in the object does not change.

Thus all derivatives of temperature at any point with respect to time are zero.

For example, a bar may be cold at one end and hot at the other, but after a state of steady state conduction is reached, the spatial gradient of temperatures along the bar does not change any further, as time proceeds.

The temperature at any given section of the rod remains constant, and this temperature varies linearly in space, along the direction of heat transfer.

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1) Matériau isolant (heat insulating materials) : mousse de polystyrène (polystyrene sponge), laine de verre (glass wool), …

2) L'équation de la conduction thermique est : $$\frac{\partial T}{\partial t} = \frac{K}{\mu c_{Cu}} \frac{\partial^2 T}{\partial x^2}$$

$$T(x) = T_1 + \frac{T_2 - T_1}{e}(x - x_1)$$

3) La puissance thermique est :

$$\Phi = -KS\frac{T_2 - T_1}{e}$$

4) Le 1er principe de la thermodynamique donne :

$$dU \approx dH = dm\, c\,(\theta_3 - \theta_4) = \delta Q + \delta W = P_{th}dt$$

$$P_{th} = D_m c(\theta_3 - \theta_4)$$

5) L'échangeur est parfait :

$$P_{th} = D_m c(\theta_3 - \theta_4) = \Phi = -KS\frac{T_2 - T_1}{e}$$

$$\boxed{K = \frac{D_m ce}{S}\frac{\theta_3 - \theta_4}{\theta_1 - \theta_2}} \quad \Rightarrow \quad \frac{\Delta K}{K} = \ ?$$

AN : $K = 374\, W.m^{-1}.K^{-1}$.

6) Incertitudes sur les mesures : températures et longueurs

Validité des hypothèses :

* Régime permanent
* Isolation latérale
* Matériau homogène
* Echangeur parfait

3) Une application de la transformée de Fourier en diffusion de la chaleur :

In general, during any period in which temperatures are changing in time at any place within an object, the mode of thermal energy flow is termed ***transient conduction***.

Another term is "***non steady-state***" conduction.

Non-steady-state situations may appear :

- After an imposed change in temperature at a boundary of an object.
- With temperature changes inside an object.
- As a result of a new source of heat suddenly introduced within the object.

Analysis of non steady-state conduction systems is more complex than steady-state systems ; except for simple shapes, it is necessary to make approximations and numerical analysis with computer.

Méthode dite "de séparation des variables" et analyse de Fourier des conditions initiales :

Diffusion thermique dans un solide suivant la direction (Ox).

Ni production, ni absorption de chaleur dans le milieu.

On appelle T(x,t) la température au sein du solide et K le coefficient thermique.

Résolution de l'équation de la chaleur par la méthode de séparation des variables :

$$T(x,t) = T_0 + f(x).g(t)$$

où T_0 désigne une constante, f(x) une fonction de x uniquement et g(t) une fonction du temps seulement.

a) Déterminer l'expression générale des fonctions f(x) et g(t).

b) On suppose qu'à t = 0, $T(x,0) = T_1 + T_2 \sin(px)$ (T_1, T_2 et p désignant des constantes). Montrer que la solution trouvée ci-dessus convient et déterminer complètement cette solution.

Equation de la chaleur : (Temps de diffusion : $\tau \approx L^2 / D$)

$$\boxed{\frac{\partial T(x,t)}{\partial t} = D \frac{\partial^2 T(x,t)}{\partial x^2}}$$

Avec :

$$T(x,t) = T_0 + f(x)g(t) \quad \Rightarrow \quad \frac{1}{D}\frac{\dot{g}(t)}{g(t)} = \frac{f''(x)}{f(x)} = cste = -k^2 < 0$$

Deux équations à résoudre :

$$f''(x) = -k^2 f(x) \quad \Rightarrow \quad f(x) = A\cos(kx) + B\sin(kx)$$

$$\dot{g}(t) = -Dk^2 g(t) \quad \Rightarrow \quad g(t) = e^{-Dk^2 t}$$

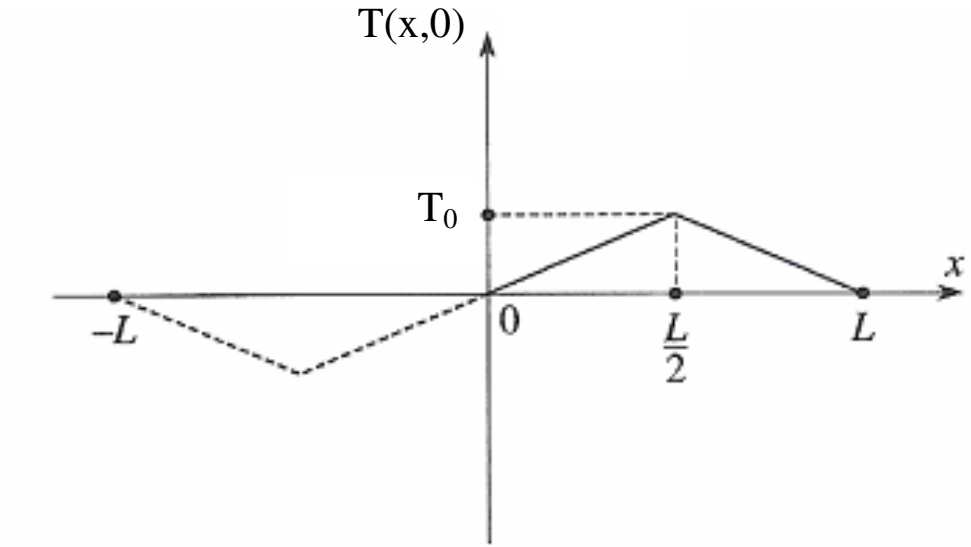
Finalement :

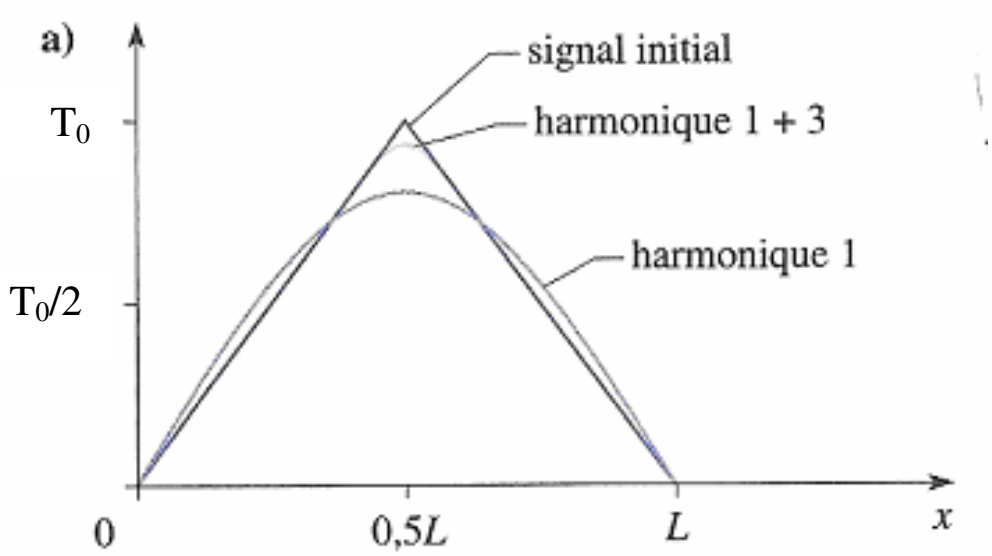
$$T(x,t) = T_0 + e^{-Dk^2 t}\left(A\cos(kx) + B\sin(kx)\right)$$

Avec les conditions initiales :

$$\boxed{T(x,t) = T_1 + T_2 e^{-Dp^2 t}\sin(px)}$$

Des conditions initiales plus réalistes :





$$T(x,0) = \sum_{p=0}^{\infty} \frac{8T_0}{\pi^2} \frac{(-1)^p}{(2p+1)^2} \sin\left((2p+1)\frac{\pi x}{L}\right)$$

$$T(x,t)=\sum_{p=0}^{\infty}\frac{8T_0}{\pi^2}\frac{(-1)^p}{(2p+1)^2}\sin\left((2p+1)\frac{\pi x}{L}\right)e^{-\frac{(2p+1)^2\pi^2 D}{L^2}t}$$

Une simulation avec MAPLE :

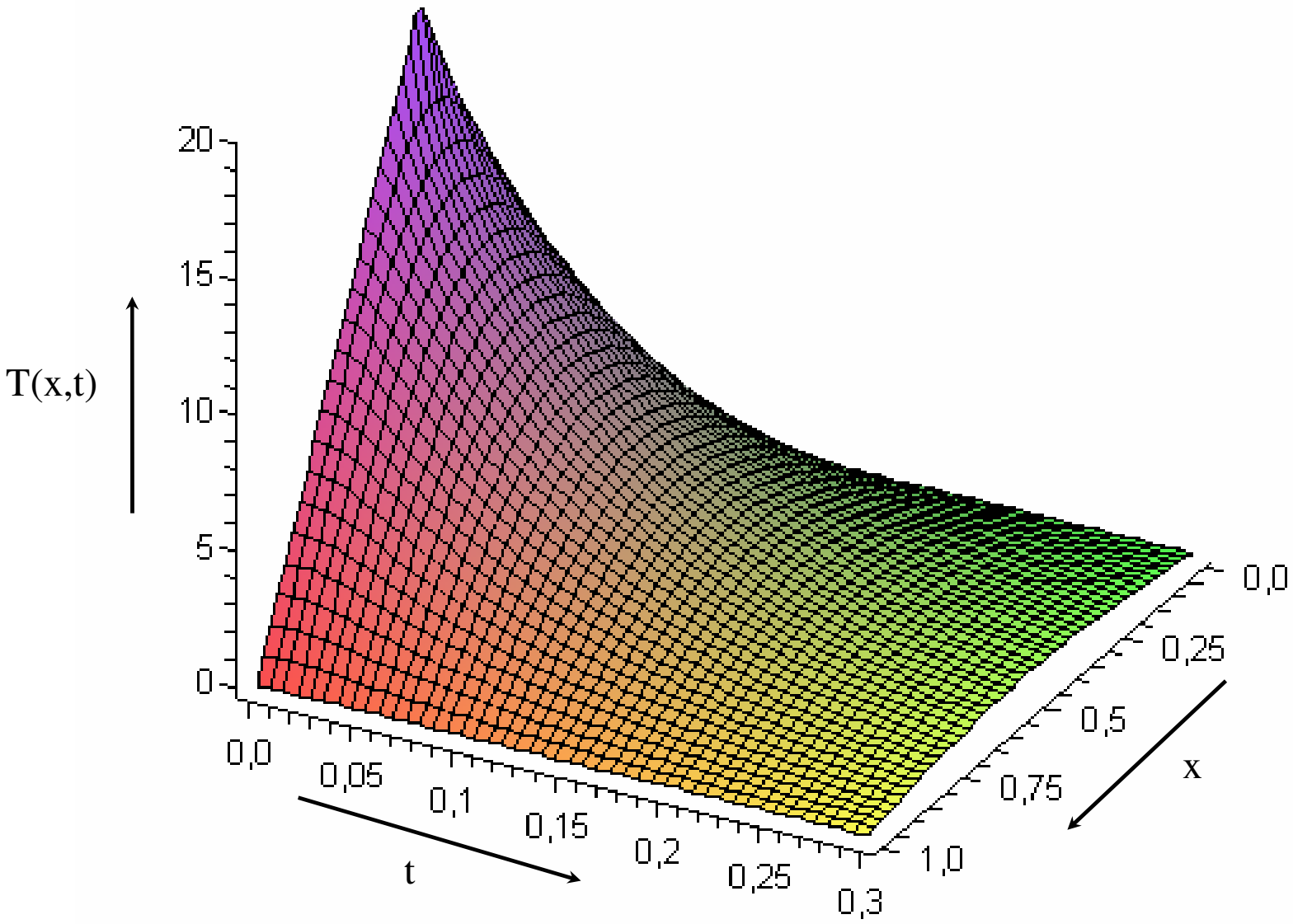
```
restart:with(plots):

T0:=20;L:=1;Dif:=1;Bp:=T0*(8/Pi^2)*((-1)^p)/(2*p+1)^2;
```

$$TO := 20$$
$$L := 1$$
$$Dif := 1$$
$$Bp := \frac{160\,(-1)^p}{\pi^2\,(2p+1)^2}$$

```
T:=(x,t)->Sum(Bp*sin((2*p+1)*Pi*x/L)*exp(-(2*p+1)^2*Pi^2*(Dif/L^2)*t),p=0..20);
```

$$T := (x,t) \rightarrow \sum_{p=0}^{20} Bp\,\sin\left(\frac{(2p+1)\,\pi\,x}{L}\right)\,e^{-\frac{(2p+1)^2\,\pi^2\,Dif\,t}{L^2}}$$

```
plot3d([x,t,T(x,t)],x=0..1,t=0..0.3,numpoints=2000);
```


T(x,t)
20
15
10
5
0
0,0
0,05
0,1
0,15
0,2
0,25
0,3
t
0,0
0,25
0,5
0,75
1,0
x