

**PHY3750**  
**DEVOIR 3**  
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**Problem 1.** (7.5) Calculer la différence d'entropie entre 1g d'azote à température  $T_2 = 20^\circ\text{C} = 293\text{K}$  et pression 1 atm, et 1g d'azote liquide à température  $T_1 = -196^\circ\text{C} = 77\text{K}$  (le point d'ébullition de l'azote), sous la même pression de 1 atm. La chaleur latente de vaporisation de l'azote à pression atmosphérique est 200 kJ/kg. Considérer l'azote comme un gaz parfait à poids moléculaire 28 et de chaleur spécifique molaire de 29.3 J/mol.K indépendante de la température.

First consider the entropy change  $\Delta S_H$  of the heating process from  $-196^\circ\text{C}$  to  $20^\circ\text{C}$ . For an ideal gas  $PV = nRT$  implies:

$$\begin{aligned} dS_H &= \frac{ncdT}{T} + \frac{P}{T}dV = \frac{ncdT}{T} + \frac{nR}{V}dV \\ \Delta S_H &= nc \int \frac{dT}{T} + nR \int \frac{dV}{V} \\ \Delta S_H &= nc \ln\left(\frac{T_2}{T_1}\right) + nR \ln\left(\frac{V_2}{V_1}\right) \end{aligned}$$

Now consider the entropy change  $\Delta S_B$  of the boiling process:

$$\Delta S_B = \frac{nl'}{T_1} = \frac{ml}{T_1} = \frac{(0.001\text{kg})(200\text{kJ/kg})}{77\text{K}} = 0.0026 \frac{\text{kJ}}{\text{K}} = 2.6 \frac{\text{J}}{\text{K}}$$

The number of moles of nitrogen gas  $N_2$  is

$$n = \frac{m}{M} = \frac{1\text{g}}{28\text{g/mol}} = \frac{1}{28}$$

We can find the two volumes using the state equation  $V = \frac{nRT}{P}$  noting that the pressure is constant:

$$\begin{aligned} V_1 &= \frac{nRT_1}{P} = \frac{(\frac{1}{28})8.31(77)}{101.3 \times 10^3} = 2.26 \times 10^{-4}\text{m}^3 \\ V_2 &= \frac{nRT_2}{P} = \frac{(\frac{1}{28})8.31(293)}{101.3 \times 10^3} = 8.58 \times 10^{-4}\text{m}^3 \end{aligned}$$

So the total entropy difference is

$$\begin{aligned} \Delta S &= \Delta S_B + \Delta S_H \\ &= 2.6 + nc \ln\left(\frac{T_2}{T_1}\right) + nR \ln\left(\frac{V_2}{V_1}\right) \\ &= 2.6 + \frac{1}{28}(29.3) \ln\left(\frac{293}{77}\right) + \frac{1}{28}(8.31) \ln\left(\frac{8.58}{2.26}\right) \\ &= 2.6 + 1.40 + 0.40 \\ \Delta S &= 4.4 \frac{\text{J}}{\text{K}} \end{aligned}$$

**Problem 2.** (7.8) Calculer le changement d'entropie de l'Univers résultant des processus suivants. La chaleur spécifique du cuivre à pression constante est  $385 \text{ J kg}^{-1} \text{ K}^{-1}$ . Dans chaque situation on s'attend suffisamment longtemps pour que le système atteigne l'équilibre thermique.

**A.** Un bloc de cuivre de masse  $0.4 \text{ kg}$  et température  $T_1 = 100^\circ\text{C} = 373\text{K}$  est mis dans un lac à température  $T_2 = 10^\circ\text{C} = 283\text{K}$ .

Assume that the lake is large enough so that the final temperature of the block is  $T_2 = 283\text{K}$ . The entropy change in the block of copper is then

$$\begin{aligned} dS_{Cu} &= \frac{\delta Q}{T} = \frac{mc dT}{T} \\ \Delta S_{Cu} &= mc \int \frac{dT}{T} = mc \ln \left( \frac{T_2}{T_1} \right) \\ \Delta S_{Cu} &= (0.4)(385) \ln \left( \frac{283}{373} \right) = -42.5 \frac{\text{J}}{\text{K}} \end{aligned}$$

The lake absorbs heat in an (approximately) isothermal process so the entropy change in the lake is given by

$$\begin{aligned} \Delta S_{lake} &= \frac{-Q}{T_2} = \frac{-mc}{T_2} \int_{T_1}^{T_2} dT = \frac{mc(T_1 - T_2)}{T_2} \\ \Delta S_{lake} &= \frac{0.4(385)(373 - 283)}{283} = 49.0 \frac{\text{J}}{\text{K}} \end{aligned}$$

This means that the entropy change in the universe is

$$\begin{aligned} \Delta S_{universe} &= \Delta S_{lake} + \Delta S_{Cu} \\ &= 49.0 - 42.5 \\ \Delta S_{universe} &= +6.5 \frac{\text{J}}{\text{K}} \end{aligned}$$

**B.** Le même bloc à  $T_1 = 10^\circ\text{C} = 283\text{K}$  est laissé tomber dans le lac d'une hauteur de  $h = 100\text{m}$ .

Note that no heat is exchanged between the block and the surrounding lake. Thus for the block,

$$dS_{Cu} = \frac{\delta Q}{T} = 0 \implies \Delta S_{Cu} = 0$$

However, the lake absorbs the kinetic energy of the block. Assuming the lake is much larger than the block, it experiences no change in internal energy. The entropy change of the lake is then

$$\begin{aligned} dS_{lake} &= \frac{\delta Q}{T} = \frac{dU + \delta W}{T} = \frac{\delta W}{T} \\ \Delta S_{lake} &= \frac{W}{T} = \frac{mgh}{T} \\ \Delta S_{lake} &= \frac{(0.4)(9.8)(100)}{283} = +1.39 \frac{\text{J}}{\text{K}} \end{aligned}$$

The entropy change in the universe is then

$$\Delta S_{universe} = \Delta S_{lake} + 0 = 1.39 \frac{\text{J}}{\text{K}}$$

**C.** Deux blocs identiques à températures  $T_A = 100^\circ\text{C} = 373\text{K}$  et  $T_B = 10^\circ\text{C} = 283\text{K}$  sont mis en contact dans une enceinte adiabatique isobare de capacité thermique négligeable.

The two blocks are isolated from their surroundings, so

$$\Delta S_{\text{universe}} = 0 + \Delta S_{\text{system}}$$

Heat flows from block A to block B:

$$\begin{aligned}\Delta S_{\text{system}} &= \Delta S_A + \Delta S_B \\ &= \frac{-Q}{T_A} + \frac{Q}{T_B} = -Q \left( \frac{1}{T_A} - \frac{1}{T_B} \right)\end{aligned}$$

Where  $Q = |Q_A| = |Q_B|$ . We can find  $Q$  by using the fact that

$$\begin{aligned}|Q_A| &= |Q_B| \\ mc(T_A - T_F) &= mc(T_F - T_B) \\ T_A - T_F &= T_F - T_B \\ T_F &= \frac{T_A + T_B}{2} = \frac{373 + 283}{2} = 328\text{K}\end{aligned}$$

Then,

$$Q = |Q_A| = mc(T_A - T_F) = 0.4(385)(373 - 328) = 6930\text{J}$$

and so

$$\Delta S_{\text{universe}} = -Q \left( \frac{1}{T_A} - \frac{1}{T_B} \right) = -6930 \left( \frac{1}{373} - \frac{1}{283} \right) = 5.45 \frac{\text{J}}{\text{K}}$$

**Problem 3.** (8.1) Les équations d'état pour un système thermodynamique sont  $P = aT - b(V - V_0)$  et  $U = \frac{b}{2}(V - V_0)^2 + cT$  où  $a$ ,  $b$  et  $c$  sont des constantes.

**A.** Démontrer que ces équations sont consistantes avec les lois de la thermodynamique (qu'elles satisfont les conditions de consistance).

First we require that

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

Note that  $\left( \frac{\partial U}{\partial V} \right)_T = b(V - V_0)$  and  $\left( \frac{\partial P}{\partial T} \right)_V = a$ . So the right side becomes

$$T \left( \frac{\partial P}{\partial T} \right)_V - P = aT - aT + b(V - V_0) = b(V - V_0) = \left( \frac{\partial U}{\partial V} \right)_T$$

as needed. Now, we calculate  $C_V$  using

$$C_V = \left( \frac{\partial U}{\partial T} \right)_V = c = \text{constant}$$

Noting that  $\left( \frac{\partial C_V}{\partial V} \right)_T = 0$ , we want the following condition to be satisfied:

$$T \left( \frac{\partial^2 P}{\partial T^2} \right)_V = \left( \frac{\partial C_V}{\partial V} \right)_T = 0$$

Since  $a$  is a constant,  $\left( \frac{\partial^2 P}{\partial T^2} \right)_V = 0$ , so that condition is satisfied. There are no other consistency conditions for this system.

**B.** Trouver l'entropie du système.

We know that

$$\left(\frac{\partial S}{\partial T}\right)_V = \frac{1}{T} \left(\frac{\partial U}{\partial T}\right)_V = \frac{c}{T}$$

We also know that

$$\left(\frac{\partial S}{\partial V}\right)_T = \frac{1}{T} \left( \left(\frac{\partial U}{\partial V}\right)_T + P \right) = \frac{1}{T} (b(V - V_0) + aT - b(V - V_0)) = \frac{aT}{T} = a$$

Now, the entropy  $S$  is a function  $S(T, V)$ , so

$$\begin{aligned} dS &= \left(\frac{\partial S}{\partial T}\right)_V dT + \left(\frac{\partial S}{\partial V}\right)_T dV \\ dS &= \frac{c}{T} dT + a dV \\ S &= c \int \frac{dT}{T} + a \int dV \\ S(T, V) &= c \ln(T) + aV + S_0 \quad \square \end{aligned}$$

**C.** Est-ce que ces équations peuvent être valides à basses températures ? Justifier votre réponse.

The third law of thermodynamics requires that for systems in thermal equilibrium ( $T_1 = T_2$ ), the following condition holds:

$$\lim_{T \rightarrow 0} (S_2 - S_1) = 0.$$

Now,

$$\begin{aligned} \lim_{T \rightarrow 0} (S_2 - S_1) &= \lim_{T \rightarrow 0} \left( c \ln \left( \frac{T_2}{T_1} \right) + a(V_2 - V_1) \right) \\ &= \lim_{T \rightarrow 0} \left( c \ln(1) + a(V_2 - V_1) \right) \\ &= a(V_2 - V_1) \end{aligned}$$

Since this term does not necessarily go to zero as the temperature drops the equations are not valid for very low temperatures.

**Problem 4.** (8.3) Un gaz obéit à l'équation d'état Redlich-Kwong  $\left(P + \frac{n^2 a}{\sqrt{T} V(V+nb)}\right)(V - nb) = nRT$ , où  $a$  et  $b$  sont des constantes caractérisant le gaz.

**A.** Démontrer qu'une capacité thermique à volume constante dans la forme  $C_V = A(T) + \frac{3na}{4bT^{3/2}} \ln \frac{V+nb}{V}$ , où  $A(T)$  est une fonction inconnue de la température, est consistante avec l'équation Redlich-Kwong.

We need to check the condition  $\left(\frac{\partial C_V}{\partial V}\right)_T = T \left(\frac{\partial^2 P}{\partial T^2}\right)_V$ .

$$\left(\frac{\partial C_V}{\partial V}\right)_T = \frac{3na}{4bT^{3/2}} \frac{V}{V+nb} \left(\frac{-nb}{V^2}\right) = \frac{-3n^2 a}{4V(V+nb)} T^{-3/2}$$

Now,

$$P = \frac{nRT}{V - nb} - \frac{n^2 a}{V(V + nb)} T^{-1/2}$$

So

$$\begin{aligned}\left(\frac{\partial P}{\partial T}\right)_V &= \frac{nR}{V-nb} + \frac{1}{2} \frac{n^2 a}{V(V+nb)} T^{-3/2} \\ \left(\frac{\partial^2 P}{\partial T^2}\right)_V &= -\frac{3}{2} \frac{1}{2} \frac{n^2 a}{V(V+nb)} T^{-5/2} = \frac{-3n^2 a}{4V(V+nb)} T^{-5/2}\end{aligned}$$

Now

$$T\left(\frac{\partial^2 P}{\partial T^2}\right)_V = \frac{-3n^2 a}{4V(V+nb)} T^{-5/2} T = \frac{-3n^2 a}{4V(V+nb)} T^{-3/2} = \left(\frac{\partial C_V}{\partial V}\right)_T$$

as required.

**B.** Trouver l'énergie interne du gaz en fonction du volume et de la température. Assumer  $A(T) = nc$ , où  $c$  est une constante.

The partial derivatives of  $U = U(T, V)$  are

$$\left(\frac{\partial U}{\partial T}\right)_V = C_V = nc + \frac{3na}{4b} \ln\left(\frac{V+nb}{V}\right) T^{-3/2}$$

and

$$\begin{aligned}\left(\frac{\partial U}{\partial V}\right)_T &= T\left(\frac{\partial P}{\partial T}\right)_V - P \\ &= T\left(\frac{nR}{V-nb} + \frac{1}{2} \frac{n^2 a}{V(V+nb)} T^{-3/2}\right) - \left(\frac{nRT}{V-nb} - \frac{n^2 a}{V(V+nb)} T^{-1/2}\right) \\ &= \frac{nRT}{V-nb} + \frac{1}{2} \frac{n^2 a}{V(V+nb)} T^{-1/2} - \frac{nRT}{V-nb} + \frac{n^2 a}{V(V+nb)} T^{-1/2} \\ &= \frac{3}{2} \frac{n^2 a}{V(V+nb)} T^{-1/2} = \frac{3}{2} \frac{n^2 a}{T^{1/2}} \frac{1}{V(V+nb)}\end{aligned}$$

Now

$$\begin{aligned}dU &= \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV \\ &= \left(nc + \frac{3na}{4b} \ln\left(\frac{V+nb}{V}\right) T^{-3/2}\right) dT + \frac{3}{2} \frac{n^2 a}{T^{1/2}} \frac{1}{V(V+nb)} dV \\ U &= nc \int dT + \frac{3na}{4b} \ln\left(\frac{V+nb}{V}\right) \int T^{-3/2} dT + \frac{3}{2} \frac{n^2 a}{T^{1/2}} \int \frac{1}{V(V+nb)} dV \\ &= ncT + \frac{3na}{4b} \ln\left(\frac{V+nb}{V}\right) (-2T^{-1/2}) + \frac{3}{2} \frac{n^2 a}{T^{1/2}} \int \frac{1}{V(V+nb)} dV \\ &= ncT - \frac{3na}{2b} \ln\left(\frac{V+nb}{V}\right) T^{-1/2} + \frac{3n^2 a}{2} T^{-1/2} \int \frac{1}{V(V+nb)} dV\end{aligned}$$

To solve the integral, note that  $\ln \frac{V+nb}{V}$  is the integral of its derivative:

$$\begin{aligned}
 \ln \left( \frac{V+nb}{V} \right) &= \int \frac{V}{V+nb} \left( \frac{1}{V} - \frac{V+nb}{V^2} \right) dV \\
 &= \int \left( \frac{1}{V+nb} - \frac{1}{V} \right) dV \\
 &= \int \left( \frac{V - V - nb}{V(V+nb)} \right) dV \\
 &= -nb \int \frac{1}{V(V+nb)} dV \\
 \int \frac{1}{V(V+nb)} dV &= \frac{-1}{nb} \ln \left( \frac{V+nb}{V} \right)
 \end{aligned}$$

Thus,

$$\begin{aligned}
 U &= ncT - \frac{3na}{2b} \ln \left( \frac{V+nb}{V} \right) T^{-1/2} + \frac{3n^2a}{2} T^{-1/2} \left( \frac{-1}{nb} \right) \ln \left( \frac{V+nb}{V} \right) \\
 &= ncT - \frac{3na}{2b} \ln \left( \frac{V+nb}{V} \right) T^{-1/2} - \frac{3na}{2b} \ln \left( \frac{V+nb}{V} \right) T^{-1/2} \\
 U(T, V) &= ncT - \frac{3na}{b} \ln \left( \frac{V+nb}{V} \right) T^{-1/2} \quad \square
 \end{aligned}$$

This method of integrating directly is incorrect since the variables are not separated in the differential...

C. Démontrer que l'entropie du gaz sous la supposition en **B.** peut être exprimée comme:

$$S(T, V) = nc \ln T + nR \ln(V - nb) - \frac{na}{2bT^{3/2}} \ln \frac{V+nb}{V} + S_0$$

We can compute the derivatives of  $S(T, V)$  using  $U(T, V)$ :

$$\begin{aligned}
 \left( \frac{\partial S}{\partial T} \right)_V &= \frac{1}{T} \left( \frac{\partial U}{\partial T} \right)_V \\
 &= \frac{1}{T} \left( nc - \frac{3na}{b} \ln \left( \frac{V+nb}{V} \right) \left( \frac{-1}{2} \right) T^{-3/2} \right) = \frac{1}{T} \left( nc + \frac{3na}{2b} \ln \left( \frac{V+nb}{V} \right) T^{-3/2} \right) \\
 \left( \frac{\partial S}{\partial T} \right)_V &= \frac{nc}{T} + \frac{3na}{2b} \ln \left( \frac{V+nb}{V} \right) T^{-5/2}
 \end{aligned}$$

and:

$$\begin{aligned}
 \left( \frac{\partial S}{\partial V} \right)_T &= \frac{1}{T} \left( \left( \frac{\partial U}{\partial V} \right)_T + P \right) \\
 &= \frac{1}{T} \left( -\frac{3na}{b} T^{-1/2} \frac{(-nb)}{V(V+nb)} \right) \\
 &= \frac{1}{T} \left( \frac{3n^2a}{V(V+nb)} T^{-1/2} \right) \\
 \left( \frac{\partial S}{\partial V} \right)_T &= \frac{3n^2a}{V(V+nb)} T^{-3/2}
 \end{aligned}$$

Now,

$$\begin{aligned}
 dS &= \left(\frac{\partial S}{\partial T}\right)_V dT + \left(\frac{\partial S}{\partial V}\right)_T dV \\
 &= \left(\frac{nc}{T} + \frac{3na}{2b} \ln\left(\frac{V+nb}{V}\right) T^{-5/2}\right) dT + \frac{3n^2a}{V(V+nb)} T^{-3/2} dV \\
 S &= nc \int \frac{dT}{T} + \frac{3na}{2b} \ln\left(\frac{V+nb}{V}\right) \int T^{-5/2} dT + \frac{3n^2a}{T^{3/2}} \int \frac{1}{V(V+nb)} dV \\
 &= nc \ln T + \frac{3na}{2b} \ln\left(\frac{V+nb}{V}\right) \left(\frac{-2}{3}\right) T^{-3/2} + \frac{3n^2a}{T^{3/2}} \left(\frac{-1}{nb}\right) \ln\left(\frac{V+nb}{V}\right) + S_0 \\
 &= nc \ln T - \frac{na}{bT^{3/2}} \ln\left(\frac{V+nb}{V}\right) - \frac{3na}{bT^{3/2}} \ln\left(\frac{V+nb}{V}\right) + S_0 \\
 S(T, V) &= nc \ln T - \frac{4na}{bT^{3/2}} \ln\left(\frac{V+nb}{V}\right) + S_0
 \end{aligned}$$

How to get to the other form? This method of integrating directly is incorrect since the variables are not separated in the differential...

**Problem 5.** (8.6) Des mesures expérimentales de la capacité thermique à volume constante  $C_V$  et la pression  $P$  dans un système thermodynamique d'un mole ont donné les expressions d'approximation suivantes:

$$\begin{aligned}
 C_V &= \frac{c}{T} - 2bVT^{-3} \\
 P &= \frac{RT}{V} e^{-aV} - \frac{b}{3T^2}
 \end{aligned}$$

où  $a$ ,  $b$  et  $c$  sont des constantes.

A. Démontrer que ces équations sont consistantes avec les lois de la thermodynamique.

We want  $\left(\frac{\partial C_V}{\partial V}\right)_T = T \left(\frac{\partial^2 P}{\partial T^2}\right)_V$ . Compute the derivatives of  $P$ ...

$$\begin{aligned}
 \left(\frac{\partial P}{\partial T}\right)_V &= \frac{R}{V} e^{-aV} - (-2) \frac{b}{3T^3} = \frac{R}{V} e^{-aV} + \frac{2b}{3T^3} \\
 \left(\frac{\partial^2 P}{\partial T^2}\right)_V &= \frac{2b(-3)}{3T^4} = \frac{-2b}{T^4}
 \end{aligned}$$

Now the derivative of  $C_V$ :

$$\left(\frac{\partial C_V}{\partial V}\right)_T = \frac{-2b}{T^3} = T \frac{-2b}{T^4} = T \left(\frac{\partial^2 P}{\partial T^2}\right)_V$$

as needed.

B. Dériver une expression pour l'énergie interne du système.

We know that

$$\left(\frac{\partial U}{\partial T}\right)_V = C_V = \frac{c}{T} - 2bVT^{-3}$$

We also know that

$$\begin{aligned}
 \left(\frac{\partial U}{\partial V}\right)_T &= T\left(\frac{\partial P}{\partial T}\right)_V - P \\
 &= T\left(\frac{R}{V}e^{-aV} + \frac{2b}{3T^3}\right) - \frac{RT}{V}e^{-aV} + \frac{b}{3T^2} \\
 &= \frac{RT}{V}e^{-aV} + \frac{2b}{3T^2} - \frac{RT}{V}e^{-aV} + \frac{b}{3T^2} \\
 \left(\frac{\partial U}{\partial V}\right)_T &= \frac{b}{T^2}
 \end{aligned}$$

Now,

$$\begin{aligned}
 \left(\frac{\partial U}{\partial V}\right)_T &= \frac{b}{T^2} \implies dU = \frac{b}{T^2}dV \\
 U &= \frac{b}{T^2}V + f(T)
 \end{aligned}$$

Taking the derivative wrt. to  $T$  of this expression:

$$\begin{aligned}
 \left(\frac{\partial U}{\partial T}\right)_V &= \frac{-2bV}{T^3} + \frac{df}{dT} \\
 \frac{-2bV}{T^3} + \frac{df}{dT} &= \frac{c}{T} - 2bVT^{-3} \\
 \frac{df}{dT} &= \frac{c}{T} \\
 f &= c \ln T + U_0
 \end{aligned}$$

Thus we get an expression for  $U(T, V)$ :

$$U(T, V) = \frac{b}{T^2}V + c \ln T + U_0 \quad \square$$

**Problem 6.** (8.9) Des mesures expérimentales sur un ressort de longueur naturel  $x_0$  à température  $T_0$  donnent les résultats suivants : la force élastique augmente linéairement avec l'élongation du ressort (loi de Hooke), et sa longueur augmente linéairement avec la température (expansion thermique); où  $f$  est la force élastique sur le ressort,  $x$  est sa longueur,  $T$  est la température et  $k$  et  $a$  sont des constantes. La capacité thermique du ressort à longueur constante est aussi mesurée et s'avère aussi constante:

$$\left(\frac{\partial f}{\partial x}\right)_T = -k, \quad \left(\frac{\partial x}{\partial T}\right)_f = a, \quad \left(\frac{\partial U}{\partial T}\right)_x = C$$

**A.** Trouver la force élastique en fonction de  $x$  et  $T$ :  $f(x, T)$ . Écrire les constantes d'intégration explicitement pour s'assurer que la force est nulle à longueur  $x_0$  et température  $T_0$ .

Starting from the derivative of  $f$ :

$$\begin{aligned}
 \left(\frac{\partial f}{\partial x}\right)_T &= -k \\
 df &= -kdx \\
 f &= -k(x - x_0) + g(T)
 \end{aligned}$$



where  $g(T)$  is some function of  $T$ . Since  $C$  is constant,

$$\begin{aligned}\left(\frac{\partial C}{\partial x}\right)_T &= 0 = T\left(\frac{\partial^2 f}{\partial T^2}\right)_x \\ \left(\frac{\partial^2 f}{\partial T^2}\right)_x &= 0\end{aligned}$$

Note that since  $\left(\frac{\partial f}{\partial T}\right)_x = \frac{dg}{dT}$ , we have

$$\left(\frac{\partial^2 f}{\partial T^2}\right)_x = \frac{d^2 g}{dT^2} = 0 \implies \frac{dg}{dT} = \text{constant}$$

This implies that  $g(T)$  is linear in  $T$  and we write

$$g(T) = b(T - T_0)$$

for some constant  $b$ . Now

$$f = -k(x - x_0) + b(T - T_0)$$

We can find a value for  $b$  using the derivative on  $x$ :

$$\begin{aligned}x &= \frac{b(T - T_0) - f}{k} + x_0 \\ \left(\frac{\partial x}{\partial T}\right)_f &= \frac{b}{k} = a \\ b &= ak\end{aligned}$$

And so we have

$$f(x, T) = -k(x - x_0) + ak(T - T_0)$$

Note that  $f(x_0, T_0) = -k(x_0 - x_0) + ak(T_0 - T_0) = 0$ .

**B. Trouver l'énergie interne du ressort en fonction de  $x$  et  $T$ .**

We already know that  $\left(\frac{\partial U}{\partial T}\right)_x = C = \text{constant}$ . We can also find  $\left(\frac{\partial U}{\partial x}\right)_T$ :

$$\begin{aligned}\left(\frac{\partial U}{\partial x}\right)_T &= T\left(\frac{\partial f}{\partial T}\right)_x - f \\ &= T(ak) + k(x - x_0) - ak(T - T_0) \\ &= k(x - x_0) + akT - akT + akT_0 \\ \left(\frac{\partial U}{\partial x}\right)_T &= k(x - x_0) + akT_0\end{aligned}$$

From  $\left(\frac{\partial U}{\partial T}\right)_x = C$  we have

$$U = C(T - T_0) + h(x)$$

for some function  $h(x)$  of  $x$ . Since  $\left(\frac{\partial U}{\partial x}\right)_T = \frac{dh}{dx}$ ,

$$\begin{aligned}\frac{dh}{dx} &= k(x - x_0) + akT_0 \\ h &= \frac{1}{2}k(x - x_0)^2 + akT_0(x - x_0)\end{aligned}$$

And we get the following expression for the internal energy:

$$U(x, T) = C(T - T_0) + \frac{1}{2}k(x - x_0)^2 + akT_0(x - x_0) \quad \square$$

C. Trouver l'entropie du ressort en fonction de  $x$  et  $T$ .

$$\left(\frac{\partial S}{\partial T}\right)_x = \frac{1}{T} \left(\frac{\partial U}{\partial T}\right)_x = \frac{1}{T} C$$

Now

$$\begin{aligned} \left(\frac{\partial S}{\partial x}\right)_T &= \frac{1}{T} \left( \left(\frac{\partial U}{\partial x}\right)_T + f \right) \\ &= \frac{1}{T} \left( k(x - x_0) + akT_0x - k(x - x_0) + ak(T - T_0) \right) \\ &= \frac{1}{T} \left( akT_0x + akT - akT_0 \right) \\ &= \frac{ak}{T} (T_0(x - 1) + T) \\ \left(\frac{\partial S}{\partial x}\right)_T &= \frac{akT_0(x - 1)}{T} + ak \end{aligned}$$

So

$$\left(\frac{\partial S}{\partial T}\right)_x = \frac{C}{T} \implies S = C \ln \frac{T}{T_0} + j(x)$$

for some function  $j(x)$ . Now

$$\begin{aligned} \left(\frac{\partial S}{\partial x}\right)_T &= \frac{dj}{dx} \\ \frac{dj}{dx} &= \frac{akT_0(x - 1)}{T} + ak \\ j &= \frac{akT_0(x - 1)^2}{2T} + ak(x - x_0) + S_0 \end{aligned}$$

So we get

$$S(x, T) = C \ln \frac{T}{T_0} + \frac{akT_0(x - 1)^2}{2T} + ak(x - x_0) + S_0$$

D. Soit  $x_0 = 20\text{cm}$ ,  $T_0 = 300\text{K}$ ,  $a = 4 \times 10^{-5}\text{m/K}$ ,  $k = 100\text{N/m}$  et  $C = 230\text{J/K}$ . Considérer un extension réversible isotherme à  $300\text{K}$  pour doubler la longueur du ressort à  $x_1 = 40\text{cm}$ . Trouver le changement d'entropie, le changement d'énergie interne, le travail effectué par le ressort et la chaleur qu'il reçoit pendant le processus.

The change in entropy is

$$\begin{aligned} S(x_1, T_0) - S(x_0, T_0) &= \frac{akT_0(x_1 - 1)^2}{2T_0} + ak(x_1 - x_0) - \frac{akT_0(x_0 - 1)^2}{2T_0} - \cancel{ak(x_0 - x_0)} \\ &= \frac{ak(x_1 - 1)^2}{2} + ak(x_1 - x_0) - \frac{ak(x_0 - 1)^2}{2} \\ &= ak \left( \frac{(x_1 - 1)^2 - (x_0 - 1)^2}{2} + (x_1 - x_0) \right) \\ &= 4 \times 10^{-5}(100) \left( \frac{(0.4 - 1)^2 - (0.2 - 1)^2}{2} + (0.4 - 0.2) \right) = 2.4 \times 10^{-4} \frac{\text{J}}{\text{K}} \end{aligned}$$

The change in internal energy is

$$\begin{aligned}
 U(x_1, T_0) - U(x_0, T_0) &= \frac{1}{2}k(x_1 - x_0)^2 + akT_0(x_1 - x_0) - \frac{1}{2}k(x_0 - x_0)^2 - akT_0(x_0 - x_0) \\
 &= \frac{1}{2}k(x_1 - x_0)^2 + akT_0(x_1 - x_0) \\
 &= \frac{1}{2}(100)(0.4 - 0.2)^2 + 4 \times 10^{-5}(100)(300)(0.4 - 0.2) \\
 &= 2.24J
 \end{aligned}$$

The work done is

$$\begin{aligned}
 W &= \int_{x_0}^{x_1} f dx \\
 &= \int_{x_0}^{x_1} -k(x - x_0) + ak(T - T_0) dx \\
 &= \frac{-1}{2}k(x_1 - x_0)^2 + \cancel{ak(T_0 - T_0)(x_1 - x_0)} \\
 &= \frac{-1}{2}(100)(0.2)^2 = -2J
 \end{aligned}$$

The work is done *on* the system. Using conservation of energy the change in heat is

$$Q = \Delta U + W = 2.24 - 2 = 0.24J$$

The rod gains heat.

**Problem 7.** (9.2) L'énergie de Helmholtz pour un système thermodynamique est donnée par

$$F = nc_V T(1 - \ln T) - nRT \ln(V - nb) - \frac{n^2 a}{V}.$$

**A.** Est-ce une équation fondamentale pour ce système? Pourquoi?

Yes, since  $F = F(T, V) = U - TS$  it completely describes the system.

**B.** Calculer l'entropie du système  $S = S(T, V)$

The entropy is given by

$$\begin{aligned}
 S &= -\left(\frac{\partial F}{\partial T}\right)_V \\
 &= -\left(nc_V(1 - \ln T) + nc_V T\left(-\frac{1}{T}\right) - nR \ln(V - nb)\right) \\
 &= -\left(nc_V(1 - \ln T) - nc_V - nR \ln(V - nb)\right) \\
 S(T, V) &= nc_V + nR \ln(V - nb) - nc_V(1 - \ln T)
 \end{aligned}$$

**C.** Calculer les équations d'état  $U = U(T, V)$  et  $P = P(T, V)$  du système.

The pressure is given by

$$\begin{aligned}
 P &= -\left(\frac{\partial F}{\partial V}\right)_T \\
 &= -\left(\frac{-nRT}{V-nb} + \frac{n^2a}{V^2}\right) \\
 P(T, V) &= \frac{nRT}{V-nb} - \frac{n^2a}{V^2}
 \end{aligned}$$

The internal energy is given by

$$\begin{aligned}
 U &= F + TS \\
 &= nc_V T(1 - \ln T) - nRT \ln(V - nb) - \frac{n^2a}{V} + T(nc_V + nR \ln(V - nb) - nc_V(1 - \ln T)) \\
 &= nc_V T(1 - \ln T) - \frac{n^2a}{V} + nc_V T - nc_V T(1 - \ln T) \\
 U(T, V) &= nc_V T - \frac{n^2a}{V} \quad \square
 \end{aligned}$$