SOLUTIONS MANUAL

THERMODYNAMICS
AND AN INTRODUCTION TO
THERMOSTATISTICS
SECOND EDITION

HERBERT B. CALLEN

Manual de soluções para o livro Thermodynamics and an introduction to thermostatistics - second edition. [SUMÁRIO]

Este manual de soluções é essencialmente uma tradução do solucionário original, feito pelo próprio Herbert B. Callen e publicado pela editora JOHN WILEY & SONS no ano de 1986 (ISBN 0 471 81993 X). O solucionário original foi feito e publicado na forma manuscrita, sendo essa a principal razão pela qual decidimos editar esse documento. A praticidade e clareza deste manual de soluções o torna uma excelente ferramenta auxiliar para as pessoas que usam o livro-texto, porém deve-se tomar o cuidado de não fazer dessa ferramenta consultiva a principal forma de resolver os problemas, sendo essa nossa principal preocupação em tornar esse material público.

O livro thermodynamics and an introduction to thermostatistics apresenta 391 problemas ao todo, e esse manual traz a solução de 346 desses problemas e ainda 7 problemas suplementares e suas respectivas soluções. Tomamos o cuidado de deixar esse documento tão mais fiel ao original quanto fosse possível, tanto nas explicações quanto na disposição das figuras, fazendo pequenas correções e alterações quando necessário e conveniente.

Esse manual é um bem público feito por nós estudantes para vocês estudantes. Por favor não o comercialize. Este material, bem como a ciência e não obstante o conhecimento, deve ser acessado por todos e para todos, sendo portanto livre o seu compartilhamento.

Comentários, correções, ou mesmo sugestões de solução para qualquer problema do livro ou deste manual, favor enviar para o e-mail solutionscallen@gmail.com, dessa forma podemos mantê-lo sempre atualizado.

Goiânia, fevereiro de 2022

$\pi i X e L$

Karlengs

WallRiDeR

Feito em LaTeX

Esse PDF foi construído pelas seguintes contribuições:

Capa (feita no inkscape)
$\pi i X e L$ e Lactovacilo

Capítulos 1, 2, 3, 4, 7, 8, 13*, 15, 16, 17, 18, 19, 20, 21.
$\pi i X e L$

Capítulos 5, 6.
WallRiDeR

Capítulos 9, 10, 11, 13*.
Karlengs

Figuras (feitas no inkscape e tikz)
$\pi i X e L$, WallRiDeR e Karlengs

Um agradecimento especial aos queridos Vinny e Mrsteps que tornaram possível o acesso à obra original.

Contato: solutionscallen@gmail.com

$AAEEIIOOOOOOUUFGMPRRRLLLNSTTVD$

Feito no Goiás

A quem interessar possa,
cuide bem desse solucionário,
ele salvou minha vida.
—*Watney*

(e um estudante da graduação)

Página do manual original (única página que não é manuscrita)

Solutions Manual for
 THERMODYNAMICS AND AN INTRODUCTION TO THERMOSTATISTICS
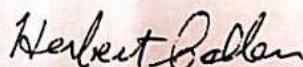   (Second Edition)

                 Herbert B. Callen
                        Published by John Wiley & Sons, 1985

        Solutions to problems in the 1985 edition are
given. A number of supplementary problems are also
included, together with their solutions. Such problems
are identified as supplementary, but they are assigned
numbers compatible with the text (cf. Prob. 1.8-8).

        It is in the interest of all instructors that
this solution manual not become common property in the
student community. Please treat this copy accordingly.

        Comments, corrections, or criticism by users of
the text would be helpful and welcome.

                        Herbert Callen
                        Department of Physics
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Sumário [SUMÁRIO]

18 QUANTUM FLUIDS 178

19 FLUCTUATIONS 182

1   THE PROBLEM AND THE POSTULATES [SUMÁRIO]

1.3   THE COMPOSITION OF THERMODYNAMIC SYSTEMS [SUMÁRIO]

1.3.1   One tenth of a kilogram of NaCl and 0.15 kg of sugar ($\mathbf{C_{12}H_{22}O_{11}}$)... [SUMÁRIO]

Solução:

Os pesos moleculares são :

$Na : 0,023\ kg$; $Cl : 0,035\ kg$;

$C : 0,012\ kg$; $O : 0,016\ kg$;

Então temos que

$NaCl : 0,058\ kg$

$C_{12}H_{12}O_{11} : 0,34\ kg$

Temos que o número de mols dos três componentes do sistema é :

$0,1\ kg\ NaCl = 1,7\ mols$

$0,15\ kg\ C_{12}H_{12}O_{11} = 0,44\ mol$

$0,5\ kg\ H_2O = 28\ mol$

$$\boxed{\therefore Total\ de\ mol = 30}$$

As frações molares são :

Fração molar de $NaCl = 0,057$

Fração molar de $C_{12}H_{12}O_{11} = 0,015$

Fração molar de $H_2O = 0,93$

$$\boxed{\therefore Volume\ molar = \frac{0,55 \times 10^{-3}m^3}{30\ mol} = 18 \times 10^{-6}\ m^3/mol}$$

1.3.2   Naturally occurring boron has an atomic mass of 10.811 g... [SUMÁRIO]

Solução:

$$X \times 10,0129 + (1 - X) \times 11,0093 = 10,811$$

Assim a fração molar de $^{10}\mathbf{B}$ é

$$\boxed{X = 0,199}$$

1.3.3   Twenty cubic centimeters each of ethyl alcohol... [SUMÁRIO]

Solução:

Álcool etílico, $C_2H_5OH : densidade = 0,79\ g/cm^3$

Álcool metílico $CH_3OH : densidade = 0,81\ g/cm^3$

Água $H_2O : densidade = 1\ g/cm^3$

$N_{C_2H_5OH} = (0,79\ g/cm^3) \times (20\ cm^3)/(46\ g/mol) = 0,34\ mol$

$N_{CH_3OH} = (0,81\ g/cm^3) \times (20\ cm^3)/(32\ g/mol) = 0,51\ mol$

$N_{H_2O} = (1\ g/cm^3) \times (20\ cm^3)/(18\ g/mol) = 1,11\ mol$

O número de mols é

$$\therefore \boxed{N = N_{C_2H_5OH} + N_{CH_3OH} + N_{H_2O} = 1,96\ mol}$$

e as frações molares dos componentes do sistema são

$$X_{C_2H_5OH} = \frac{0,34\ mol}{1,96\ mol} = 0,17$$

$$X_{CH_3OH} = \frac{0,51\ mol}{1,96\ mol} = 0,26$$

$$X_{H_2O} = \frac{1,11\ mol}{1,96\ mol} = 0,57$$

1.3.4   A 0.01 kg sample is composed of 50 molecular percent H_2... [SUMÁRIO]

SOLUÇÃO:

Seja N o número de mols na amostra inicialmente. Portanto
$\qquad$ massa do $H_2 = 0,5N \times 2 \times 10^{-3}\ kg = 10^{-3}\ N\ kg$
$\qquad$ massa do $HD = 0,3N \times 2 \times 10^{-3}\ kg = 0,9 \times 10^{-3}\ N\ kg$
$\qquad$ massa do $D_2 = 0,2N \times 4 \times 10^{-3}\ kg = 0,8 \times 10^{-3}\ N\ kg$

Massa total $= 0,01\ kg = (1 + 0,9 + 0,8) \times 10^{-3}\ N\ kg$

$$\therefore N = \frac{10^{-2}}{2,7 \times 10^{-3}} = 3,7\ mol$$

Número inicial de mols de $D_2 = 0,2 \times 3,7 = 0,74\ mol$
Seja N' o número de mols de D_2 a ser adicionado.
Então

$$0,3 = \frac{0,74\ mol + N'}{3,7\ mol + N'}$$

$$N' = 0,53 mol$$

$$\therefore Massa\ de\ D_2 = 0,53 \times 4 \times 10^{-3}\ kg = 2,1 \times 10^{-3}\ kg$$

1.3.5   A solution of sugar ($C_{12}H_{22}O_{11}$) in water is 20% sugar by weight... [SUMÁRIO]

SOLUÇÃO:

Massa da Água(water) $= M^{(water)} = 0,8M^{(solution)}$
Massa de açúcar(sugar) $= M^{(sugar)} = 0,2M^{(Solution)}$

$$N^{(water)} = \frac{0,8M^{(solution)}}{0,018} = 44,44M^{(solution)}$$

$$N^{(sugar)} = \frac{0,2M^{(solution)}}{0,34} = 0,588M^{(solution)}$$

$$\therefore X^{sugar} = \frac{N^{(sugar)}}{N^{(sugar)} + N^{(water)}} = \frac{0,588M^{(solution)}}{0,588M^{(solution)} + 44,44M^{(solution)}} = 0,013$$

Ou

$$\therefore X^{sugar} = 1,3\%$$

1.3.6 An aqueous solution of an unidentified solute has a total mass... [SUMÁRIO]

Solução:

Seja M_s a massa molecular ("peso molecular") do soluto e N o número total de mols na amostra original

$$\therefore (0,1N) \times M_s + (0,9N) \times 18 \times 10^{-3} = 0,1029 \times 10^{-3} \; kg$$

Depois de adicionar 2 mols $(= 36 \times 10^{-3} \; kg)$ de H_2O :

$$\frac{0,1N}{N+2} = 0,07 \quad \text{ou} \quad N = 4,67$$

Onde $M_s = 0,0584 \; kg$

$$\boxed{\text{Consequentemente } NaCl \text{ é um palpite razoável.}}$$

1.3.7 One tenth of a kg of an aqueous solution of HCl is poured... [SUMÁRIO]

Solução:

Massa molar de $HCl = 1,01 + 35,45 = 36,46$
Massa molar de $NaOH = 22,99 + 16 + 1,01 = 40,00$
Massa molar de $H_2O = 2,02 + 16 = 18,02$
Massa molar de $NaCl = 22,99 + 35,45 = 58,44$

Solução ácida: Massa$= 0,9N \times M_{H_2O} + 0,1N \times M_{HCl} = (0,9 \times 18,02 + 0,1 \times 36,46)N \times 10^{-3} = 0,1 \; kg$

$$N = 5,034 \; mol$$

$$\therefore N^0_{H_2O} = 0,9N = 4,53 \; mol \qquad N^0_{HCl} = 0,1N = 0,50 \; mol$$

Solução básica: $0,2 \; kg = (0,75 \times 18,02 + 0,25 \times 40) \times 10^{-3} = 23,52N'$

$$N' = 8,503 \; mol$$

$$\therefore N^0_{H_2O} = \frac{3}{4} \times 8,503 = 6,38 \; mol \qquad N^0_{NaOH} = 0,25N' = 2,13 \; mol$$

Então

$$NaOH + HCl \longrightarrow NaCl + H_2O$$

O HCl é a quantidade limite, e apenas $0,5 \; mol$ de $NaOH$ podem reagir.
A composição final é

$$NaCl : 0,5 \; mol \qquad NaOH : 1,63 \; mol \qquad HCl : 0 \; mol$$

$$H_2O : 4,53 + 6,38 + 0,5 = 11,41 \; mol$$

O número total de mols é $= 13,54$, que está de acordo com o número original (Note que a reação química preserva o número total de mols). Então

$$\boxed{X_{NaCl} = 0,04 \; ; \qquad X_{NaOH} = 0,12 \; ; \qquad X_{H_2O} = 0,84}$$

1.8   QUANTITATIVE DEFINITION OF HEAT-UNITS [SUMÁRIO]

1.8.1   For the system considered in Example 1, calculate... [SUMÁRIO]

Solução:

Denote este estado por E; Note que é a meio caminho entre os estados B e D. Note também que ao longo da linha de V constante, a energia é diretamente proporcional a P. Isto é

$$dU = \frac{3}{2}VdP \quad (V\,constante)$$

Consequentemente

$$U_E = \frac{1}{2}(U_D + U_B) = \frac{1}{2}(967,5 - 112,5)$$

Tomando $U_A = 0$ temos

$$\boxed{U_E = 427,5J}$$

1.8.2   Calculate the heat transferred to the system considered in... [SUMÁRIO]

Solução:

$W = -\int Pdv = -(\acute{A}rea\ \ sombreada)$

A área sombreada é um trapézio.

$\acute{A}rea_{trap\acute{e}zio} = \dfrac{B+b}{2} \times h$

$W = -7,5 \times 10^4 \times 7 \times 10^{-3} = -525J$

$U_E = 427,5J\ (Do\ problema\ 1.8\text{-}1)$

$U_E - U_A = W_{A\to E} + Q_{A\to E}$

$427,5 = -525 + Q_{A\to E}$

$\boxed{\therefore Q_{A\to E} = 952,5J}$
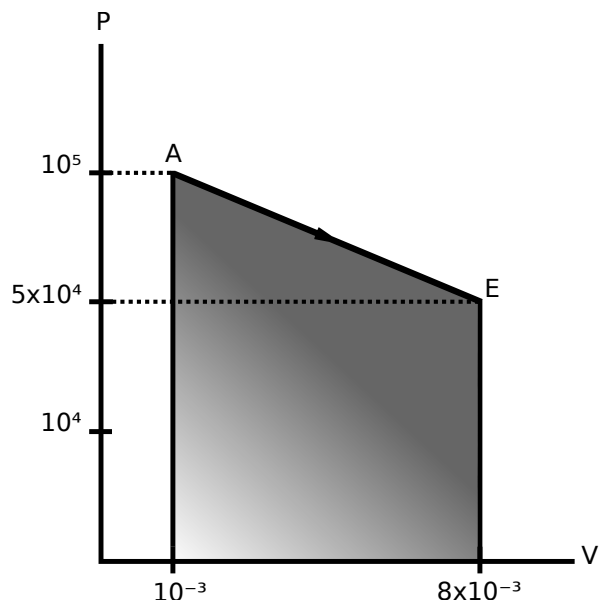
1.8.3 For a particular gaseous system it has been determined that...

SOLUÇÃO:

Faça $U_A \equiv 0$,

Então $U = 2,5PV - 5 \times 10^3 J$

$\therefore U_B = 10^4 J$, $U_C = 7,5 \times 10^3 J$

$W_{AB} = -\int_A^B P dV = -P\Delta V = -4 \times 10^3 Joules$

e $U_B - U_A = W_{AB} + Q_{AB}$

$\therefore Q_{AB} = 14 \times 10^3 J$ ($Um\ fluxo\ de\ energia\ na$ $forma\ de\ calor\ \underline{entra}\ no\ sistema$)

de forma similar :

$W_{BC} = -\int_B^C P dV = \text{área abaixo da linha } BC = 7 \times 10^3 J$

$Q_{BC} = U_C - U_B - W_{BC} = -2,5 \times 10^3 - 7 \times 10^3 = -9,5 \times 10^3 Joules$

Finalmente $W_{CA} = 0$

$U_A - U_C = Q_{CA} + W_{CA}$, $Q_{CA} = -7,5 \times 10^3 J$ ($Fluxo\ de\ energia\ na\ forma\ de\ calor\ \underline{sai}\ do\ sistema$)

Para checar, note que o trabalho realizado no ciclo é $W_{AB} + W_{BC} + W_{CA} = 3 \times 10^3 J$ e a energia na forma de calor que entrou no ciclo é $14 \times 10^3 J - 9,5 \times 10^3 J - 7,5 \times 10^3 J = -3 \times 10^3 J$. A Soma do trabalho e da energia na forma de calor transferidos é zero, exatamente como deveria ser.

Agora nos resta calcular Q e W para o processo de A para B ao longo da parábola $P = 10^5 + 10^9(V - 0,02)^2$

$W_{AB} = -\int_{0,01}^{0,03} P dV$

$= -\int_{0,01}^{0,03}[10^5 + 10^9(V - 0,02)^2]dV$

$W_{AB} = -\left[10^5(V_B - V_A) + \frac{10^9(V - 0,02)^3}{3}\right]_{0,01}^{0,03}$

Então $\boxed{W_{AB} = -2,7 \times 10^3 J}$

$Q = \Delta U - W = 10^4 + 2,7 \times 10^3$

$\boxed{\therefore Q = 12,7 \times 10^3 Joules}$
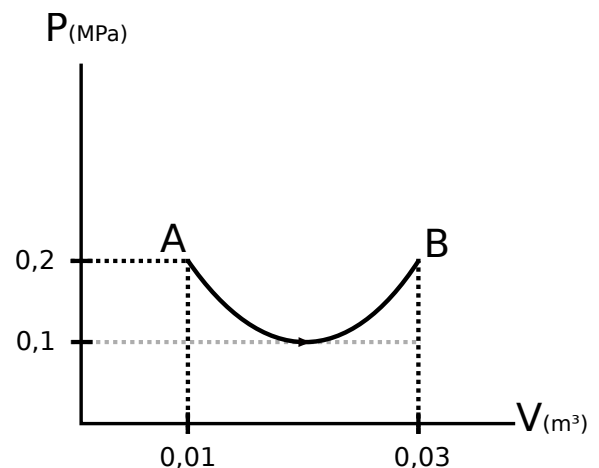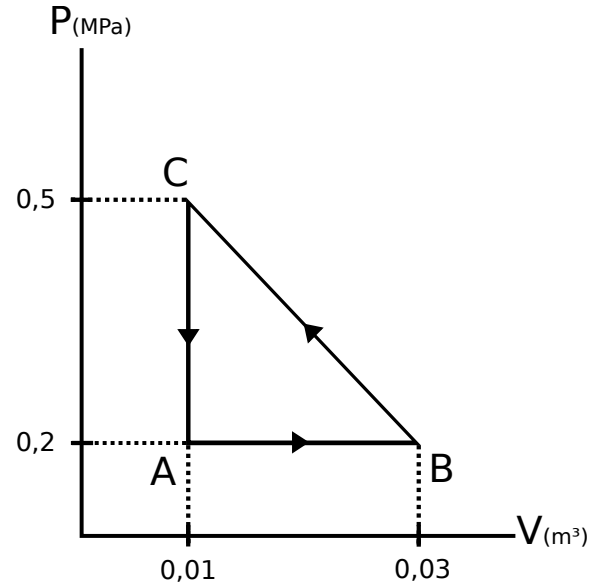
1.8.4   For the system of Problem 1.8-3 find the equation of the adiabats... [SUMÁRIO]

Solução:

$$U = 2,5PV + const.$$

$$\text{Então } dU = 2,5PdV + 2,5VdP$$

$$\text{Mas ao longo de uma adiabata, temos que } dU = -PdV$$

$$\therefore 2,5PdV + 2,5VdP = -PdV, \text{ assim}$$

$$7\frac{dV}{V} + 5\frac{dP}{P} = 0$$

$$\text{Integrando, ficamos com } 7\ln\left(\frac{V}{V_0}\right) + 5\ln\left(\frac{P}{P_0}\right) = 0$$

$$\boxed{\therefore V^7 P^5 = V_0^7 P_0^5}$$

1.8.5   The energy of a particular system, of one mole, is given by ... [SUMÁRIO]

Solução:

$$dU = 2APVdP + AP^2dV = -PdV$$

$$\therefore A\frac{dP}{1+AP} = -\frac{1}{2}\frac{dV}{V}$$

$$\ln(1+AP) = -\frac{1}{2}\ln V + const.$$

$$\boxed{(1+AP)V^{1/2} = const}$$

$$Obs: \text{ } Para \text{ } onde \text{ } foi \text{ } o \text{ } A \text{ } que \text{ } multiplica \text{ } \frac{dP}{1+AP} \text{ } na \text{ } segunda \text{ } linha?$$

Figura 1: reprodução da solução original, feita pelo próprio Callen, onde ele questiona sobre o "A"

1.8.6 For a particular system it is found that if the volume is kept ...

Solução:
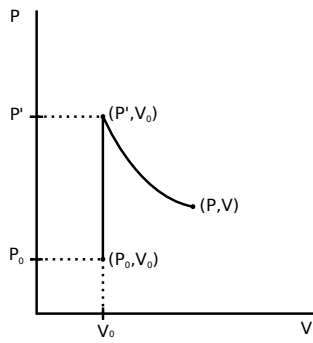
Primeiro, encontre a energia ao longo da isocórica $V = V_0$.
Ao longo da isocórica nenhum trabalho é realizado, portanto :

$U(P', V_0) = U_0 + Q' = U_0 + A(P' - P_0)$

Agora considere o ponto (P, V). A adiabata através desse ponto intercepta a isocórica V_0 em $P' = P(V/V_0)^\gamma$. Consequentemente

$$U(P, V) - U(P', V_0) = -\int_{V_0}^{V} P'' dV'' = -P \int_{V_0}^{V} (V/V'')^\gamma dV''$$

$$= -PV^\gamma \frac{[V^{1-\gamma} - V_0^{1-\gamma}]}{1-\gamma} = -\frac{P}{1-\gamma}\left[V - V_0 \left(\frac{V}{V_0}\right)^\gamma \right]$$

ou $\boxed{U(P, V) = U_0 + A\left[P \left(\frac{V}{V_0}\right)^\gamma - P_0 \right] + \frac{PV}{\gamma - 1}\left[1 - \left(\frac{V}{V_0}\right)^{\gamma-1} \right]}$

1.8.7 Two moles of a particular single-component system are found...

Solução:

$$\text{Resposta} \quad \boxed{U = \frac{2}{N} A P V^2}$$

1.8.8 **(Supplementary Problem) A particular single-component system of one mole has adiabats of the form $P^{5/3}$ = constant (that is, the pressure and the volume obey the given relationship when when the system is enclosed by an adiabatic, impermeable wall). The system is fitter with a stirrer, as in the example of this section. If the system is adiabatically insulated and maintained at constant volume, and if an amount of work dW ($= \text{torque} \times d\theta$) is transmitted (by an external torque turning the stirrer through an angle dθ), the pressure of the system is observed to increase by an amount dP, where**

$$(\mathbf{AV} + \mathbf{BV^{5/3}})\mathbf{dP} = \text{đW} \ (\mathbf{torque} \times \mathbf{d\theta})$$

Find the internal energy as a function of P, V and N. [SUMÁRIO]

> **SOLUÇÃO:**
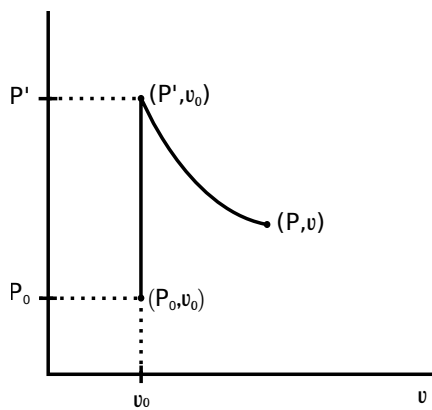
Primeiro encontramos a escala de energia ao longo da isocórica $v = v_0$:

$$u = u_0 + (Av_0 + Bv_0^{5/3}) \times (P - P_0)$$

Agora escolhemos um ponto arbitrário P_1, v_1. A adiabata através desse ponto intercepta a isocórica $v = v_0$ no ponto $P' = P_1 \left(\dfrac{v_1}{v_0}\right)^{5/3}$.

O trabalho realizado no processo de levar o sistema de (P', v_0) para (P_1, v_1) ao longo da adiabata é :

$$W = -\int_{v_0}^{v_1} P dv = -\int_{v_0}^{v_1} P_1 \left(\frac{v_1}{v}\right)^{5/3} dv = -\frac{3}{2} P_1 v_1 \left[\left(\frac{v_1}{v_0}\right)^{2/3} - 1\right]$$

então

$$u(P_1, v_1) = u(P', v_0) - \frac{3}{2} P_1 v_1 \left[\left(\frac{v_1}{v_0}\right)^{2/3} - 1\right]$$

E portanto

$$u(P_1, v_1) = u_0 + (Av_0 + Bv_0^{5/3}) \left[P_1 \left(\frac{v_1}{v_0}\right)^{5/3} - P_0\right] - \frac{3}{2} P_1 v_1 \left[\left(\frac{v_1}{v_0}\right)^{2/3} - 1\right]$$

Então, para um sistema de N moles (e também retirando os subscritos em P_1 e v_1):

$$\boxed{U(P, V, N) = Nu_0 + N(Av_0 + Bv_0^{5/3}) \left[P \left(\frac{v}{v_0}\right)^{5/3} - P_0\right] - \frac{3}{2} NPv \left[\left(\frac{v}{v_0}\right)^{2/3} - 1\right]}$$

1.10 THE ENTROPY MAXIMUM POSTULATES

1.10.1 The following ten equations are purported to be fundamental...

> **SOLUÇÃO:**

Precisamos encontrar as 5 equações supostamente fundamentais que são fisicamente inadimissíveis e indicar quais postulados são violados por cada uma.

Fisicamente aceitável

(a) $S = \left(\dfrac{R^2}{v_0\theta}\right)^{1/3}(NVU)^{1/3}$ Não viola nenhum postulado.

Viola algum postulado

(b) $S = \left(\dfrac{R}{\theta^2}\right)^{1/3}\left(\dfrac{NU}{V}\right)^{2/3}$ Não é homogênea de primeira ordem.

Fisicamente aceitável

(c) $S = \left(\dfrac{R}{\theta}\right)^{1/2}\left(NU + \dfrac{R\theta V^2}{v_0^2}\right)^{1/2}$ Não viola nenhum postulado.

Viola algum postulado

(d) $S = \left(\dfrac{R^2\theta}{v_0^3}\right)V^3/NU$ Não é uma função monotonicamente crescente e também viola o postulado de Nernst.

Fisicamente aceitável

(e) $S = \left(\dfrac{R^3}{v_0\theta^2}\right)^{1/5}[N^2VU^2]^{1/5}$ Não viola nenhum postulado.

Viola algum postulado

(f) $S = NRln(UV/N^2R\theta v_0)$ Viola o postulado de Nernst.

Fisicamente aceitável

(g) $S = \left(\dfrac{R}{\theta}\right)^{1/2}[NU]^{1/2}\exp(-V^2/2N^2v_0^2)$ Não viola nenhum postulado

---

Viola algum postulado

(h) $S = \left(\dfrac{R}{\theta}\right)^{1/2}(NU)^{1/2}\exp\left(-\dfrac{UV}{NR\theta v_0}\right)$ Não é homogênea de primeira ordem nem uma função monotonicamente crescente de U

(i) $U = \left(\dfrac{v_0\theta}{R}\right)\dfrac{S^2}{V}\exp(S/NR)$ Não viola nenhum postulado.

(j) $U = \left(\dfrac{R\theta}{v_0}\right)NV\left(1 + \dfrac{S}{NR}\right)exp(-S/NR)$ Não é homogênea de primeira ordem nem uma função monotonicamente crescente de U

Obs: O postulado de Nernst ao qual o autor se refere é o postulado reformulado por Planck, e que o Callen chama de "Postulado IV". Discussões mais detalhadas a respeito desse postulado podem ser vistas na página 30 do capítulo 1 e no capítulo 11 do livro.

Postulado IV. A entropia de qualquer sistema se anula no estado para o qual

$(\partial U/\partial S)_{V,N_1,\ldots,N_r} = 0$ (isto é, no zero de temperatura)

1.10.2   For each of the five physically acceptable fundamental equations... [SUMÁRIO]

SOLUÇÃO:

$(a)\ U = \dfrac{1}{NV}\left(\dfrac{v_0\theta}{R^2}\right)S^3$

$(c)\ U = \dfrac{\theta S^2}{NR} - \dfrac{R\theta V^2}{Nv_0^2}$

$(e)\ U = N^{-1}V^{-1/2}\left(\dfrac{v_0\theta}{R^3}\right)^{1/2}S^{5/2}$

$(g)\ U = \left(\dfrac{\theta S^2}{NR}\right)\exp\left(\dfrac{V^2}{N^2v_0^2}\right)$

$(i)\ U = \left(\dfrac{v_0\theta}{R}\right)\dfrac{S^2}{V}\exp\left(\dfrac{S}{NR}\right)$

1.10.3 The fundamental equation of a system A is $S = \left(\dfrac{R^2}{v_0\theta}\right)^{1/3}(NVU)^{1/3}$ and similarly... [SUMÁRIO]

$\boxed{\textsc{Solução:}}$

$$S_A = \left(\frac{R^2}{v_0\theta}\right)^{1/3}(N_A V_A U_A)^{1/3} \qquad\qquad V_A = 9\times 10^{-6}m^3 \ , \ N_A = 3$$

$$S_B = \left(\frac{R^2}{v_0\theta}\right)^{1/3}(N_B V_B U_B)^{1/3} \qquad\qquad V_B = 4\times 10^{-6}m^3 \ , \ N_B = 2$$

$$U_A + U_B = 80J$$

Faça $S' = \dfrac{S}{R^2 v_0\theta} \qquad \therefore \ S'_A = 3\times 10^{-2}U_A^{1/3} \qquad e \qquad S'_B = 2\times 10^{-2}U_B^{1/3}$

$$S' = S'_A + S'_B = 3\times 80^{1/3}\times 10^{-2}\times\left[\xi^{1/3} + \frac{2}{3}(1-\xi)^{1/3}\right] \qquad \text{Onde} \qquad \xi = U_A/80$$
$$1-\xi = U_B/80$$

Para maximizar fazemos $\dfrac{dS'}{d\xi} = 0$

$$\frac{dS'}{d\xi} = 3\times 80^{1/3}\times 10^{-2}\times\left[\frac{1}{3}\xi^{-2/3} - \frac{2}{9}(1-\xi)^{-2/3}\right] = 0$$

Então

$$\xi = \left(\frac{2}{3}\right)^{-3/2}(1-\xi) \Rightarrow \xi = 0,6475295549 \text{ ou arredondando } \xi = 0,65$$

$$\boxed{\therefore \ U_A = 80\xi = 52J \ \ e \ \ U_B = 80(1-\xi) = 28J}$$
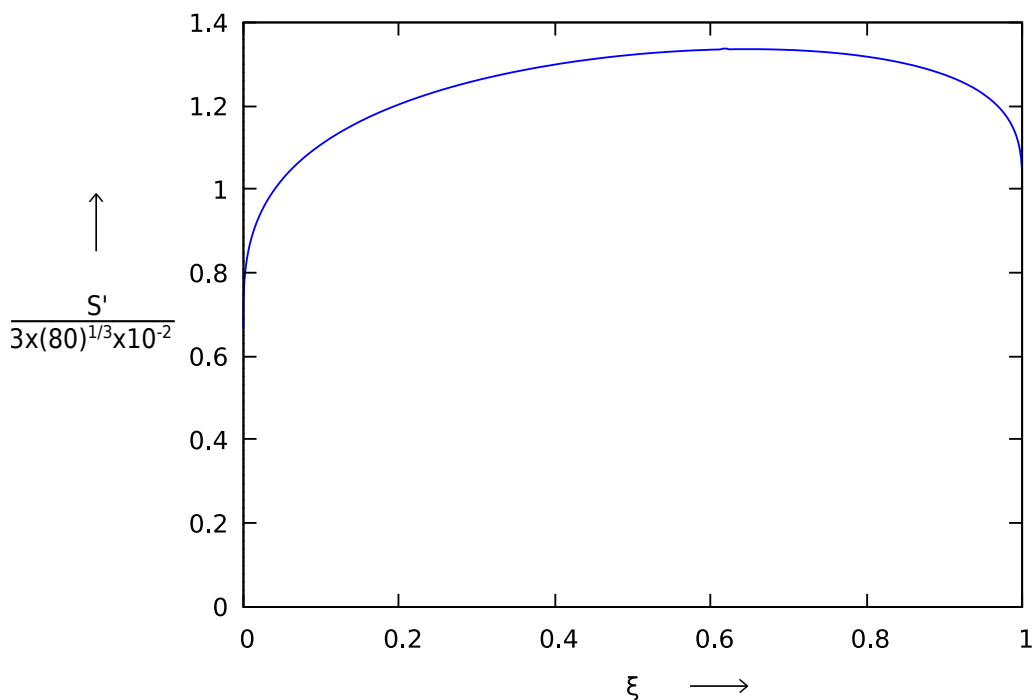
Figura 2: Entropia como função de $U_A/(U_A + U_B)$ com o máximo em $\xi = 0,65$

2 THE CONDITIONS OF EQUILIBRIUM [SUMÁRIO]

2.2 EQUATIONS OF STATE [SUMÁRIO]

2.2.1 Find the three equations of state for a system with the fundamental equation $\mathbf{U} = \left(\dfrac{\mathbf{v_0\theta}}{\mathbf{R^2}} \right) \dfrac{\mathbf{S^3}}{\mathbf{NV}}$... [SUMÁRIO]

> **SOLUÇÃO:**

$$T = \left(\frac{\partial U}{\partial S}\right) = 3\left(\frac{v_0\theta}{R^2}\right)\frac{S^2}{NV}$$

$$-P = \left(\frac{\partial U}{\partial V}\right) = -\left(\frac{v_0\theta}{R^2}\right)\frac{S^3}{NV^2}$$

$$\mu = \left(\frac{\partial U}{\partial N}\right) = -\left(\frac{v_0\theta}{R^2}\right)\frac{S^3}{N^2V}$$

Para corroborar com o fato de que as três equações de estado são homogêneas de ordem zero (Isto é, T, P e μ são parâmetros intensivos) fazemos :

$$T(\lambda S, \lambda V, \lambda N) = 3\left(\frac{v_0\theta}{R^2}\right)\frac{(\lambda S)^2}{(\lambda N)(\lambda V)} = 3\left(\frac{v_0\theta}{R^2}\right)\frac{S^2}{NV} = T(S,V,N)$$

$$-P(\lambda S, \lambda V, \lambda N) = -\left(\frac{v_0\theta}{R^2}\right)\frac{(\lambda S)^3}{(\lambda N)(\lambda V)^2} = -\left(\frac{v_0\theta}{R^2}\right)\frac{S^3}{NV^2} = -P(S,V,N)$$

$$\mu(\lambda S, \lambda V, \lambda N) = -\left(\frac{v_0\theta}{R^2}\right)\frac{(\lambda S)^3}{(\lambda N)^2(\lambda V)} = -\left(\frac{v_0\theta}{R^2}\right)\frac{S^3}{N^2V} = \mu(S,V,N)$$

2.2.2 For the system of problem 2.2-1 find μ as a function of T, V e N [SUMÁRIO]

> **SOLUÇÃO:**

Eliminando S das equações de estado $T(S,V,N)$ e $\mu(S,V,N)$ do problema 2.2-1,

$$\boxed{\mu = -3^{-3/2}\left(\frac{v_0\theta}{R^2}\right)^{-1/2}T^{3/2}v^{1/2}}$$

2.2.3 Show by a diagram (drawn to arbitrary scale) the dependence of... [SUMÁRIO]

> **SOLUÇÃO:**

Eliminando S das equações de estado $T(S,V,N)$ e $-P(S,V,N)$ do problema 2.2-1

$$\boxed{P = \frac{1}{3}\left(\frac{R^2}{3v_0\theta}\right)^{1/2}\left(\frac{NT^3}{V}\right)^{1/2}}$$
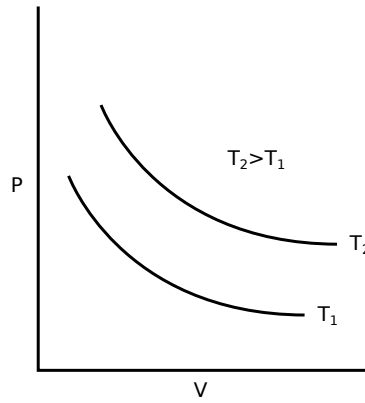
Figura 3: Isotermas no diagrama PV

2.2.4 Find the three equations of state for a system with the fundamental equation $u = \left(\dfrac{\theta}{R}\right) s^2 - \left(\dfrac{R\theta}{v_0^2}\right) v^2$ [**SUMÁRIO**]

$\boxed{\textsc{Solução:}}$

$u = \left(\dfrac{\theta}{R}\right) s^2 - \left(\dfrac{R\theta}{v_0^2}\right) v^2$ ou $U = \dfrac{\theta}{R}\dfrac{S^2}{N} - \dfrac{R\theta}{v_0^2}\dfrac{V^2}{N}$

$T = \left(\dfrac{\partial u}{\partial s}\right)_v = 2\dfrac{\theta}{R}s \quad , \quad P = -\left(\dfrac{\partial u}{\partial v}\right)_s = 2\dfrac{R\theta}{v_0^2}v$

$\mu = \dfrac{\partial U}{\partial N} = -\dfrac{\theta}{R}\dfrac{S^2}{N^2} + \dfrac{R\theta}{v_0^2}\dfrac{V^2}{N^2} = -\dfrac{\theta}{R}s^2 + \dfrac{R\theta}{v_0^2}v^2$

$$\boxed{\therefore \mu = -u}$$

2.2.5 Express μ as a function of T and P for the system of problem 2.2-4 [**SUMÁRIO**]

$\boxed{\textsc{Solução:}}$

Eliminando S e v das três equações de estado do problema anterior, temos que :

$$\boxed{\mu = -\dfrac{1}{4}\dfrac{R}{\theta}T^2 + \dfrac{v_0^2}{4R\theta}P^2}$$

2.2.6   Find the three equations of state for a system with the fundamental equation
$$u = \left(\frac{v_0\theta}{R}\right)\frac{s^2}{v}e^{s/R} \quad \text{[SUMÁRIO]}$$

> **SOLUÇÃO:**

$$T = \left(\frac{\partial u}{\partial s}\right)_v = 2\frac{v_0\theta}{R}\frac{s}{v}e^{s/R} + \frac{v_0\theta}{R^2}\frac{s^2}{v}e^{s/R}$$

$$-P = \left(\frac{\partial u}{\partial v}\right)_s = -\frac{v_0\theta}{R}\frac{s^2}{v^2}e^{s/R}$$

Para encontrar μ, reescreva a equação fundamental como $U = \left(\frac{v_0\theta}{R}\right)\frac{S^2}{V}e^{S/NR}$

$$\boxed{\therefore \mu = \left(\frac{v_0\theta}{R}\right)\frac{S^2}{V}e^{S/NR} \times \left(-\frac{S}{N^2R}\right) = -\frac{v_0\theta}{R^2}\frac{S^3}{N^2}e^{S/NR}}$$

2.2.7   A particular system obeys the relation $u = Av^{-2}\exp(s/R)$... [SUMÁRIO]

> **SOLUÇÃO:**

$$T = \frac{\partial u}{\partial s} = \frac{A}{R}v^{-2}e^{s/R} \qquad\qquad P = -\frac{\partial u}{\partial v} = 2Av^{-3}e^{s/R}$$

Com s constante, então

$$\frac{T_f}{T_0} = \left(\frac{v_0^2}{v_f^2}\right) \qquad \text{e} \qquad \frac{P_f}{P_0} = \left(\frac{v_0}{v_f}\right)^3$$

$$\boxed{\therefore \frac{T_f}{T_0} = \left(\frac{P_f}{P_0}\right)^{2/3}} \qquad \text{Ou} \qquad T_f = \frac{T_0}{2^{2/3}} = 0,63T_0 \Rightarrow \boxed{T_f = 0,63T_0}$$

2.2.8   Show that, in analogy with equation 2.25, for a system with r components...
[SUMÁRIO]

> **SOLUÇÃO:**

$$\text{Seja } u = u(s,v,x_1,...,x_r), \qquad\qquad x_j \equiv N_j/N, \qquad N \equiv \sum_{j=1} N_j$$

$$du = \frac{\partial u}{\partial s}ds + \frac{\partial u}{\partial v}dv + \sum_{j=1}^{r}\frac{\partial u}{\partial x_j}dx_j$$

$$= Tds - Pdv + \sum_{j=1}^{r}\mu_j dx_j$$

$$\text{mas} \qquad \sum_{j=1}^{r} dx_j = 0 \qquad \text{ou} \qquad dx_r = -\sum_{j=1}^{r-1} dx_j$$

$$\boxed{\therefore \quad du = Tds - Pdv + \sum_{j=1}^{r-1}(\mu_j - \mu_r)dx_j}$$

2.2.9 Show that if a single-component system is such that PV^k is constant...

$\boxed{\textsc{Solução:}}$

Nos é dado que $PV^k = g(s)$, onde g é uma função arbitrária.

Agora seja $u = u(s,v)$ e $P = -\dfrac{\partial u}{\partial v} = -\dfrac{g(s)}{v^k}$

Integrando,

$$u = -\frac{g(s)}{(k-1)v^{k-1}} + h(s), \qquad h \text{ é uma função arbitrária}$$

$$\therefore \quad u = \frac{Pv^k}{(k-1)v^{k-1}} + h(s) = \frac{Pv}{k-1} + h(s)$$

Mas de $Pv^k = g(s)$ sabemos que s é uma função de Pv^k

$$\therefore \quad u = \frac{Pv}{k-1} + f(Pv^k), \qquad f \text{ é uma função arbitrária}$$

$$\text{ou} \qquad \boxed{U = \frac{1}{k-1}PV + Nf(PV^k/N^k)}$$

2.3 ENTROPIC INTENSIVE PARAMETERS [SUMÁRIO]

2.3.1 Find the three equations of state in the entropy representation for... [SUMÁRIO]

> **SOLUÇÃO:**

$$s = \left(\frac{R^{3/2}}{v_0^{1/2}\theta} \right)^{2/5} u^{2/5}v^{1/5}$$

$$\frac{1}{T} = \frac{\partial s}{\partial u} = \frac{2}{5}\left(\frac{R^{3/2}}{v_0^{1/2}\theta} \right)^{2/5} u^{-3/5}v^{1/5} \quad \underline{Reescrevendo} \quad \boxed{\frac{1}{T} = \frac{2}{5}\left(\frac{v_0^{1/2}\theta}{R^{3/2}} \right)^{-2/5} \frac{v^{1/5}}{u^{3/5}}}$$

$$\frac{P}{T} = \frac{\partial s}{\partial v} = \frac{1}{5}\left(\frac{R^{3/2}}{v_0^{1/2}\theta} \right)^{2/5} u^{2/5}v^{-4/5} \quad \underline{Reescrevendo} \quad \boxed{\frac{P}{T} = \frac{1}{5}\left(\frac{v_0^{1/2}\theta}{R^{3/2}} \right)^{-2/5} \frac{u^{2/5}}{v^{4/5}}}$$

Para a equação de estado $\frac{\mu}{T} = -\frac{\partial S}{\partial N}$ utilizamos as relações $s = \frac{S}{N} = SN^{-1}$, $v = \frac{V}{N} = VN^{-1}$ e $u = \frac{U}{N} = UN^{-1}$, que para esse problema, são, $s = SN^{-1}$, $v^{1/5} = V^{1/5}N^{-1/5}$ e $u^{2/5} = U^{2/5}N^{-2/5}$. Assim, temos

$$SN^{-1} = \left(\frac{R^{3/2}}{v_0^{1/2}\theta} \right)^{2/5} U^{2/5}N^{-2/5}V^{1/5}N^{-1/5} \implies SN^{-1} = \left(\frac{R^{3/2}}{v_0^{1/2}\theta} \right)^{2/5} U^{2/5}V^{1/5}N^{-2/5}N^{-1/5}$$

$$SN^{-1} = \left(\frac{R^{3/2}}{v_0^{1/2}\theta} \right)^{2/5} U^{2/5}V^{1/5}N^{-3/5} \implies \underbrace{S = \left(\frac{R^{3/2}}{v_0^{1/2}\theta} \right)^{2/5} U^{2/5}V^{1/5}N^{2/5}}_{\text{Calcularemos } \frac{\mu}{T} \text{ a partir dessa equação}}$$

$$\frac{\mu}{T} = -\frac{\partial S}{\partial N} = -\frac{2}{5}\left(\frac{R^{3/2}}{v_0^{1/2}\theta} \right)^{2/5} U^{2/5}V^{1/5}N^{-3/5}, \qquad \text{Note que } (N^{-3/5} = N^{-2/5}N^{-1/5})$$

$$\implies \frac{\mu}{T} = -\frac{2}{5}\left(\frac{R^{3/2}}{v_0^{1/2}\theta} \right)^{2/5} U^{2/5}V^{1/5}N^{-2/5}N^{-1/5} \implies \frac{\mu}{T} = -\frac{2}{5}\left(\frac{R^{3/2}}{v_0^{1/2}\theta} \right)^{2/5} U^{2/5}N^{-2/5}V^{1/5}N^{-1/5}$$

$$\implies \frac{\mu}{T} = -\frac{2}{5}\left(\frac{R^{3/2}}{v_0^{1/2}\theta} \right)^{2/5} u^{2/5}v^{1/5} \quad \underline{Reescrevendo} \quad \boxed{\frac{\mu}{T} = -\frac{2}{5}\left(\frac{v_0^{1/2}\theta}{R^{3/2}} \right)^{-2/5} u^{2/5}v^{1/5}}$$

Portanto, as três equações de estado na representação entrópica são :

$$\boxed{\frac{1}{T} = \frac{2}{5}\left(\frac{v_0^{1/2}\theta}{R^{3/2}} \right)^{-2/5} \frac{v^{1/5}}{u^{3/5}}} , \boxed{\frac{P}{T} = \frac{1}{5}\left(\frac{v_0^{1/2}\theta}{R^{3/2}} \right)^{-2/5} \frac{u^{2/5}}{v^{4/5}}} , \boxed{\frac{\mu}{T} = -\frac{2}{5}\left(\frac{v_0^{1/2}\theta}{R^{3/2}} \right)^{-2/5} u^{2/5}v^{1/5}}$$

2.3.2 Show by a diagram (drawn to arbitrary scale) the dependence of temperature on volume ... [SUMÁRIO]

> **Solução:**

Obtemos a relação de dependência entre T e v eliminando u das equações de estado $\dfrac{1}{T}$ e $\dfrac{P}{T}$ do problema anterior, que são :

$$\frac{1}{T} = \frac{2}{5}\left(\frac{R^{3/2}}{v_0^{1/2}\theta}\right)^{2/5} u^{-3/5}v^{1/5}$$

$$\frac{P}{T} = \frac{1}{5}\left(\frac{R^{3/2}}{v_0^{1/2}\theta}\right)^{2/5} u^{2/5}v^{-4/5}$$
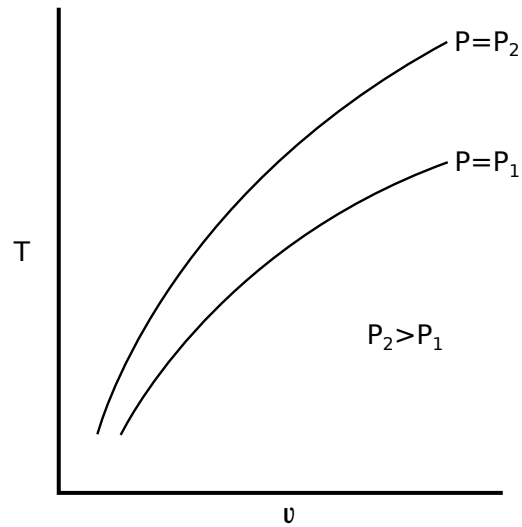
Isolando u na primeira equação $\dfrac{1}{T}$, temos :

$$u = \left(\frac{2}{5}\right)^{5/3}\left(\frac{R^3}{v_0\theta^2}\right)^{1/3} v^{1/3}T^{5/3}$$

Substituindo u na equação de estado $\dfrac{P}{T}$, encontramos :

$$\frac{P}{T} = \frac{1}{5}\left(\frac{R^3}{v_0\theta^2}\right)^{1/5}\left[\left(\frac{2}{5}\right)^{2/3}\left(\frac{R^3}{v_0\theta^2}\right)^{2/15} v^{2/15}T^{2/3}\right]v^{-4/5} \Longrightarrow P = \underbrace{\left(\frac{2}{5}\right)^{2/3}\frac{1}{5}\left(\frac{R^3}{v_0\theta^2}\right)^{1/3}}_{= A\ (=\text{Constante})}\frac{T^{5/3}}{v^{2/3}}$$

Assim

$$\boxed{\frac{T^5}{v^2} = AP^3}\ \text{ou ainda}\ \boxed{T = AP^{3/5}v^{2/5}},\ onde\ A = Cte = \left(\frac{2}{5}\right)^{2/3}\frac{1}{5}\left(\frac{R^3}{v_0\theta^2}\right)^{1/3}$$

2.3.3 Find the three equations of state in the entropy representation for … [SUMÁRIO]

SOLUÇÃO:

$$s = \left(\frac{R}{\theta}\right)^{1/2} u^{1/2} e^{-v/v_0}$$

A partir dessa equação fundamental, as equações de estado calculadas são :

$$\frac{1}{T} = \left(\frac{\partial s}{\partial u}\right)_v = \frac{1}{2}\left(\frac{R}{\theta}\right)^{1/2} u^{-1/2} e^{-v/v_0}$$

$$\frac{P}{T} = \left(\frac{\partial s}{\partial v}\right)_u = -\frac{1}{v_0}\left(\frac{R}{\theta}\right)^{1/2} u^{1/2} e^{-v/v_0}$$

$$\frac{\mu}{T} = -\left(\frac{\partial S}{\partial N}\right)_{V,U} = -\frac{\partial}{\partial N}\left[\left(\frac{R}{\theta}\right)^{1/2} U^{1/2} N^{1/2} e^{-V/N v_0}\right]$$

$$= \left(\frac{R}{\theta}\right)^{1/2} u^{1/2} e^{-v/v_0}\left[\frac{1}{2} - \frac{v}{v_0}\right]$$

2.3.4 Consider the fundamental equation $S = AU^n V^m N^r$ where A is a positive constant… [SUMÁRIO]

SOLUÇÃO:

a) Para que S seja homogênea de primeira ordem, devemos ter :

$$n + m + r = 1 \quad , \quad \text{ou } r = 1 - n - m \quad \text{daí}$$
$$S = NA\left(\frac{U}{N}\right)^n \left(\frac{V}{N}\right)^m$$

b) $\dfrac{1}{T} = \dfrac{\partial S}{\partial U} = nA\left(\dfrac{U}{N}\right)^{n-1}\left(\dfrac{V}{N}\right)^m$ ou $T = \dfrac{1}{nA} u^{1-n} v^m$

mas se $u \to 0$ em $T = 0$ devemos ter $1 - n > 0$ ou
$$\boxed{n < 1}$$

Também, multiplicando as equações acima por T e S
$$TS = \frac{1}{n}U \quad , \quad \text{ou} \quad U = nTS$$
e eliminando U na equação de estado acima
$$T^n = n^{-n} A^{-1} s^{1-n} v^{-m}$$
e se $T \to 0$ na medida em que $s \to 0$ devemos ter
$$\boxed{0 < n < 1}$$

c)
$$\text{Finalmente } \frac{P}{T} = \frac{\partial S}{\partial V} = mA\left(\frac{U}{N}\right)^n \left(\frac{V}{N}\right)^{m-1}$$
e eliminando T da equação térmica de estado (primeira linha de **(b)**)
$$P = \frac{m}{n}\left(\frac{U}{V}\right)$$
Se P cresce com U/V, $m/n > 0$, ou $\boxed{m > 0}$
Consequentemente devemos ter $m > 0$ e $0 < n < 1$

2.3.5 Find the three equations of state for a system with the fundamental relation... [SUMÁRIO]

> **Solução:**

a,b) $\dfrac{1}{T} = R\left[v + \dfrac{1}{u^2 v}\right] > 0, \quad \dfrac{P}{T} = R\left[u + \dfrac{1}{uv^2}\right], \quad -\dfrac{\mu}{T} = R\left[-uv - \dfrac{3}{uv}\right]$

c) $s = \dfrac{1}{T}u + \dfrac{P}{T}v - \dfrac{\mu}{T} = Ru\left[v + \dfrac{1}{u^2 v}\right] + R\left[uv + \dfrac{1}{uv}\right] - R\left[uv + \dfrac{3}{uv}\right] = uv - (uv)^{-1}$

d) Dividindo as duas primeiras equações de estado, $P = u/v$ ou $u = Pv$ e substituindo na relação fundamental

$\dfrac{s}{R} = uv - \dfrac{1}{uv}$

$\quad = Pv^2 - \dfrac{1}{Pv^2}$

Ou ainda $Pv^2 =$Função de s.
Portanto as adiabatas são dadas por

$$\boxed{Pv^2 = const}$$
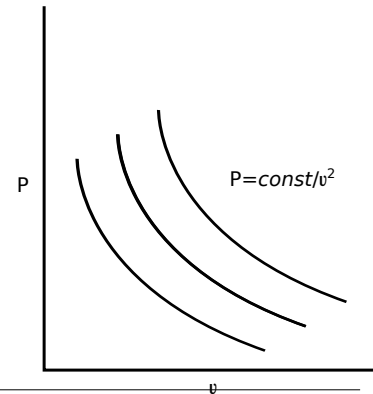
2.6 TEMPERATURE UNITS [SUMÁRIO]

2.6.1 The temperature of a system composed of ice, water, and water vapor... [SUMÁRIO]

> **Solução:**

$T(\text{℃}) = T(K) - 273,15 = (373,15 - 273,15) \pm 0,01 = (100,00 \pm 0,01)\text{℃}$

$T(°R) = \dfrac{9}{5}T(K) = (671,67 \pm 0,02)°R$

$T(°F) = T(°R) - 459,67 = \dfrac{9}{5}T(\text{℃}) - 32 = (212,00 \pm 0,02)°F$

2.6.2 The "gas constant" R is defined as the product of Avogrado's number... [SUMÁRIO]

> **Solução:**

$$R = 8,314 \times \frac{5}{9} J/mol\ °F = 4,619 J/mol\ °F$$

2.6.3 Two particular systems have the following equations of state... [SUMÁRIO]

> **Solução:**

$T^{(1)} = T^{(2)} \implies \dfrac{2}{3}\dfrac{U^{(1)}}{RN^{(1)}} = \dfrac{2}{5}\dfrac{U^{(2)}}{RN^{(2)}} \quad ou \quad 5U^{(1)} = 2U^{(2)}$.

Também $U^{(1)} + U^{(2)} = 2,5 \times 10^3 J \quad \implies \quad \boxed{U^{(1)} = 714,3J \ \ e \ \ U^{(2)} = 1785,7J}$

2.6.4 Two systems with the equations of state given in Problem 2.6-3 ... [SUMÁRIO]

> **SOLUÇÃO:**

$$U_0^{(1)} = \frac{3}{2} R N^{(1)} T_0^{(1)} = \frac{3}{2} \times 8,314 \times 2 \times 250 = 6235,5 J$$

$$U_0^{(2)} = \frac{5}{2} R N^{(2)} T_0^{(2)} = \frac{5}{2} \times 8,314 \times 3 \times 350 = 21824,25 J$$

$$\therefore \ U^{(1)} + U^{(2)} = 28060 J$$

e novamente $5U^{(1)} = 2U^{(2)} \Longrightarrow \boxed{U^{(1)} = 8017J \ \ e \ \ U^{(2)} = 20043J}$

2.7 MECHANICAL EQUILIBRIUM [SUMÁRIO]

2.7.1 Three cylinders are fitted with four pistons, as shown in Fig. 2.2 ... [SUMÁRIO]

> **SOLUÇÃO:**
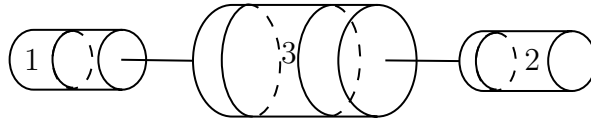
Figura 4: Three volume-coupled system

$$\delta U^{(1)} + \delta U^{(2)} + \delta U^{(3)} = 0$$

$$\text{e } \delta V^{(3)} = -3\delta V^{(1)} - \frac{3}{2}\delta V^{(2)}$$

Então

$$\delta S = \frac{1}{T^{(1)}}\delta U^{(1)} + \frac{1}{T^{(2)}}\delta U^{(2)} + \frac{1}{T^{(3)}}\delta U^{(3)} - \frac{P^{(1)}}{T^{(1)}}\delta V^{(1)} - \frac{P^{(2)}}{T^{(2)}}\delta V^{(2)} - \frac{P^{(3)}}{T^{(3)}}\delta V^{(3)}$$

Eliminando $\delta U^{(3)}$ e $\delta V^{(3)}$ das duas últimas equações,

$$\delta S = \left(\frac{1}{T^{(1)}} - \frac{1}{T^{(3)}}\right)\delta U^{(1)} + \left(\frac{1}{T^{(2)}} - \frac{1}{T^{(1)}}\right)\delta U^{(2)} - \left[\frac{P^{(1)}}{T^{(1)}} - 3\frac{P^{(3)}}{T^{(3)}}\right]\delta V^{(1)} - \left[\frac{P^{(2)}}{T^{(2)}} - \frac{3}{2}\frac{P^{(3)}}{T^{(3)}}\right]\delta V^{(2)}$$

portanto $\delta S = 0$

Cada uma das quatro diferenciais $\delta U^{(1)}, \ \delta U^{(2)}, \ \delta V^{(1)}, \ \delta V^{(2)}$ são arbitrárias, daí

$$\boxed{T^{(1)} = T^{(2)} = T^{(3)} \quad , \quad P^{(1)} = 3P^{(3)} \quad , \quad 2P^{(2)} = 3P^{(3)}}$$

2.7.2 Two particular systems have the following equations of state : ...

SOLUÇÃO:

$$\frac{1}{T^{(1)}} = \frac{3}{2}R\frac{N^{(1)}}{U^{(1)}} \quad \text{e} \quad \frac{P^{(1)}}{T^{(1)}} = R\frac{N^{(1)}}{V^{(1)}} \qquad , \qquad N^{(1)} = 0,5mol = \frac{1}{2}mol$$

$$\frac{1}{T^{(2)}} = \frac{5}{2}R\frac{N^{(2)}}{U^{(2)}} \quad \text{e} \quad \frac{P^{(2)}}{T^{(2)}} = R\frac{N^{(2)}}{V^{(2)}} \qquad , \qquad N^{(2)} = 0,75mol = \frac{3}{4}mol$$

$$T_0^{(1)} = 200K \quad , \quad T_0^{(2)} = 300K \quad , \quad V_0^{(1)} + V_0^{(2)} = 20 \; litros \; = \; 20 \times 10^{-3}m^3$$

Se o pistão intermediário é móvel e diatérmico, encontrar os volumes, energias, pressões e temperaturas finais.

$$\frac{1}{T^{(1)}} = \frac{1}{T^{(2)}} \quad \text{e} \quad \frac{P^{(1)}}{T^{(1)}} = \frac{P^{(2)}}{T^{(2)}}. \text{ Logo, } T^{(1)} = T^{(2)} \text{ e } P^{(1)} = P^{(2)}$$

Mas $U^{(1)} + U^{(2)} = \frac{3}{2}N^{(1)}RT^{(1)} + \frac{5}{2}N^{(2)}RT^{(2)} = (1245 + 4669)J = 5914J$

$$\therefore \quad \left[\frac{3}{2} \times \frac{1}{2} + \frac{5}{2} \times \frac{3}{4}\right] \times R \times T^f = 5914J \qquad R = 8,314472 \; Joule/mol - Kelvin$$

$$\boxed{T^f = 271 \; K}$$

$$\frac{P^{(1)}}{T^{(1)}} = \frac{P^{(2)}}{T^{(2)}} \quad \text{ou} \quad \frac{N^{(1)}}{V^{(1)}} = \frac{N^{(2)}}{V^{(2)}} \qquad \therefore \quad V^{(2)} = \frac{3}{2}V^{(1)}$$

Também $V^{(1)} + V^{(2)} = 20 \times 10^{-3}m^3$

Consequentemente $V^{(1)} = 8 \times 10^{-3}m^3 = 8 \; litros \quad , \quad V^{(2)} = 12 \times 10^{-3}m^3 = 12 \; litros$

$$P^{(1)} = P^{(2)} = \frac{0,5 \times R \times 271K}{8 \times 10^{-3}m^3}$$

$$\boxed{P^{(1)} = P^{(2)} = 1,41 \times 10^5 Pa}$$

$U^{(1)} = \frac{3}{2}N^{(1)}RT$ e $U^{(2)} = \frac{5}{2}N^{(2)}RT$

$$\boxed{U^{(1)} = 1690J} \qquad \text{e} \qquad \boxed{U^{(2)} = 4220J}$$

2.7.3 The hypothetical problem of equilibrium in a closed composite system ...

SOLUÇÃO:

A equação fundamental é

$$S = S^{(1)}(U^{(1)}, V^{(1)}) + S^{(2)}(U^{(2)}, V^{(2)})$$

note que suprimimos o número de mols na notação. A condição para o volume é (condição de fechamento ou completeza)

$$V^{(1)} + V^{(2)} = V = constante$$

E nós devemos formalizar o significado de restrição adiabática. Desde que nenhum fluxo de energia na forma de calor seja permitido pela parede, a troca de energia de cada subsistema é devida inteiramente pelo termo do trabalho, e a restrição adiabática é expressa pela condição que (condição adiabática)

$$dU^{(1)} = -P^{(1)}dV^{(1)}; \quad dU^{(2)} = -P^{(2)}dV^{(2)}$$

A mudança na entropia total em um processo virtual é agora,

$$dS = \frac{1}{T^{(1)}}dU^{(1)} + \frac{P^{(1)}}{T^{(1)}}dV^{(1)} + \frac{1}{T^{(2)}}dU^{(2)} + \frac{P^{(2)}}{T^{(2)}}dV^{(2)}$$

Inserindo a condição adiabática, a quantidade dS se anula identicamente. Era de se esperar inserir a condição do volume (condição de fechamento ou completeza) e então fazer $dS = 0$ para obter a condição de equilíbrio, mas o desaparecimento da quantidade dS no meio do caminho durante os cálculos certamente inviabiliza a continuação da análise. Como esperado dos fundamentos físicos, uma solução matemática do problema não existe. Entretanto, uma solução parcial pode ser obtida, para a segunda condição de fechamento que ainda não escrevemos, que deve ser aplicada para todo problema na representação entrópica. Esta é a condição de fechamento para a energia

$$U^{(1)} + U^{(2)} = U = constante$$

Assim, temos

$$dU^{(1)} = -dU^{(2)}$$

E, inserindo as condições adiabáticas

$$-P^{(1)}dV^{(1)} = P^{(2)}dV^{(2)}$$

Finalmente, da equação da condição do volume encontramos $dV^{(1)} = -dV^{(2)}$, Consequentemente

$$P^{(1)} = P^{(2)}$$

Novamente, esta caracterização necessária mas não suficiente do estado de equilíbrio está em concordância com nossas expectativas nos fundamentos físicos.

2.8 EQUILIBRIUM WITH RESPECT TO MATTER FLOW [SUMÁRIO]

2.8.1 The fundamental equation of a particular type of two-component system is... [SUMÁRIO]

SOLUÇÃO:

Para cada subsistema temos $\frac{1}{T} = \frac{\partial S}{\partial U} = \frac{3}{2}\frac{NR}{U}$ e $\frac{P}{T} = \frac{NR}{V}$,

e ainda $-\frac{\mu_1}{T} = A + R\ln\left(\frac{U^{3/2}V}{N^{5/2}}\right) - \frac{5}{2}R - R\ln\left[\frac{N_1}{(N_1 + N_2)}\right] = R\ln\frac{U^{3/2}V}{N_1 N^{3/2}} + \left[A - \frac{5}{2}R\right]$

Mas $\frac{1}{T^{(1)}} = \frac{1}{T^{(2)}}$ ou $\frac{N_1^{(2)} + N_2^{(2)}}{U^{(1)}} = \frac{N_1^{(2)} + N_2^{(2)}}{U^{(2)}}$

e $\frac{\mu_1^{(1)}}{T^{(1)}} = \frac{\mu_1^{(2)}}{T^{(2)}}$ ou $\frac{[U^{(1)}]^{3/2}}{[N_1^{(1)} + N_2^{(1)}]^{3/2}N_1^{(1)}} = \frac{[U^{(2)}]^{3/2}}{[N_1^{(2)} + N_2^{(2)}]^{3/2}N_1^{(2)}}$

Elevando a primeira dessas equações a $3/2$, e multiplicando as equações, obtemos

$$N_1^{(1)} = N_1^{(2)}, \quad consequentemente \quad \boxed{N_1^{(1)} = N_1^{(2)} = 0,75}$$

Para encontrar as energias e temperaturas :
As energias iniciais eram :

$$U^{(1)} = \frac{3}{2} N^{(1)} R T^{(1)} = 562,5R$$

$$U^{(2)} = \frac{3}{2} N^{(2)} R T^{(2)} = 562,5R$$

As energias finais são : $U^{(1)} = \frac{3}{2} \times 1,5 \times RT$, $\quad U^{(2)} = \frac{3}{2} \times 1,5 \times RT$ Portanto,

$$U^{(1)} + U^{(2)} = 4,125RT$$

Então,

$$4,125RT = 2 \times 562,5R \Longrightarrow \boxed{T = 272,7K}$$

Encontrando as pressões : $(PV = NRT)$

$$P^{(1)}V^{(1)} = N^{(1)} R T^{(1)} \Longrightarrow \boxed{P^{(1)} = 6,8 \times 10^5 Pa}$$

$$P^{(2)}V^{(2)} = N^{(2)} R T^{(2)} \Longrightarrow \boxed{P^{(2)} = 5,7 \times 10^5 Pa}$$

2.8.2 A two-component system gaseous system has a fundamental equation of the form... [SUMÁRIO]

SOLUÇÃO:

Para cada subvolume $\frac{1}{T} = \frac{1}{3} A U^{-2/3} V^{1/3} N^{1/3}, \quad \frac{P}{T} = \frac{1}{3} A U^{1/3} V^{-2/3} N^{1/3}$

Ou ainda $T = \frac{3}{A} \left(\frac{U^2}{NV} \right)^{1/3}, \quad P = U/V, \quad -\frac{\mu_1}{T} = \frac{1}{3} A U^{1/3} V^{1/3} N^{-2/3} + B \left(\frac{N_2}{N} - \frac{N_1 N_2}{N^2} \right)$

Então

$$U = \left(\frac{A^3}{3} T^3 (NV)^{1/2} \right)$$

E isto é suficiente para determinar T_e :

$$\boxed{2T_e^3 = T_l^3 + T_r^3}$$

Se $T_r = 2T_l \Longrightarrow 2T_e^3 = 9T_l^3 \Longrightarrow \boxed{T_e = 1,651 T_l}$
Também, eliminando U da equação para μ/T :

$$-\frac{\mu_1}{T} = \frac{1}{9} A^2 T \left(\frac{V}{N} \right)^{1/2} + B \left[\frac{N_2}{N} - \frac{N_1 N_2}{N^2} \right]$$

Então, igualando μ_1/T em cada subsistema,

$$\frac{1}{9} A^2 T_e V^{1/2} N_{1l}^{-1/2} = \frac{1}{9} A^2 T_e V^{1/2} \left[N_{1r} + \frac{1}{2} \right]^{-1/2} + B \left[\frac{N_2}{N_{1r} + N_2} - \frac{N_{1r} N_2}{(N_{1r} + N_2)^2} \right]$$

Mas

$$B = \left(\frac{A}{3}\right)^2 T_l V^{1/2}$$

Portanto,

$$T_e N_{1l}^{-1/2} = T_e \left[N_{1r} + \frac{1}{2}\right]^{-1/2} + T_l \left[\frac{1}{2N_{1r}+1} - \frac{2N_{1r}}{(2N_{1r}+1)^2}\right]$$

Assim temos que,

$$\left(\frac{3}{2} - N_{1r}\right)^{-1/2} = \left(N_{1r} + \frac{1}{2}\right)^{-1/2} + \frac{T_l}{T_e}(2N_{1r}+1)^{-2}$$

Então,

$$\left(\frac{3}{2} - N_{1r}\right)^{-1/2} - \left(N_{1r} + \frac{1}{2}\right)^{-1/2} - 0,6057(2N_{1r}+1)^2 = 0$$

Isto pode ser resolvido por tentativa e erro utilizando uma calculadora ou um computador. Feito corretamente, você deve concluir que,

$$\boxed{N_{1r} = 0,84}$$

$$\boxed{N_{1l} = 1,5 - 0,84 = 0,66}$$

2.9 CHEMICAL EQUILIBRIUM [SUMÁRIO]

2.9.1 The hydrogenation of propane (C_3H_8) to form methane (CH_4) proceeds by the reaction... [SUMÁRIO]

SOLUÇÃO:

$$\mu_{C_1 H_8} + 2\mu_{H_2} = 3\mu_{CH_4}$$

O que é formalmente indentico ao exemplo 1 da seção 2.7

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3 SOME FORMAL RELATIONSHIPS, AND SAMPLE SYSTEMS [SUMÁRIO]

3.1 THE EULER EQUATION [SUMÁRIO]

3.1.1 Write each of the five physically acceptable fundamental equations... [SUMÁRIO]

SOLUÇÃO:

(a)

$$S = C[UVN]^{1/3}, \quad C \equiv \left(\frac{R^2}{v_0 \theta}\right)^{1/3}$$

Então,

$$S = \underbrace{\left[\frac{C}{3}U^{-2/3}V^{1/3}N^{1/3}\right]}_{1/T}U + \underbrace{\left[\frac{C}{3}U^{1/3}V^{-2/3}N^{1/3}\right]}_{P/T}V + \underbrace{\left[\frac{C}{3}U^{1/3}V^{1/3}N^{-2/3}\right]}_{-\mu/T}N$$

(c)

$$S = C\left[NU + \frac{R\theta}{v_0^2}V^2\right]^{1/2}, \quad C \equiv \left(\frac{R}{\theta}\right)^{1/2}$$

Então,

$$S = \underbrace{\frac{CN}{2}\left[NU + \frac{R\theta}{v_0^2}V^2\right]^{-1/2}}_{1/T}U + \underbrace{\frac{CR\theta}{v_0^2}V\left[NU + \frac{R\theta}{v_0^2}V^2\right]^{-1/2}}_{P/T}V + \underbrace{\frac{C}{2}U\left[NU + \frac{R\theta}{v_0^2}V^2\right]^{-1/2}}_{-\mu/T}N$$

(e)

$$S = C[N^2VU]^{1/5}$$

$$S = \underbrace{\frac{2}{5}CU[N^2VU]^{-4/5}}_{1/T}U + \underbrace{\frac{1}{5}C[N^2VU]^{-4/5}}_{P/T}V + \underbrace{\frac{2}{5}CN[N^2VU]^{-4/5}}_{-\mu/T}N$$

(g) e **(i)** são similares

3.2 THE GIBBS-DUHEM RELATION [SUMÁRIO]

3.2.1 Find the relation among T, P, and μ for the system with the fundamental equation... [SUMÁRIO]

> **SOLUÇÃO:**

A equação fundamental é :

$$U = \left(\frac{v_0^2\theta}{R^3}\right)\frac{S^4}{NV^2}$$

Então,

$$T = 4\left(\frac{v_0^2\theta}{R^3}\right)\frac{S^3}{NV^2}$$

$$P = 2\left(\frac{v_0^2\theta}{R^3}\right)\frac{S^4}{NV^3}$$

$$\mu = -\left(\frac{v_0^2\theta}{R^3}\right)\frac{S^4}{N^2V^2}$$

Das duas primeiras equações $\implies T/P = 2V/S$

Da primeira e terceira equação $\implies \mu/T = -S/4N$
Reescrevendo a primeira equação temos,

$$T = 4\left(\frac{v_0^2\theta}{R^3}\right)\frac{S}{N}\left(\frac{S}{V}\right)^2$$

$$= 4\left(\frac{v_0^2\theta}{R^3}\right)\left(-4\frac{\mu}{T}\right)\left(2\frac{P}{T}\right)^2$$

$$\therefore \boxed{T = -(2)^6\left(\frac{v_0^2\theta}{R^3}\right)\mu P^2}$$

3.3   SUMMARY OF FORMAL STRUCTURE [SUMÁRIO]

3.3.1   A particular system obeys the two equations of state... [SUMÁRIO]

$\boxed{\text{SOLUÇÃO:}}$

Dadas as equações $T = 3As^2/v$ e $P = As^3/v$, encontre $\mu(s,v)$ e a equação fundamental.
(a)

$$d\mu = -sdT + vdP$$

$$= -sd[3As^2/v] + vd[As^3/v]$$

$$= -3A\frac{s^2}{v}ds + A\frac{s^3}{v^2}dv$$

$$= -d[As^3/v]$$

$$\Rightarrow d\mu = -d[As^3/v]$$

$$\int d\mu = \int -d[As^3/v]$$

$$\therefore \mu = -As^3/v + cte$$

Podemos tomar a constante igual a zero ($cte = 0$)
Assim,

$$\boxed{\mu(s,v) = -As^3/v}$$

Então a equação de Euler será:

$$U = TS - PV + \mu N$$

ou ainda

$$u = Ts - Pv + \mu$$

$$\therefore \boxed{u = \left(\frac{3As^2}{v}\right)s - \left(A\frac{s^3}{v}\right)v - \left(A\frac{s^3}{v}\right)}$$

Ou de forma mais sucinta,

$$\boxed{U = A\frac{S^3}{NV}}$$

(b)

Pela integração direta da equação de Euler na forma molar :

$$du = Tds - Pdv$$
$$= \left(3A\frac{s^2}{v} \right) ds - \left(A\frac{s^3}{v} \right) dv$$
$$= d[A\frac{s^3}{v}]$$
$$\Rightarrow \int du = \int d \left[A\frac{s^3}{v} \right]$$

Fazendo a constante de integração igual a zero, concluímos que :

$$\boxed{U = A\frac{S^3}{NV}}$$

3.3.2 It is found that a particular system obeys the relations U = PV and P = BT² [SUMÁRIO]

$\boxed{\textsc{Solução:}}$

As equações envolvem U e estão portanto na representação entrópica. Escreva como :

$$\frac{1}{T} = B^{1/2}\frac{v^{1/2}}{u^{1/2}} \quad \text{e} \quad \frac{P}{T} = B^{1/2}\frac{u^{1/2}}{v^{1/2}}$$

Então,

$$ds = \frac{1}{T}du + \frac{P}{T}dv$$
$$= B^{1/2}\frac{v^{1/2}}{u^{1/2}}du + B^{1/2}\frac{u^{1/2}}{v^{1/2}}dv$$
$$= 2B^{1/2}d[u^{1/2}v^{1/2}]$$

$$\therefore \boxed{s = 2B^{1/2}u^{1/2}v^{1/2} + const.} \quad ou \quad \boxed{S = 2B^{1/2}U^{1/2}V^{1/2} + Ns_0}$$

3.3.3 A system obeys the equations $P = -\dfrac{NU}{NV - 2AVU}$ and $T = 2C\dfrac{U^{1/2}V^{1/2}}{N - 2AU}e^{AU/N}$... [SUMÁRIO]

$\boxed{\textsc{Solução:}}$

Escreva as equações na forma $\dfrac{P}{T} = -\dfrac{1}{2}C^{-1}\dfrac{u^{1/2}}{v^{3/2}}e^{Au}$ e $\dfrac{1}{T} = \dfrac{1}{2}C^{-1}u^{-1/2}v^{-1/2}[1 - 2Au]e^{-Au}$

$$\therefore ds = \frac{1}{2}C^{-1}e^{-Au} \left[\frac{1 - 2Au}{\sqrt{uv}}du - \frac{u^{1/2}}{v^{3/2}}dv \right]$$

Faça $s = Du^n v^m e^{-Au}$ (tentativa e erro!)

$$\therefore ds = D[(nu^{n-1}v^m - Au^n v^m)]e^{-Au}du + mu^n v^{m-1}e^{-Au}dv$$

Isto está de acordo se tomarmos $n = 1/2$, $m = -1/2$, $D = C^{-1}$

$$\therefore \boxed{s = C^{-1}\sqrt{\frac{u}{v}}e^{-Au}}$$

3.3.4   A system obeys the two equations $u = \frac{3}{2}Pv$ and $u^{1/2} = BTv^{1/3}$... [SUMÁRIO]

$\boxed{\textbf{Solução:}}$

As equações estão na representação entrópica, então escrevemos

$$\frac{1}{T} = Bu^{-1/2}v^{1/3} \quad \text{e} \quad \frac{P}{T} = \frac{2}{3}Bu^{1/2}v^{-2/3}$$

Então

$$
\begin{aligned}
ds &= \frac{1}{T}du + \frac{P}{T}dv \\
&= Bv^{1/3}\frac{du}{u^{1/2}} + \frac{2}{3}Bu^{1/2}\frac{dv}{v^{2/3}} \\
&= 2Bd(u^{1/2}v^{1/3})
\end{aligned}
$$

$$\therefore \boxed{s = 2Bu^{1/2}v^{1/3} + s_0} \quad ou \quad \boxed{S = 2BU^{1/2}V^{1/3}N^{1/6} + Ns_0}$$

3.4   THE SIMPLE IDEAL GAS AND MULTICOMPONENT SIMPLE IDEAL GASES [SUMÁRIO]

3.4.1   A "constant volume ideal gas thermometer"is contructed as shown (schematically) in Fig. 3.3. ... [SUMÁRIO]

$\boxed{\textbf{Solução:}}$

$\boxed{\textcolor{red}{\textbf{NENHUMA SOLUÇÃO PARA ESSE PROBLEMA NO MOMENTO}}}$

3.4.2   Show that the relation between the volume and the pressure of a monoatomic ideal gas ... [SUMÁRIO]

$\boxed{\textbf{Solução:}}$

Para um gás simples $S = Ns_0 + NR\ln\left[\left(\frac{U}{U_0}\right)^{-c}\frac{V}{V_0}\left(\frac{N_0}{N}\right)\right]^{c+1}$

Se $S = const$, $u^c v = u_0^c v_0 e^{[(s-s_0)/R]}$

$$\therefore (cRT)^c v = (cRT_0)^c v_0 e^{[(s-s_0)/R]}$$

$$(Pv)^c v = (P_0 v_0)^c v_0 e^{[(s-s_0)/R]}$$

$$Pv^{\frac{c+1}{c}} = P_0 v_0^{\frac{c+1}{c}} e^{(s-s_0)/c} = const.$$

Então, para um gás ideal monoatômico, $c = 3/2$

$$\boxed{Pv^{5/3} = \left[P_0 v_0^{5/3} e^{-2s_0/3R} \right] e^{2s/3R} = const}$$

3.4.3 Two moles of a monoatomic ideal gas are at a temperature of 0°Cand a volume... [SUMÁRIO]

SOLUÇÃO:

$$S = \frac{N}{N_0} S_0 + NR \ln \left[\left(\frac{U}{U_0} \right)^{3/2} \frac{V}{V_0} \left(\frac{N}{N_0} \right)^{-5/2} \right]$$

Em $S = const.$,

$$U^{3/2} V = const \implies \left(\frac{3}{2} NRT \right)^{3/2} V = const. \implies T^{3/2} V = const.$$

$$V_f = v_i \left(\frac{T_i}{T_f} \right)^{3/2} = 45 \left(\frac{273}{223} \right)^{3/2} litros = 61 \ litros = 61 \times 10^{-3} m^3$$

Também,

$$PV = NRT$$

Portanto,

$$\boxed{P_i = \frac{NRT_i}{V_i} = 0,101 MPa} \quad e \quad \boxed{P_f = \frac{NRT_f}{V_f} = 0,061 MPa}$$

3.4.4 By carring out the integral $\int PdV$, compute the work done by the gas in Problem 3.4-3.. [SUMÁRIO]

SOLUÇÃO:

Do problema 3.4-2, $PV^{5/3} = const.$

$$(-W) = \int PdV = \int_{V_i}^{V_f} P_i \left(\frac{V_i}{V} \right)^{5/3} dV = -\frac{3}{2} P_i V_i^{5/3} [V_f^{-2/3} - V_i^{-2/3}] = -\frac{3}{2} P_i V_i \left[\left(\frac{V_f}{V_i} \right)^{-2/3} - 1 \right]$$

Então

$$(-W) = -\frac{3}{2} \times (1,01 \times 10^5) \times (45 \times 10^{-3}) \left[\left(\frac{61}{45} \right)^{-2/3} - 1 \right]$$

Logo

$$(-W) = 12,5 \times 10^2 \, Joules$$

Também

$$U_i = \frac{3}{2}NRT_i = 3 \times 8,314 \times 273 = 6810 \; Joules$$
$$U_f = \frac{3}{2}NRT_f = 3 \times 8,314 \times 223 = 5560 \; Joules$$
$$\Delta U = 12,4 \times 10^2 \; Joules$$

3.4.5 In a particular engine a gas is compressed in the initial stroke of the piston... [SUMÁRIO]

SOLUÇÃO:

(a)

$$W = -\int_{V_0}^{V_1} PdV = -NR\int_{V_0}^{V_1} T\frac{dV}{V} = -\frac{NRT_0}{V_0^\eta}\int_{V_0}^{V_1} V^{\eta-1}dV = -\frac{NRT_0}{\eta}\left[\left(\frac{V_1}{V_0}\right)^\eta - 1\right]$$

$$\boxed{W = \frac{NR}{\eta}(T_0 - T_1)}$$

(b)

$$\boxed{\Delta U = \frac{3}{2}NR(T_1 - T_0)} \quad \text{Onde } T_1 = \left(\frac{V_1}{V_0}\right)^\eta T_0$$

(c)

$$Q = \Delta U - W = \frac{3}{2}NR(T_1 - T_0) + \frac{NR}{\eta}(T_1 - T_0)$$

$$\therefore \boxed{Q = \left(\frac{3}{2} + \frac{1}{\eta}\right)NR(T_1 - T_0)}$$

(d)

$$S = Ns_0 + \frac{3}{2}NR \, \ln\left(\frac{U}{U_0}\right) + NR \, \ln\left(\frac{V}{V_0}\right) - \frac{5}{2}NR \, \ln\left(\frac{N}{N_0}\right)$$
$$= Ns_0 + \frac{3}{2}NR \, \ln\left(\frac{T}{T_0}\right) + NR \, \ln\left(\frac{V}{V_0}\right) - \frac{5}{2}NR \, \ln\left(\frac{N}{N_0}\right)$$

$$\therefore dS = \frac{3}{2}NR\frac{dT}{T} + NR\frac{dV}{V}$$

$$= \frac{3}{2}NR\eta\frac{dV}{V} + NR\frac{dV}{V} = \left(\frac{3}{2}\eta + 1\right)NR\frac{dV}{V}$$

$$\therefore Tds = \left(\frac{3}{2}\eta + 1\right)NRT_0\frac{V^{\eta-1}}{V_0^{\eta}}dV$$

Então

$$Q = \int TdV = \left[\left(\frac{3}{2}\eta + 1\right)NRT_0\frac{1}{\eta}\left(\frac{V}{V_0}\right)^{\eta}\right]_{V_0}^{V_1} = \left(\frac{3}{2} + \frac{1}{\eta}\right)NRT_0\left[\left(\frac{V_1}{V_0}\right)^{\eta} - 1\right]$$

$$\therefore \boxed{\left(\frac{3}{2} + \frac{1}{\eta}\right)NR(T_1 - T_0)} \quad \text{O que bate com a letra (c)}$$

(e) Para checar $\eta = -\frac{2}{3}$ se $Q = 0$

Então

$$PV = NRT = NR\left(\frac{V}{V_0}\right)^{\eta}T_0$$

ou ainda

$$\boxed{PV^{1-\eta} = const \quad \text{ou} \quad PV^{5/3} = const.}$$

E esta é a conhecida forma de uma adiabata.

3.4.6 Find the three equations of state of the "simple ideal gas"(equation 3.34... [SUMÁRIO]

$$\boxed{\text{SOLUÇÃO:}}$$

$$S = Ns_0 + NcR\ \ln\left(\frac{U}{Nu_0}\right) + NR\ \ln\left(\frac{V}{Nv_0}\right)$$

Então

$$\frac{1}{T} = \frac{NcR}{U} \quad \text{e} \quad \frac{P}{T} = \frac{NR}{V}$$

$$\therefore \boxed{-\frac{\mu}{T} = \frac{\partial S}{\partial N} = s_0 + cR\ \ln\left(\frac{U}{Nu_0}\right) + R\ \ln\left(\frac{V}{Nv_0}\right) - (1+c)R}$$

3.4.7 Find the four equations of state of a two-component mixture if simple ideal gases... [SUMÁRIO]

$$\boxed{\text{SOLUÇÃO:}}$$

$$S = \sum_j N_j s_{j_0} + \sum_j N_j c_j R\ \ln\left(\frac{T}{T_0}\right) + \sum_j N_j R\ \ln\left(\frac{V}{N_j V_0}\right) \ ; \ U = \left(\sum_j N_j c_j\right)RT$$

$$\therefore S = \sum_j N_j s_{j_0} + \left(\sum_j N_j c_j \right) R \ln \left[\frac{U}{\left(\sum_j N_j c_j \right) R T_0} \right] + \sum_j N_j R \ln \left(\frac{V}{N_j V_0} \right)$$

Então

$$\frac{1}{T} = \sum_j N_j c_j \frac{R}{U}$$

$$\frac{P}{T} = \sum_j N_j \frac{R}{V}$$

$$-\frac{\mu}{T} = s_{j_0} + c_j R \ln \left(\frac{U}{\sum_j N_j c_j R T_0} \right) - c_j R + R \ln \left(\frac{V}{N_j V_0} \right) - R$$

Para verificar a equação de Euler, calculamos $\dfrac{U}{T} + \dfrac{P}{T}V - \sum_j \dfrac{\mu_j N_j}{T}$

$$\tfrac{U}{T} + \tfrac{P}{T}V - \sum_j \tfrac{\mu_j N_j}{T} = U \sum_j \tfrac{N_j c_j R}{U} + V \sum_j \tfrac{N_j R}{V} + \sum_j \left[s_{j_0} + c_j R \ln \left(\tfrac{U}{\sum_j N_j c_j R T_0} \right) - c_j R + R \ln \left(\tfrac{V}{N_j V_0} \right) - R \right] N_j$$

O lado direito desta equação é exatamente o S da segunda linha da solução.

3.4.8 If a monoatomic ideal gas is permitted to expand into an evacuated region, thereby increasing its volume... [SUMÁRIO]

> **Solução:**

Responda na ordem inversa, ou seja, **(c)**, **(b)** e depois **(a)**.

$$S = N s_0 + N R \ln \left[\left(\frac{U}{U_0} \right)^{3/2} \left(\frac{V}{V_0} \right) \left(\frac{N}{N_0} \right)^{-5/2} \right]$$

(a) De $PV = NRT$

$$\frac{P_f}{P_i} = \frac{V_i}{V_f} = \frac{1}{\lambda} \Longrightarrow \boxed{P_f = \frac{P_i}{\lambda}}$$

(b) de $U = \dfrac{3}{2} NRT \Longrightarrow \boxed{T_f = T_i}$

(c) Se $U_f = U_i$ e $V_f/V_i = \lambda$ então

$$\Delta S = S_f - S_i = NR \ln(V_f) - NR \ln(V_i) = NR \ln \left(\frac{V_f}{V_i} \right)$$

$$\therefore \boxed{\Delta S = NR \ln(\lambda)}$$

3.4.9 A tank has a volume of 0.1m³ and is filled with He gas at a pressure of... [SUMÁRIO]

SOLUÇÃO:

$$U_1 = \frac{3}{2}P_1V_1 \quad , \quad U_2 = \frac{3}{2}P_2V_2, \quad U_f = \frac{3}{2}P_fV_f = \frac{3}{2}P_f(V_1+V_2) \quad \text{e} \quad U_f = U_1 + U_2$$

$$\text{Então} \quad \frac{3}{2}P_f(V_1+V_2) = \frac{3}{2}P_1V_1 + \frac{3}{2}P_2V_2$$

$$\therefore \boxed{P_f = \frac{P_1V_1 + P_2V_2}{V_1+V_2} = \frac{5\times 10^6 \times 0.1 + 6\times 10^6 \times 0,15}{0,25} = 5,6\times 10^6 Pa}$$

3.4.10 ... [SUMÁRIO]

SOLUÇÃO:

(a)

$$P_1V_1 = N_1RT_1 \quad \text{ou} \quad 5\times 10^6 \times 0,1 = N_1 \times 8,314 \times 300 \quad \text{então} \quad N_1 = 200,5 \ mols$$

$$P_2V_2 = N_2RT_2 \quad \text{ou} \quad 6\times 10^6 \times 0,15 = N_2 \times 8,314 \times 350 \quad \text{então} \quad N_2 = 309,3 \ mols$$

$$P_fV_f = (N_1+N_2)RT_f \quad \text{ou} \quad 5,6\times 10^6 \times 0,25 = 509,8 \times 8,134 \times T_f$$

$$\therefore \boxed{T_f = 330 \ K}$$

(b)

$$\text{Novamente} \quad N_1 = 200,5 \quad \text{e} \quad N_2 = 309,3 \quad \text{Então} \quad U_1 + U_2 = U_f$$

Logo

$$\frac{3}{2}N_1RT_1 + \frac{5}{2}N_2RT_2 = \frac{3}{2}N_1RT_f + \frac{5}{2}N_2RT_f \Longrightarrow \boxed{T_f = 336 \ K}$$

$$\text{Note também que} \quad \frac{3}{2}P_1V_1 + \frac{5}{2}P_2V_2 = \left(\frac{3}{2}N_1 + \frac{5}{2}N_2\right)\frac{P_fV_f}{N_1+N_2} \Longrightarrow \boxed{P_f = 5,7\times 10^6 Pa}$$

3.4.11 Show that the pressure of a multicomponent simple ideal gas can be written as the sum... [SUMÁRIO]

SOLUÇÃO:

$$P = \frac{NRT}{V} \quad \text{e} \quad N = \sum_i Ni \Longrightarrow \boxed{P = \sum_i \left(\frac{N_iRT}{V}\right) \equiv \sum_i P_i}$$

3.4.12 Show that μ_j, the electrochemical potential of the jth component in a ... [SUMÁRIO]

SOLUÇÃO:

Nós temos $S = \sum_j N_j s_{j_0} + \sum_j N_j c_j R \ln\left(\dfrac{T}{T_0}\right) + \sum_j N_j R \ln\left(\dfrac{V}{N_j v_0}\right)$ quando $T = \dfrac{U}{R \sum_j N_j c_j}$

$$-\frac{\mu_j}{T} = \left(\frac{\partial S}{\partial N_j}\right)_{U_1,\dots} = s_{j_0} + c_j R \ln\left(\frac{T}{T_0}\right) + \frac{1}{T}\left(\sum_j N_j c_j\right) R \left(\frac{\partial T}{\partial N_j}\right)_U + R \ln\left(\frac{V}{N_j v_0}\right) - R$$

$$\text{Mas} \quad \left(\frac{\partial T}{\partial N_j}\right) = -\frac{U}{R}\frac{c_j}{(\sum_j N_j c_j)^2} = -\frac{T c_j}{\sum_j N_j c_j}$$

$$\therefore -\frac{\mu_j}{T} = s_{j_0} + c_j R \ln\left(\frac{T}{T_0}\right) - c_j R + R \ln\left(\frac{V}{N_j v_0}\right) - R$$

$$\implies \mu_j = -RT \ln\left(\frac{V}{N_j v_0}\right) + RT\left[1 + c_j - c_j \ln\left(\frac{T}{T_0}\right) - \frac{s_{j_0}}{R}\right]$$

$$\therefore \boxed{\mu_j = RT \ln\left(\frac{P_j}{RT v_0}\right) + RT\left[1 + c_j - c_j \ln\left(\frac{T}{T_0}\right) - \frac{s_{j_0}}{R}\right]}$$

3.4.13 An impermeable, diathermal, and rigid partition divides a container into two subvolumes... [SUMÁRIO]

SOLUÇÃO:

Do problema anterior $\mu_j = -RT \ln\left(\dfrac{V}{N_j v_0}\right) + RT\left[1 + c_j - c_j \ln\left(\dfrac{T}{T_0}\right) - \dfrac{s_{j_0}}{R}\right]$

$$\text{e} \quad \mu_{H_2}^{(1)} = \mu_{H_2}^{(2)}$$

$$\therefore -RT \ln\left(\frac{V_0}{N_{H_2}^{(1)} v_0}\right) = -RT \ln\left(\frac{V_0}{N_{H_2}^{(2)} v_0}\right)$$

$$\text{Ou} \quad N_{H_2}^{(1)} = N_{H_2}^{(2)} = \frac{1}{2} \text{ mol}$$

$$\therefore \boxed{P^{(1)} = \frac{N_{H_2}^{(1)} RT}{V_0} = \frac{1}{2}\frac{RT}{V_0}} \quad \text{e} \quad \boxed{P^{(2)} = \frac{[N_{H_2}^{(2)} + N_{Ne}^{(2)}]RT}{V_0} = \frac{7}{2}\frac{RT}{V_0}}$$

3.4.14 Use the results of problem 3.4-11 and 3.4-12 to stablish the results $P_\alpha = P_\gamma$ e... [SUMÁRIO]

SOLUÇÃO:

A pressão parcial de A em β, ou P_β^A, é igual a P_α

A pressão parcial de B em β, ou P_β^B, é igual a P_γ

$$\therefore P_\beta = P_\beta^A + P_\beta^B = P_\alpha + P_\gamma$$

Também, por simetria,

$$P_\alpha = P_\gamma \implies \boxed{P_\beta = 2P_\alpha}$$

3.4.15 An impermeable, diathermal and rigid partition divides a container into two subvolumes... [SUMÁRIO]

$\boxed{\textbf{Solução:}}$

Note que $U = \displaystyle\sum_j N_j c_j RT,$ e desde que a energia total seja constante, a temperatura é constante.

$$\text{Inicialmente} \quad P_{H_2} = \frac{nRT}{nV_0} = \frac{RT}{V_0}$$
$$P_{He} = \frac{mRT}{mV_0} = \frac{RT}{V_0}$$

$$\text{Finalmente} \quad P = \frac{(n+m)RT}{(n+m)V_0} = \frac{RT}{V_0} \implies \text{não há variação na pressão}$$

Então a variação na entropia é igual a "entropia de mistura". Veja o texto logo abaixo da equação 3.40 no livro-texto (entropy of mixing-pg 69).

$$\therefore \boxed{\Delta s = -R \sum_j N_j \, \ln\left(\frac{N_j}{N}\right) = -R\left[n \, ln\left(\frac{n}{n+m}\right) + m \, ln\left(\frac{m}{n+m}\right)\right]}$$

3.5 THE "IDEAL VAN DER WAALS FLUID"[SUMÁRIO]

3.5.1 Are each of the listed pairs of equations of state compatible (recall equations 3.46)... [SUMÁRIO]

$\boxed{\textbf{Solução:}}$

(a)

$$U = aPv \quad \text{e} \quad Pv^2 = bT$$

Escreva as equações como $\dfrac{P}{T} = \dfrac{b}{v^2}$, e (dividindo por $P = u/av$), $\implies \dfrac{1}{T} = \dfrac{ab}{uv}$

Então $\dfrac{\partial}{\partial u}\left(\dfrac{P}{T}\right) \overset{?}{=} \dfrac{\partial}{\partial v}\left(\dfrac{1}{T}\right)$ se torna $\dfrac{\partial}{\partial u}\left(\dfrac{b}{v^2}\right) \overset{?}{=} \dfrac{\partial}{\partial v}\left(\dfrac{ab}{uv}\right)$, ou $0 \overset{?}{=} -\dfrac{ab}{uv^2} \implies \underline{\text{não é compatível}}$

(b)

$$U = aPv^2 \quad \text{e} \quad Pv^2 = bT$$

$$\therefore \frac{P}{T} = \frac{b}{v^2} \quad \text{e} \quad \frac{1}{T} = \frac{ab}{u}$$

$$\text{Então} \quad \frac{\partial}{\partial u}\left(\frac{P}{T}\right) = \frac{\partial}{\partial v}\left(\frac{1}{T}\right), \quad \text{ou} \quad 0 = 0 \Longrightarrow \underline{\text{Compatível}}$$

(c)

$$P = \frac{u}{v}\frac{c + buv}{a + buv} \quad \text{e} \quad T = \frac{u}{a + buv}$$

$$\therefore \frac{P}{T} = \frac{c}{v} + bu \quad \text{e} \quad \frac{1}{T} = \frac{a}{u} + bv$$

$$\therefore \frac{\partial}{\partial u}\left(\frac{P}{T}\right) = \frac{\partial}{\partial v}\left(\frac{1}{T}\right) \quad (= b) \Longrightarrow \underline{\text{compatível}}$$

Para encontrar as equações fundamentais para os casos **(b)** e **(c)** :

(b) $\quad ds = \frac{1}{T}du + \frac{P}{T}dv = \frac{ab}{u}du + \frac{b}{v^2}dv \Rightarrow \boxed{S - S_0 = abN \ \ln\left(\frac{U}{N}\right) - b\frac{N^2}{V}}$

(c) $\quad ds = \left(\frac{a}{u} + bv\right)du + \left(\frac{c}{v} + bu\right)dv \Rightarrow \boxed{S = Ns_0 + a \ \ln\left(\frac{U}{U_0}\right) + b\frac{UV}{N} - bu_0v_0 + c \ \ln\left(\frac{V}{Nv_0}\right)}$

3.5.2 Find the relationship between the volume and the temperature of an ideal Van Der Waals fluid... [SUMÁRIO]

SOLUÇÃO:

$$S = NR \ \ln[(v - b)(cRT)^c] + Ns_0 \Longrightarrow \boxed{(v - b)T^c = const.}$$

3.5.3 Repeat the problem 3.4-3 for CO$_2$, rather than for a monoatomic ideal gas... [SUMÁRIO]

SOLUÇÃO:

Recordando $S = NR \ \ln[(v - b)(u + a/v)^c] + S_0$ Consequentemente, numa expansão adiabática,

$$(v - b)\left[u + \frac{a}{v}\right]^c = const.$$

$$\text{também} \quad u + \frac{a}{u} = cRT$$

$$\text{de onde} \quad (v - b)T^c = const.$$

Então $\quad \dfrac{(v_f - b)T_f^c}{(v_i - b)T_i^c} = 1,$ e da tabela 3.1(pg.77 do livro), $c = 3,5$ e $b = 42,7 \times 10^{-6}m^3$

Tem-se também que $v_i = 45 \times 10^{-3}m^3$

Neste caso b pode ser desprezado, então

$$\frac{v_f}{v_i} \simeq \left(\frac{T_i}{T_f}\right)^c = \left(\frac{273}{223}\right)^{3,5} = 2,03$$

$$\text{e ainda} \quad \boxed{v_f = 91,4 \ litros = 0,091m^3}$$

$$\boxed{P_i = \frac{RT_i}{v_i - b} - \frac{a}{v_i^2} = 1,01 \times 10^5 Pa}$$

$$\boxed{P_f = \frac{RT_f}{v_f - b} - \frac{a}{v_f^2} = 0,06 \times 10^5 Pa}$$

Se $\frac{a}{v^2} \simeq \frac{1}{10}\frac{RT}{v}$, $\quad P \simeq \frac{1}{10}\frac{(RT)^2}{a} \simeq 12 \times 10^5 Pa \simeq 12\ atm$

3.5.4 Repeat parts (a), (b), e (c) do problema 3.4-5, assuming that $\eta = -1/2$ and that gas... [SUMÁRIO]

SOLUÇÃO:

Nós temos $u + \dfrac{a}{v} = cRT$ e $P = \dfrac{RT}{(v - b)} - \dfrac{a}{v^2}$

$$\therefore W = -\int_{V_0}^{V_1} P dV = -NR\int_{v_0}^{v_1}\frac{T dv}{v - b} + Na\int_{v_0}^{v_1}\frac{dv}{v^2} = -NRT_0\sqrt{v_0}\int_{v_0}^{v_1}\frac{v^{-1/2}}{v - b}dv - Na\left[\frac{1}{v_1} - \frac{1}{v_0}\right]$$

Para resolver esta integral, faça a mudança $\xi = v^{-1/2}$, o que resultará em

$$W = -\frac{NRT_0}{\sqrt{b/v_0}}\ \ln\left[\frac{1 - \sqrt{b/v_1}}{1 + \sqrt{b/v_1}}\frac{1 + \sqrt{b/v_0}}{1 - \sqrt{b/v_0}}\right] + \frac{Na}{v_0 v_1}(v_1 - v_0)$$

Também

$$\Delta U = N\Delta u = N\Delta\left(cRT - \frac{a}{v}\right) = NcR(T_1 - T_0) + \frac{Na}{v_0 v_1}(v_1 - v_0)$$

$$\therefore Q = \Delta U - W = NcR(T_1 - T_0) + NRT_0\sqrt{\frac{v_0}{b}}\ \ln\left[\frac{1 - \sqrt{b/v_1}}{1 + \sqrt{b/v_1}}\frac{1 + \sqrt{b/v_0}}{1 - \sqrt{b/v_0}}\right]$$

3.5.5 Consider a Van Der Waals gas contained in the apparatus described in Problem 3.4-1 ... [SUMÁRIO]

SOLUÇÃO:

NENHUMA SOLUÇÃO PARA ESSE PROBLEMA NO MOMENTO

3.5.6 One mole of a monoatomic ideal gas and one mole of Cl_2 are contained in a rigid cylinder and... [SUMÁRIO]

SOLUÇÃO:

As pressões e os volumes molares são iguais

$$\therefore \frac{RT}{v} = \frac{RT}{v - b} - \frac{a}{v^2}$$

$$\implies v = \frac{b}{1 - \dfrac{b}{a}RT} = 71,4 \times^{-6} m^3$$

$$\therefore \boxed{P = \frac{RT}{v} = 35 \times 10^6 Pa = 3,5 \times 10^7 Pa}$$

3.5.7 **(Supplementary problem) Suppose we wish to account (crudely) for a long-range repulsion of the molecules of a gas by adding a small temperature-independent term P_0 to the Van der Waals pressure (with $a = 0$):**

$$P = RT/(v - b) + P_0$$

What is the simplest amendment to the thermal equation of state $u = cRT$ consistent therewith? What is the corresponding fundamental equation ?
[SUMÁRIO]

SOLUÇÃO:

$$\frac{P}{T} = \frac{R}{v - b} + \frac{P_0}{T}$$

$$\therefore \frac{\partial}{\partial u}\left(\frac{P}{T}\right)_v = P_0 \frac{\partial}{\partial u}\left(\frac{1}{T}\right)_v$$

$$\therefore \frac{\partial}{\partial v}\left(\frac{1}{T}\right)_u = P_0 \frac{\partial}{\partial u}\left(\frac{1}{T}\right)_v$$

Se tomarmos por tentativa $\dfrac{1}{T} \overset{?}{=} \dfrac{cR}{u + \alpha v}$ (α é indeterminado)

Então, substituindo,

$$-\frac{cR\alpha}{(u + \alpha v)^2} \overset{?}{=} P_0\left[-\frac{cR}{(u + \alpha v)^2}\right]$$

Que é satisfeita para $\alpha = P_0$

$$\therefore \frac{1}{T} = \frac{cR}{u + P_0 v} \quad \text{ou} \quad \boxed{u = cRT - P_0 v}$$

Então $ds = \dfrac{1}{T}du + \dfrac{P}{T}dv$

$$= \frac{cR}{u + P_0 v}dv + \left(\frac{R}{v - b} + \frac{P_0 cR}{u + P_0 v}\right)dv$$

E então,

$$\boxed{s = s_0 + R\,ln[(u + P_0 v)^c(v - b)]}$$

3.6 ELECTROMAGNETIC RADIATION [SUMÁRIO]

3.6.1 The universe is considered by cosmologists to be an expanding electromagnetic cavity containing radiation... [SUMÁRIO]

SOLUÇÃO:

$$\frac{1}{T} = b^{1/4}(V/U)^{1/4} \quad \text{(equação 3.55-pg.79 do livro)}$$

$$S = \frac{4}{3}b^{1/4}U^{3/4}V^{1/4} \quad \text{(equação 3.57-pg.79 do livro)}$$

Eliminando U : $S = \frac{4}{3}bVT^3$

$$\text{Em } S \text{ constante,} \quad T \sim V^{-1/3}, \quad \text{ou} \quad T/T_0 = (V_0/V)^{1/3}$$

$$\text{Se } V = 2V_0, \quad T = T_0/2^{1/3} = 2,7/2^{1/3} \Longrightarrow \boxed{T = 2,1 \ K}$$

3.6.2 Assuming the electromagnetic radiation filling the universe to be in equilibrium at T = 2.7 K... [SUMÁRIO]

SOLUÇÃO:

$$P = \frac{1}{3}\frac{U}{V} \quad \text{e} \quad U = bVT^4, \quad b = 7,56 \times 10^{-16} J/m^3 K^4$$

$$\therefore \boxed{P = \frac{1}{3}bT^4 = 1,34 \times 10^{-14} Pa = 1,33 \times 10^{-19} \ atm}$$

3.6.3 The density of matter (primarily hydrogen atoms) in intergalactic space is such that... [SUMÁRIO]

SOLUÇÃO:

(a) $PV = NRT = \tilde{N}k_B T$ Onde $\tilde{N} \equiv$ nº de átomos

$$\therefore \boxed{\frac{\tilde{N}}{V} = \frac{P}{k_B T} = 10^{-23}/1,38 \times 10^{-23} \times 2,7 \sim 3 \text{ átomos}/m^3}$$

(a) $U = \frac{3}{2}PV$ para um gás, enquanto que $U = bVT^4$ para radiação.

$$\therefore \boxed{U_H/U_{rad} = \frac{\frac{3}{2}PV}{bVT^4} = 4 \times 10^{-26}}$$

(c) A energia cinética das partículas é desprezível se comparada a mc^2

$$\boxed{\frac{mc^2}{bT^4} = \frac{1,7 \times 10^{-27} \times (3 \times 10^8)^2}{7,6 \times 10^{-16} \times (2,7)^4} = 4 \times 10^3}$$

3.7   THE "RUBBER BAND"[SUMÁRIO]

3.7.1   For the rubber band model, calculate the fractional change in $(\mathbf{L} - \mathbf{L_0})$ that results from an increase $\delta\mathbf{T}$... [SUMÁRIO]

SOLUÇÃO:

$$\mathscr{T} = bT\frac{L - L_0}{L_1 - L_0}$$

$$\therefore \left(\frac{\partial L}{\partial T}\right)_{\mathscr{T}} = -\frac{1}{T}\frac{(L - L_0)(L_1 - L_0)}{L_1 - L_0} \quad \text{Ou ainda} \quad \boxed{\frac{1}{L - L_0}\left(\frac{\partial L}{\partial T}\right)_{\mathscr{T}} = -\frac{1}{T}}$$

3.7.2   A rubber band is stretched by an amount dL, at constant T. Calculate the heat transfer đQ... [SUMÁRIO]

SOLUÇÃO:

$$S = S_0 + cL \, \ln\left(\frac{U}{U_0}\right) - \frac{b}{2(L_1 - L_0)}(L - L_0)^2 \quad \text{(equação 3.62-pg. 81 do livro)}$$

e

$$U = cL_0 T \quad \text{(equação 3.58-pg. 80 do livro)}$$

$$\therefore S = S_0 + cL \, \ln\left(\frac{T}{T_0}\right) - \frac{b}{2(L_1 - L_0)}(L - L_0)^2$$

$$\therefore đQ = T\left(\frac{\partial S}{\partial L}\right)dL = -bT\frac{L - L_0}{L_1 - L_0}dL$$

$$\text{também} \quad \mathscr{T} = bT\frac{L - L_0}{L_1 - L_0}$$

$$\text{Então} \quad đW = \mathscr{T}dL = bT\frac{L - L_0}{L_1 - L_0}$$

Consequentemente vemos que

$$đQ + đW = 0$$

Isto é consistente com o fato de que U é uma função apenas da temperatura (e $dU=đQ+đW$)

3.7.3   If the energy of the unstretched rubber band were found to increase quadratically with T... [SUMÁRIO]

SOLUÇÃO:

$$U = cL_0 T^2 \quad \text{e novamente} \quad \mathscr{T} = bT(L - L_0)/(L_1 - L_0)$$

$$\frac{\partial}{\partial L}\left(\frac{1}{T}\right)_U = \frac{\partial}{\partial U}\left(-\frac{\mathscr{T}}{T}\right)_L$$

Então

$$dS = \frac{1}{T}dU - \frac{\mathscr{T}}{T}dL$$
$$= \left(\frac{cL_0}{U}\right)^{1/2}dU - b\frac{L-L_0}{L_1-L_0}dL$$
$$S - S_0 = 2(cL_0)^{1/2}U^{1/2} - \frac{b}{L_1-L_0}\left(\frac{1}{2}L^2 - LL_0\right)$$

Note que esta equação é uma equação homogênea de primeira ordem, assim como L_0 é extensivo. (L_0 pode ser visto como um análogo para N)

3.8 UNCONSTRAINABLE VARIABLES; MAGNETIC SYSTEMS
[SUMÁRIO]

3.8.1 Calculate the three equations of state of the paramagnetic model of equation 3.66. That is, calculate... [SUMÁRIO]

SOLUÇÃO:

$$U = NRT_0 \ \exp\left[\frac{S}{NR} + \frac{\mu_0}{2\chi_1 R}\frac{I^2}{N^2}\right]$$
$$T = \frac{\partial U}{\partial S} = \frac{U}{NR} \qquad B_e = \frac{\partial U}{\partial I} = \frac{\mu_0}{\chi_1 R}\frac{IU}{N^2}$$
$$\mu = \frac{\partial U}{\partial N} = \frac{U}{N}\left[1 - \frac{S}{NR} - \frac{\mu_0}{\chi_1 R}\frac{I^2}{N^2}\right]$$

Considere $TS + B_e I + \mu N$

$$\boxed{TS + B_e I + \mu N = \frac{U}{NR}S + \frac{\mu_0}{\chi_1 R}\frac{I^2 U}{N^2} + U\left[1 - \frac{S}{NR} - \frac{\mu_0}{\chi_1 R}\frac{I^2}{N^2}\right] = U}$$

3.8.2 Repeat problem 3.8-1 for a system with the fundamental equation $U = \mu_0 I^2/2N\chi + ...$ [SUMÁRIO]

SOLUÇÃO:

$$T = \frac{\partial U}{\partial S} = \frac{2\varepsilon}{k_B}\ \exp\left(\frac{2S}{Nk_B}\right) \quad , \quad B_e = \frac{\partial U}{\partial I} = \frac{\mu_0}{N\chi}I$$
$$\mu = \frac{\partial U}{\partial N} = -\frac{1}{2}\frac{\mu_0}{N\chi}I^2 + \varepsilon\ \exp\left(\frac{2S}{Nk_B}\right) - \frac{2S\varepsilon}{k_B N}\ \exp\left(\frac{2S}{Nk_B}\right)$$

Considere $TS + B_e I + \mu N$

$$TS + B_e I + \mu N = \frac{2\varepsilon S}{k_B} \exp\left(\frac{2S}{Nk_B}\right) + \frac{\mu_0 I^2}{N\chi} - \frac{1}{2}\frac{\mu_0}{N\chi}I^2 + \left(N\varepsilon - \frac{2S\varepsilon}{k_B}\right) \exp\left(\frac{2S}{Nk_B}\right)$$

$$= \frac{1}{2}\frac{\mu_0 I^2}{N\chi} + N\varepsilon \ \exp\left(\frac{2S}{Nk_B}\right)$$

$$\therefore \boxed{TS + B_e I + \mu N = U}$$

3.9 MOLAR HEAT CAPACITY AND OTHER DERIVATIVES [SUMÁRIO]

3.9.1 ... [SUMÁRIO]

$\boxed{\textbf{Solução:}}$

(a)
Relembre de

$$S = \sum_j N_j s_{j_0} + \sum_j N_j c_j R \ln\left(\frac{T}{T_0}\right) + \sum_j N_j R \ln\left(\frac{V}{N_j v_0}\right) \ ; \ U = \sum_j N_j c_j R T \ ; \ PV = NRT$$

Então

$$c_v = \frac{T}{N}\left(\frac{\partial S}{\partial T}\right)_v = \frac{T}{N}\sum_j \frac{N_j c_j}{T}R = R\bar{c} \qquad \Longrightarrow \boxed{c_v = R\bar{c}}$$

$$\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P = \frac{1}{V}\frac{NR}{P} = \frac{1}{T} \qquad \Longrightarrow \boxed{\alpha = 1/T}$$

$$\kappa_T = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T = -\frac{1}{V}\left(-\frac{NRT}{P^2}\right) = \frac{1}{P} \qquad \Longrightarrow \boxed{\kappa_T = 1/P}$$

Para calcular κ_S, escreva $S = \sum_j N_j s_{j_0} + N\bar{c}R \ \ln\left(\frac{PV}{N}\frac{N_0}{P_0 v_0}\right) + \sum_j N_j R \ \ln\frac{V}{N_j V_0}$, e então diferenciando com relação a P mantendo S constante, temos

$$\kappa_T = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_S$$

$$0 = \sum_j N_j c_j R\left[\frac{1}{P} + \frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_S\right] + \sum_j N_j R \frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_S$$

$$0 = \frac{N\bar{c}}{P} + N(\bar{c}+1)\kappa_S \ \ \text{ou} \ \ \boxed{\kappa_S = \frac{\bar{c}}{\bar{c}+1}\frac{1}{P}}$$

Para calcular c_p escreva $S = \sum_j N_j s_{j_0} + N\bar{c}R \ \ln\left(\frac{T}{T_0}\right) + \sum_j N_j R \ \ln\left(\frac{NRT}{PN_j V_0}\right)$

$$c_p = \frac{T}{N}\left(\frac{\partial S}{\partial T}\right)_P$$

$$c_p = \frac{T}{N}\left(\frac{\partial S}{\partial T}\right) = \frac{T}{N}\left(\frac{1}{T}\sum_j N_j c_j R + \frac{1}{T}\sum_j N_j R\right) \Longrightarrow \boxed{c_p = \bar{c}R + R = (\bar{c}+1)R}$$

(b)

$$\bar{c} = \frac{3}{2} \text{ para um gás ideal monoatômico}$$

3.9.2 Corroborate equation 3.70 for a multicomponent simple ideal gas, showing that both the right- and left-hand... [SUMÁRIO]

$\boxed{\textsc{Solução:}}$

escrevendo $U = T\bar{c}NR$;

$$S = \sum_j N_j s_{j_0} + (\sum_j N_j c_j)R \ \ln \frac{U}{Nu_0} + NR \ \ln \frac{V}{Nv_0} - R\sum_j N_j \ \ln \frac{N_j}{N}$$
$$= \sum_j N_j s_{j_0} + N\bar{c}R \ \ln \frac{T\bar{c}R}{u_0} + NR \ \ln \frac{V}{Nv_0} - R\sum_j N_j \ \ln \frac{N_j}{N}$$

Então, diferenciando com respeito a V mantendo S constante (e $N_1, N_2, ...$)

$$0 = 0 + \frac{N\bar{c}R}{T}\left(\frac{\partial T}{\partial V}\right)_S + \frac{NR}{V} \ \ \text{ou} \ \ \boxed{\left(\frac{\partial T}{\partial V}\right)_S = -\frac{1}{\bar{c}}\frac{1}{T}}$$

Também, a S constante,

$$U^{\bar{c}}V = const$$
$$\therefore P = -\left(\frac{\partial U}{\partial V}\right)_S = \frac{const}{\bar{c}}V^{-\frac{1}{\bar{c}}-1} = \frac{1}{\bar{c}}\frac{U}{V}$$
$$\left(\frac{\partial P}{\partial S}\right)_V = \frac{1}{\bar{c}}\frac{1}{V}\left(\frac{\partial U}{\partial S}\right)_V = \frac{T}{\bar{c}V}$$

Consequentemente

$$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V = -\frac{T}{\bar{c}V}$$

3.9.3 Compute the coefficient of expansion α and the isothermal compressibility $\kappa_{\mathbf{T}}$ in terms... [SUMÁRIO]

$\boxed{\textsc{Solução:}}$

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

Diferenciando com respeito a T, mantendo a pressão constante :

$$-\frac{2a}{v^2}(v-b)\alpha + \left(P + \frac{a}{v^2}\right)v\alpha = R$$

$$\alpha = \frac{Rv^2}{Pv^3 - av + 2ab}$$

Similarmente, diferenciando a equação de Van der Waals com respeito a P, com temperatura T constante,

$$\boxed{\kappa_T = \frac{v^2(v-b)}{Pv^3 - av + 2ab}}$$

3.9.4 Compute C_P, C_V, κ_S, e κ_T for the system in Problem 1.10-(a). With these values... [SUMÁRIO]

SOLUÇÃO:

$$S = D(UVN)^{1/3} \;\;,\;\; D \equiv \left(\frac{R^2}{v_0\theta}\right)^{1/3}$$

Nós encontramos

$$v = \frac{1}{3^3}D^3\frac{T^3}{P^2}$$
$$c_v = \frac{D^3}{2\times 3^2}\frac{T^2}{P}$$
$$c_p = \frac{2}{3^2}D^3\frac{T^2}{P}$$
$$\alpha = \frac{3}{T}$$
$$\kappa_T = \frac{2}{P}$$
$$\kappa_S = \frac{1}{2P}$$

E a equação de estado é $27P^2v = D^3T^3$ Então

$$\boxed{c_p - c_v = \frac{Tv\alpha^2}{\kappa_T} = \frac{1}{6}\frac{D^3T^2}{P}}$$

E

$$\boxed{\kappa_T - \kappa_S = \frac{Tv\alpha^2}{c_p} = \frac{3}{2P}}$$

3.9.5 From equations 3.75 and 3.76 show that $c_p/c_v = \kappa_T/\kappa_S$ [SUMÁRIO]

SOLUÇÃO:

$$c_p - c_v = \frac{Tv\alpha^2}{\kappa_T} \quad \text{(Equação 3.75)}$$

$$\kappa_T - \kappa_S = \frac{Tv\alpha^2}{c_p} \quad \text{(Equação 3.76)}$$

$$\frac{c_p - c_v}{\kappa_T - \kappa_S} = \frac{c_p}{\kappa_T}$$

$$1 - \frac{c_v}{c_p} = 1 - \frac{\kappa_S}{\kappa_T}$$

$$\therefore \boxed{\frac{\kappa_S}{\kappa_T} = \frac{c_v}{c_p}}$$

3.9.6   A simple fundamental equation that exhibits some of the qualitative properties of typical crystaline solids... [SUMÁRIO]

SOLUÇÃO:

(a) $T = \dfrac{\partial u}{\partial s} = A e^{b(v-v_0)^2} \left[\dfrac{4}{3} s^{1/3} + \dfrac{1}{3k_B} s^{4/3} \right] e^{s/3k_B} \to 0$ quando $s \to 0$

(b) $c_v = T \left(\dfrac{\partial s}{\partial T} \right)_v = \dfrac{\left(\dfrac{4}{3} s + \dfrac{1}{3k_B} s^2 \right)}{\left(\dfrac{4}{9} + \dfrac{8}{9k_B} s + \dfrac{1}{9k_B^2} s^2 \right)} \to 0$ quando $s \to 0$

Mas $T \sim s^3$ para s pequeno, portanto $c_v \sim T^3$ para T pequeno

(c) De **(b)**, $c_v = T \left(\dfrac{\partial s}{\partial T} \right)_v = \dfrac{\left(\dfrac{4}{3} s + \dfrac{1}{3k_B} s^2 \right)}{\left(\dfrac{4}{9} + \dfrac{8}{9k_B} s + \dfrac{1}{9k_B^2} s^2 \right)}$

E mantendo apenas termos em s^2 (para s ou T grandes), $\boxed{c_v \to 3k_B}$

(d) $P = -\left(\dfrac{\partial u}{\partial v} \right)_s = -2b(v - v_0)u$

$$\therefore \text{Se} \quad P = 0, \ v = v_0, \ a = const \ \ \text{e} \quad \alpha = 0$$

(OBSERVAÇÃO) Note que se quisermos calcular α explicitamente, então

$$(v\alpha)^{-1} = \left(\frac{\partial T}{\partial v} \right)_P$$

faça $T = T(s, v)$ e então $dT = u_{ss} ds + u_{sv} dv$

e $(v\alpha)^{-1} = \left(\dfrac{\partial T}{\partial v} \right)_P = u_{ss} \left(\dfrac{\partial s}{\partial v} \right)_P + u_{sv} = u_{ss} \left[-\dfrac{u_{vv}}{u_{sv}} \right] + u_{sv}$

Ou $v\alpha = \dfrac{u_{sv}}{[u_{sv}^2 - u_{ss} u_{vv}]}$ que é facilmente calculada

---

3.9.7 The density of mercury at various temperatures is given here in grams/cm³... [SUMÁRIO]

Solução:

$$\rho = \frac{M}{V} \Longrightarrow d\rho = -\frac{M}{V^2}dV \Longrightarrow d\rho = -\frac{\rho}{V}dV$$

Ou

$$\frac{d\rho}{\rho} = -\frac{dV}{V}$$

e

$$\alpha = -\frac{1}{V}\frac{dV}{dT} = \frac{1}{\rho}\frac{d\rho}{dT}$$

Interpolando a partir dos dados fornecidos

$$\begin{aligned}
\alpha &= 0,000182 \ K^{-1} \text{ a } 0\text{°C} \\
&= 0,000181 \ K^{-1} \text{ a } 45\text{°C} \\
&= 0,000179 \ K^{-1} \text{ a } 105\text{°C} \\
&= 0,000182 \ K^{-1} \text{ a } 305\text{°C}
\end{aligned}$$

$\alpha = \frac{AdL}{ALdT}$ Onde A é a área transversal (cross-sectional area) e L é o comprimento da coluna de Hg.

$$\therefore dL = \alpha L dT$$

$$\therefore \frac{dL}{L} \ \text{ deve ser proporcional a } \alpha \text{ se } dT \text{ for constante}$$

3.9.8 For a particular material C_P, α, e κ_T can be represented empirically by power series... [SUMÁRIO]

Solução:

Do exemplo na página 86-87

$$\ln\frac{v'}{v_0} = \int_{T_0}^{T'} \alpha(T, P_0)dT - \int_{P_0}^{P} \kappa_T(T', P)dP$$

Mas se $\tau = T - T_0$

$$\int_{T_0}^{T'} \alpha(T, P_0)dT = \int_0^{T'-T_0} \alpha(\tau, p)d\tau = \alpha^0\tau' + \frac{1}{2}A_\alpha\tau'^2 + \frac{1}{3}B_\alpha\tau'^3 + E_\alpha p_0^2\tau' + \frac{1}{2}F_\alpha\tau'^2 p_0$$

$$\int_{P_0}^{P'} \kappa_T(T', P)dP = \int_0^{p'} \kappa_T(T', p)dp = \kappa_T^0 p' + (A_\kappa\tau' + B_\kappa\tau'^2)p' + \frac{1}{2}D_\kappa p'^2 + \frac{1}{3}E_\kappa p'^3 + \frac{1}{2}F_\kappa p'^2$$

O que dá então o resultado pretendido.

3.9.9 Calculate the molar entropy $s(T, P_0)$ for fixed pressure P_0 and for temperature T in the vicinity of...

SOLUÇÃO:

$$ds = \frac{c_p}{T}dT$$

Mas para $p = P - P_0 = 0$ temos, como no problema anterior,

$$c_p = c_p^0 + A_c\tau + B_c\tau^2$$

ou

$$ds = \frac{c_p^0 + A_c\tau + B_c\tau^2}{T_0 + \tau}d\tau$$

Para τ/τ_0 pequeno,

$$ds = [c_p^0 + A_c\tau + B_c\tau^2]\frac{1}{T_0}[1 - \frac{\tau}{T_0} + \frac{\tau^2}{T_0^2} + ...]d\tau$$

$$= \frac{1}{T_0}\left[c_p^0 + \left(A_c - \frac{c_p^0}{T_0}\right)\tau + \left(B_c - \frac{A_c}{T_0} + \frac{c_p^0}{T_0^2}\right)\tau^2 + ...\right]d\tau$$

$$\therefore \boxed{s - s_0 = \frac{c_p^0}{T_0}\tau + \frac{1}{2T_0}\left(A_c - \frac{c_p^0}{T_0}\right)\tau^2 + \frac{1}{3T_0}\left(B_c - \frac{A_c}{T_0} + \frac{c_p^0}{T_0^2}\right)\tau^3 + ...}$$

3.9.10 By analogy with equations 3.70 and 3.71 show that for a paramagnetic system

$$\left(\frac{\partial B_e}{\partial S}\right)_{I,V,N} = \left(\frac{\partial T}{\partial I}\right)_{S,V,N}$$

Or inverting

$$T\left(\frac{\partial S}{\partial B_e}\right)_{I,V,N} = T\left(\frac{\partial I}{\partial T}\right)_{S,V,N}$$

SOLUÇÃO:

$$U = U(S, V, I, N)$$

$$\frac{\partial^2 U}{\partial S \partial I} = \frac{\partial^2 U}{\partial I \partial S} \quad \text{Ou} \quad \left(\frac{\partial B_e}{\partial S}\right)_{I,V,N} = \left(\frac{\partial T}{\partial I}\right)_{S,V,N}$$

Invertendo,

$$T\left(\frac{\partial S}{\partial B_e}\right)_{I,V,N} = T\left(\frac{\partial I}{\partial T}\right)_{S,V,N}$$

Ou

$$\left(\frac{đQ}{dB_e}\right)_{I,V,N} = T\left(\frac{\partial I}{\partial T}\right)_{S,V,N}$$

A quantidade de energia absorvida na forma de calor por unidade com a variação em B_e, a I constante, é igual à variação adiabática em I por unidade com a variação em T

3.9.11 **By analogy with equations 3.70 and 3.71 show that for a paramagnetic system**

$$\left(\frac{\partial B_e}{\partial V}\right)_{S,I,N} = -\left(\frac{\partial P}{\partial I}\right)_{S,V,N}$$

Solução:

$$\boxed{\frac{\partial^2 U}{\partial V \partial I} = \frac{\partial^2 U}{\partial I \partial V} \implies \left(\frac{\partial B_e}{\partial V}\right)_{S,I,N} = -\left(\frac{\partial P}{\partial I}\right)_{S,V,N}}$$

3.9.12 **The magnetic analogues of the molar heat capacities C_P and C_v are C_B and C_I. Calculate...**

Solução:

$$U = NRT_0 \ \exp\left[\frac{S}{NR} + \frac{\mu_0}{2\chi_0 R}\frac{I^2}{N^2}\right] \quad \therefore U = NRT \ \text{ e } \ I = \frac{N\chi_0}{\mu_0 T}B_e$$

Então

$$S = NR \ \ln\left(\frac{U}{NRT_0}\right) - \frac{\mu_0}{2\chi_0}\frac{I^2}{N}$$

$$c_I = \frac{T}{N}\left(\frac{\partial S}{\partial T}\right)_I = \frac{T}{N}\frac{\partial}{\partial T}\left[NR \ \ln\frac{T}{T_0}\right] = R$$

analogamente, escrevemos

$$S = NR \ ln\frac{T}{T_0} + \frac{1}{2\chi_0 N\mu_0}\frac{B^2}{T^2}$$

$$c_{B_e} = \frac{T}{N}\left(\frac{\partial S}{\partial T}\right)_{B_e} = R + \frac{\chi_0}{\mu_0}\frac{B_e^2}{T^2}$$

3.9.13 **The (isothermal) molar magnetic susceptibility is defined by**

$$\chi \equiv \frac{\mu_0}{N}\left(\frac{\partial I}{\partial B_e}\right)_T$$

Solução:

$$U = NRT_0 \ \exp\left[\frac{S}{NR} + \frac{\mu_0}{2\chi_1 R}\frac{I^2}{N^2}\right]$$

$$\therefore B_e = \frac{\partial U}{\partial I} = \frac{\mu_0}{\chi_1 R}\frac{UI}{N^2} \ \text{ e } \ T = \frac{\partial U}{\partial S} = \frac{U}{NR}$$

$$\therefore B_e = \frac{\mu_0}{\chi_1}T\frac{I}{N} \ \text{ ou } \ I = N\frac{\chi_1}{\mu_0}\frac{B_e}{T} \ \text{ e } \ \chi = \frac{\mu_0}{N}\left(\frac{\partial I}{\partial B_e}\right)_T = \frac{\chi_1}{T}$$

3.9.14   Calculate the adiabatic molar susceptibility

$$\chi_s \equiv \frac{\mu_0}{N} \left(\frac{\partial I}{\partial B_e} \right)_S$$

as a function of T and B_e for the paramagnetic model of equation 3.66 [SUMÁRIO]

SOLUÇÃO:

$$U = NRT_0 \ \exp\left[\frac{S}{NR} + \frac{\mu_0}{2\chi_1 R} \frac{I^2}{N^2} \right]$$

E as equações de estado são

$$T = \frac{U}{NR} \quad , \quad I = \frac{N\chi_1}{T} \frac{B_e}{\mu_0}$$

$$\therefore B_e = \frac{\mu_0 I T}{N\chi_1} = \frac{\mu_0 I}{N\chi_1} \frac{U}{NR} = \frac{\mu_0 I T}{N\chi_1} T_0 \ \exp\left[\frac{S}{NR} + \frac{\mu_0}{2\chi_1 R} \frac{I^2}{N^2} \right]$$

$$\frac{1}{\mu_0} \left(\frac{\partial B_e}{\partial I} \right)_S = \left[\frac{T_0}{N\chi_1} + \frac{IT_0}{N\chi_1} \left(\frac{\mu_0 I}{\chi_1 RN^2} \right) \right] \exp\left[\frac{S}{NR} + \frac{\mu_0}{2\chi_1 R} \frac{I^2}{N^2} \right]$$

$$= \frac{T}{N\chi_1} + \frac{\mu_0 I^2}{N^3 \chi_1^2 R} T$$

$$= \frac{T}{N\chi_1} + \frac{B_e^2}{\mu_0 NRT}$$

$$\therefore \boxed{\chi_s = \frac{\mu_0}{N} \left(\frac{\partial I}{\partial B_e} \right)_S = \frac{\chi_1 RT}{RT^2 + \chi_1 B_e^2/\mu_0} = \frac{\chi_1}{T + \chi_1 B_e^2/\mu_0 RT}}$$

3.9.15   Calculate the isothermal and adiabatic molar susceptibilities (defined in Problem 3.9-13 and 3.9-14)... [SUMÁRIO]

SOLUÇÃO:

$$B_e = \left(\frac{\partial U}{\partial I} \right)_S = \frac{\mu_0 I}{N\chi} \quad \text{E também} \quad T = \left(\frac{\partial U}{\partial S} \right)_I = \frac{2\varepsilon}{k_B} e^{2s/Nk_B}$$

Portanto, S constante implica em T constante !

$$\chi_s = \chi_T = \frac{\mu_0}{N} \frac{\partial I}{\partial B_e} = \chi$$

3.9.16   Show that for the system of Problem 3.8-2... [SUMÁRIO]

SOLUÇÃO:

$$U = \frac{\mu_0}{2N\chi} I^2 + N\varepsilon \ \exp\left(\frac{2S}{Nk_B} \right)$$

$$\therefore B_e = \left(\frac{\partial U}{\partial I}\right)_S = \frac{\mu_0}{N\chi}I \quad \text{e} \quad T = \frac{\partial U}{\partial S} = \frac{2\varepsilon}{k_B}\exp\left(\frac{2S}{Nk_B}\right)$$

A separação das variáveis magnéticas e das variáveis térmicas em termos diferentes na equação fundamental leva ao desaparecimento de "termos cruzados".

3.9.17 Calculate the heat transfer to a particular system if 1 mole is taken from $(\mathbf{T_0}, \mathbf{P_0})$ to $(\mathbf{2T_0}, \mathbf{2P_0})$... [SUMÁRIO]

> **Solução:**

$$đQ = Tds = T\left(\frac{\partial s}{\partial T}\right)_P dT + T\left(\frac{\partial s}{\partial P}\right)_T dP = c_p dT - Tv\alpha dP$$

Ao longo do caminho $P = (P_0/T_0)T$ e portanto $dP = (P_0/T_0)dT$

$$\therefore đQ = c_p dT - Tv\alpha\left(\frac{P_0}{T_0}\right)dT = \left[c_p - \frac{P_0}{T_0}\alpha Tv\right]dT$$

$$\text{Entretanto} \quad dv = \left(\frac{\partial v}{\partial T}\right)_P dT + \left(\frac{\partial v}{\partial P}\right)_T dP = v\alpha dT - v\kappa_T dP$$

$$\therefore \frac{dv}{v} = \left[\alpha - \kappa_T\frac{P_0}{T_0}\right]dT \quad \text{e} \quad v = v_0 e^{[\alpha - \kappa_T P_0/T_0](T-T_0)}$$

$$đQ = c_p - \frac{P_0}{T_0}\alpha T e^{[\alpha - \kappa_T P_0/T_0](T-T_0)}$$

$$Q = c_p T_0 - P_0\alpha T_0 e^{(\kappa_T P_0 - \alpha T_0)}\int_1^2 xe^{Bx}dx \quad , \quad \text{onde} \quad x \equiv T/T_0, \quad \text{e} \quad B \equiv \alpha T_0 - \kappa_T P_0$$

Integrando por partes ($e^{Bx}dx \to dv$ e $x \to u$),

$$Q = c_p T_0 - P_0\alpha T_0 e^{\kappa_T P_0 - \alpha T_0}\left[\frac{Bx-1}{B^2}e^{Bx}\right]_{x=1}^{x=2}$$

$$\therefore \boxed{Q = c_p T_0 - P_0\alpha T_0 e^{\kappa_T P_0 - \alpha T_0}\left[\frac{2B-1}{B^2}e^{2B} - \frac{B-1}{B}e^B\right]}$$

3.9.18 (Supplementary Problem) A particular substance is known to have $\alpha = \mathbf{5/(4T)}$, $\kappa_T = \mathbf{2/(P+P_0)}$, and $\mathbf{c_p = AT^{\frac{1}{4}}/(P+P_0)}$. It is also specified that at $\mathbf{T = T_0}$ and $\mathbf{P = P_0}$ the value of v is $\mathbf{v_0 = 4AT_0/(5P_0^2)}$ and the value of s is $\mathbf{s_0 = 2AT_0^{\frac{1}{4}}/P_0}$. Calculate the fundamental equation of one mole of this substance. [SUMÁRIO]

> **Solução:**

Nós procuramos $\mu(T, P) \equiv G(T, P, N)/N$ Para esta substância, e $d\mu = -sdT + vdP$. Consequentemente queremos encontrar $s(T, P)$ e $v(T, P)$.
Mas

$$ds = \frac{1}{T}c_p dT - v\alpha dP = AT^{-3/4}(P+P_0)^{-1}dT - \frac{5v}{4T}dP$$

e

$$\frac{dv}{v} = -\kappa_T dP + \alpha dT = -\frac{2}{(P + P_0)}dP + \frac{5}{4T}dT$$

Ou

$$\frac{v}{v_0} = \left(\frac{T}{T_0}\right)^{5/4}\left(\frac{2P_0}{P + P_0}\right)^2$$

Voltando para ds:

$$ds = \frac{AT^{-3/4}}{(P + P_0)}dT - \frac{4AT^{1/4}}{(P + P_0)^2}dP$$

e

$$s = \frac{4AT^{1/4}}{P + P_0} \quad \text{(recorde a condição de contorno dada)}$$

Então

$$\boxed{d\mu = -sdT + vdP = -\frac{4AT^{1/4}}{P + P_0}dT + \frac{16A}{5}\frac{T^{5/4}}{(P + P_0)^2}dP}$$

e

$$\boxed{\mu = -\frac{16AT^{5/4}}{5(P + P_0)}}$$

Ou

$$\boxed{G = -\frac{16ANT^{5/4}}{5(P + P_0)}}$$

4 REVERSIBLE PROCESSES AND THE MAXIMUM WORK THEOREM [SUMÁRIO]

4.1 POSSIBLE AND IMPOSSIBLE PROCESSES [SUMÁRIO]

4.1.1 One mole of a monatomic ideal gas and one mole of an idela Van der Waals fluid (Section 3.5) ... [SUMÁRIO]

SOLUÇÃO:

Para um gás ideal $u = \frac{3}{2}RT$ $\qquad$ Para um flúido de Van der Waals $u = \frac{3}{2}RT - \frac{a}{v}$

$$\therefore \frac{3}{2}RT_1 + \left(\frac{3}{2}RT_2 - \frac{a}{v_2}\right) = \frac{3}{2}RT_2 + \left(\frac{3}{2}RT - \frac{a}{v_1}\right)$$

$$\therefore \boxed{T = T_1 + \frac{2a}{3R}\left[\frac{1}{v_1} - \frac{1}{v_2}\right]}$$

$$S_i \leq S_f$$

$$\ln[T_1^{3/2}v_1] + \ln[T_2^{3/2}(v_2 - b)] \leq \ln[T_2^{3/2}v_2] + \ln[T^{3/2}(v_1 - b)]$$

$$\therefore v_2 T^{3/2}(v_1 - b) \geq v_1 T_1^{3/2}(v_2 - b)$$

$$T \geq T_1\left[\frac{v_1(v_2 - b)}{v_2(v_1 - b)}\right]^{2/3}$$

$$\therefore \boxed{T_1 + \frac{2a}{3R}\left[\frac{1}{v_1} - \frac{1}{v_2}\right] \geq T_1 \left[\frac{v_1(v_2 - b)}{v_2(v_1 - b)}\right]^{2/3}}$$

Ou equivalentemente,

$$\boxed{T_1 > \frac{2a}{3R}\frac{v_1 - v_2}{v_1 v_2}\left[1 - \frac{v_1(v_2 - b)}{v_2(v_1 - b)}\right]^{-2/3}}$$

4.1.2 A rubber band (Section 3.7) is initially at temperature T_B and length L_B. One mole of a monatomic ideal gas ... [SUMÁRIO]

SOLUÇÃO:

Para um gás $\Delta U = \frac{3}{2}R\left(T'_G - T_G\right)$, $\Delta S = \frac{3}{2}NR\ln\left(T'_G/T_G\right)$
Para o elástico de borracha (rubber band) :

$$\Delta U = cL_0\left(T'_B - T_B\right) \quad , \Delta S = cL_0\ln T'_B/T_B - \frac{b}{2\left(L_1 - L_0\right)}\left\{\left(L'_B - L_0\right)^2 - \left(L_B - L_0\right)^2\right\}$$

Conservação da energia : $\frac{3}{2}R\left(T'_G - T_G\right) + cL_0\left(T'_B - T_B\right) = 0 \quad ou \quad T'_B/T_B = 1 - \frac{3R}{2}\frac{T'_G - T_0}{T_B}$

e ainda $\Delta S = cL_0\ln\left[1 - \frac{3R}{2cL_0}\frac{T'_G - T_G}{T_B}\right] - \frac{b}{2\left(L_1 - L_0\right)}\left\{\left(L'_B - L_0\right)^2 - \left(L_B - L_0\right)^2\right\} > 0$

Ou fazendo $L_B - L_0 \equiv \ell$

$$\boxed{\ell^2 - \ell'^2 \geqslant \frac{2}{b}\left(L_1 - L_0\right)cL_0\ln\left[1 - \frac{3R}{2cL_0}\frac{T'_G - T_0}{T_B}\right]^{-1}}$$

4.1.3 Supose the two systems in Example 1 were to have heat capacities of the form $C(T) = DT^n$, with $n > 0$ ... [SUMÁRIO]

SOLUÇÃO:

$$\frac{D}{n+1}\left[T_{10}^{n+1} + T_{20}^{n+1}\right] = \frac{2D}{n+1}T_f^{n+1} + W$$

$$e \quad \frac{1}{2}\left[T_{10}^{n+1} + T_{20}^{n+1}\right] = T_f^n$$

$$\therefore \boxed{W = \frac{D}{n+1}\left[T_{10}^{n+1} + T_{20}^{n+1} - \frac{1}{2^{1/n}}\left(T_{10}^n + T_{20}^n\right)^{\frac{n+1}{n}}\right] \quad , n = 2}$$

4.2 QUASI-STATIC AND REVERSIBLE PROCESSES

4.2.1 Does every reversible process coincide with a quasi-static locus? Does every quasi-static locus coincide with a reversible process ? ...

$\boxed{\text{SOLUÇÃO:}}$

- Does every reversible process coincide with a quasi-static locus ?
  Resposta: Sim, por definição.

- Does every quasi-static locus coincide with a reversible process ?
  Resposta: Não. Coincide só se o locus quasi-stático é isentrópico.

- For any real process starting in a state A nad terminating in a state H, does there exist some quasi-static locus with the same two terminal states A and H ?
  Resposta: Sim. existe um número infinito de tais locus.

- Does there exist some reversible process with the same two terminal states ?
  Resposta: Geralmente não - Só se o processo real é reversível.

4.2.2 Consider a monatomic ideal gas in a cylinder fitted with a piston. The walls of the cylinder and the piston are adiabatic. ...

$\boxed{\text{SOLUÇÃO:}}$

$$S = Ns_0 + NR\ln\left[\left(\frac{U}{U_0}\right)^{3/2}\frac{V}{V_0}\left(\frac{N_0}{N}\right)^{5/2}\right]$$

$$\therefore \delta S = \frac{3}{2}NR\frac{\delta U}{U} + NR\frac{\delta V}{V}$$

$$\text{mas } \delta U = -P\delta V$$

$$\therefore \delta S = -\frac{3}{2}NRP\frac{\delta V}{U} + NR\frac{\delta V}{V}$$

$$\text{mas } U = \frac{3}{2}PV \quad \text{ou} \quad \frac{3}{2}\frac{P}{U} = \frac{1}{V}$$

$$\therefore \boxed{\delta S = 0}$$

4.2.3 A monatomic ideal gas is permitted to expand by a free expansion from V to V + dV ...

$\boxed{\text{SOLUÇÃO:}}$

$$\delta s = \frac{1}{T}\delta U + \frac{P}{T}\delta V = \frac{NR}{V}\delta V$$

E integrando temos que $\boxed{S = NR\ln\left(\dfrac{V_f}{V_i}\right)}$

4.2.4 In the temperature range of interest a system obeys the equations $\mathbf{T = Av^2/s}$ and $\mathbf{P = -2Av\ln(s/s_0)}$ ... [SUMÁRIO]

SOLUÇÃO:

$$\delta u = T\delta s - P\delta v = A\left[\frac{v^2}{s}\delta s + 2v\ln s \,\delta v\right]$$

$$\therefore u = u_0 + Av^2\ln s \qquad (eq.\,fundamental)$$

Então

$$u = Av^2\ln(Av^2/T) + u_0$$

E a u constante

$$(Av^2/T)^{v^2} = const.$$

ou

$$T_f = Av_f^2\left(\frac{T_0}{Av_0^2}\right)^{(v_0/v_f)^2}$$

Também,

$$s = Av^2/T$$

$$\Delta s = A\left[\frac{v_f^2}{T_f} - \frac{v_0^2}{T_0}\right]$$

Com o T_f como dado acima.

4.3 RELAXATION TIMES AND IRREVERSIBILITY [SUMÁRIO]

4.3.1 A cylinder of length L and cross-sectional area A is divided into two equal-volume chambers by a piston, held at ... [SUMÁRIO]

SOLUÇÃO:

Conservação da energia: $\dfrac{3}{2}NRT_0 = \dfrac{3}{2}NRT_f + \dfrac{1}{2}K_{spring}(x - L/2)^2$

Equilíbrio mecânico: $PA = K_{spring}(x - L/2)$

Eq. de estado: $PV = NRT_f$ ou $P\left(\dfrac{L}{2} + x\right)A = NRT_f$

Das últimas duas equações, $\dfrac{L}{2} + x = NRT_f/K_{spring}(x - L/2)$

Ou ainda

$$\frac{3}{2}NRT_0 = \frac{3}{2}K_{spring}\left(x^2 - \frac{L^2}{4}\right) + \frac{1}{2}K_{spring}(x - L/2)^2$$

$$\therefore \frac{x}{L} = \frac{1}{8}\left[1 \pm \sqrt{9 + 48NRT_0/K_{spring}L^2}\right]$$

Então
$$V = A\left[\frac{L}{2} + x\right] = \frac{AL}{2}\left[1 + 2\frac{x}{L}\right]$$

E
$$T_f = T_0 - \frac{L^2}{3NR}\left(x - \frac{L}{2}\right)^2 = T_0 - \frac{k_{spring}L^2}{12NR}\left(2\frac{x}{L} - 1\right)^2$$

4.4 HEAT FLOW: COUPLED SYSTEMS AND REVERSAL OF PROCESSES [SUMÁRIO]

4.4.1 Each of two bodies has a heat capacity given, in the temperature range of interest, by C = A + BT ... [SUMÁRIO]

Tome energia=0 em $T = 200K$. Então
$$U = \int_{200}^{\top}(A + BT)dT = 10^{-2}T^2 + 8T - 2000$$
$$\therefore U_i = 1600 + 3200 - 2000 = 2800J\,(= U_f)$$

Faça $\tau = 10^{-2}T$. Então
$$U_f = U_i = 2\left[10^{-2}T^2 + 8T - 20 \times 10^2\right] = 2800$$

Ou
$$\tau^2 + 8\tau - 34 = 0$$
$$\therefore T = 307K$$

Também, para cada corpo,
$$S(T) = S(200) + \int_{200}^{T}\frac{A + BT}{T}dt = S(200) + A\ln\frac{T}{200} + B(T - 200)$$

$$\therefore S_{\text{inicial}} = S(200) + S(400) = 2S(200) + 8\ln 2 + 2 \times 10^{-2} \times 200 = 2S(200) + 9,55$$
$$S_{\text{final}} = 2\left[S(200) + 8\ln\frac{307}{200} + 2 \times 10^{-2} \times 107\right] = 2S(200) + 11.4$$
$$\therefore \boxed{\Delta S = 1.59 \text{ J/K}}$$

4.4.2 Consider again the system of Problem 4.4-1. LEt a third body be available, with heat capacity C₃ = BT ... [SUMÁRIO]

$$U_3 = \int_{20}^{T}BTdT = \frac{1}{2}B\left(T^2 - 4 \times 10^4\right) = 10^{-2}T^2 - 400$$

$$S_3 = \int_{200}^{T} B\, dT = B(T - 200) = 2 \times 10^{-2} T - 4$$

$$\Delta U_3 + \Delta U_2 = 0$$

$$10^{-2}\left(200^2 - T_{30}^2\right) + \left[10^{-2} \times 307^2 + 8 \times 307 - 20 \times 10^2\right] - \left[10^{-2} \times 200^2 + 8 \times 200 - 20 \times 10^2\right] = 0$$

$$\boxed{T_{30} = 424K}$$

$$\Delta S_2 = A \ln \frac{T_f}{T_i} + B\left(T_f - T_i\right) = 8 \ln \frac{424}{307} + 2 \times 10^{-2}(424 - 307)$$

$$\boxed{\Delta S_2 = 4.9 J/K}$$

4.4.3 Prove that the entropy change in a heat flow process, as given in equation 4.5, is intrinsically positive. [SUMÁRIO]

SOLUÇÃO:

$$\Delta s = c_1 \ln \frac{T_f}{T_{10}} + c_2 \ln \frac{T_f}{T_{20}} \quad (eq.4.5)$$

$$\therefore \Delta S > 0 \text{ se } \left(\frac{T_f}{T_{10}}\right)^{c_1}\left(\frac{T_f}{T_{20}}\right)^{c_2} > 0$$

Ou se

$$T_f > T_{10}^{\frac{c_1}{c_1 + c_2}} T_{20}^{\frac{c_2}{c_1 + 2_2}}$$

Mas

$$T_f = \frac{c_1}{c_1 + c_2} T_{10} + \frac{c_2}{c_1 + c_2} T_{20}$$

Faça $x \equiv \dfrac{c_1}{c_1 + c_2}$ e faça $Z \equiv T_{10}/T_{20}$ (note que $0 \le Z \le 1$)

Devemos provar que:
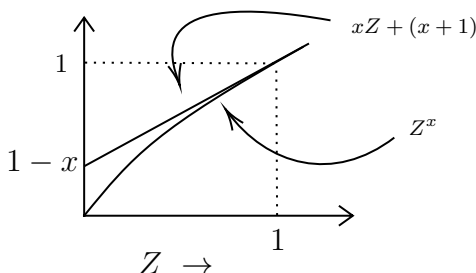
$$xZ + (1 - x) > Z^x, \quad 0 < x < 1, \quad 0 < Z < 1$$

Note que para $x = 1$, ambos os lados são idênticos. A razão das inclinações dessas curvas é:

$$\frac{\text{inclinação de } Z^x}{\text{inclinação de } xZ + (1 - x)} = \frac{xZ^{x-1}}{x} = Z^{x-1} > 1$$

Consequentemente

$$[xZ + (1 - x)] > Z^x \text{ para } 0 < x < 1 \text{ e } 0 < Z < 1$$

4.4.4 Show that if two bodies have equal heat capacities, eqach of which is constant (independent of temperature), the equilibrium temperature ... [SUMÁRIO]

SOLUÇÃO:

$$U = U_0 + c\left(T - T_0\right) \quad \text{Para cada corpo}$$

$$U_f = U_{10} + U_{20}$$

$$\therefore \quad 2\,\cancel{U_0} + 2C\left(T_f - \cancel{T_0}\right) = 2\,\cancel{U_0} + C\left(T_{10} - \cancel{T_0}\right) + C\left(T_{20} - \cancel{T_0}\right)$$

$$T_f = \tfrac{1}{2}\left(T_{10} + T_{20}\right)$$

4.4.5 Over a limited temperature range the heat capacity at constant volume of a particular type of system is inversely proportional... [SUMÁRIO]

SOLUÇÃO:

$$U\left(T_{10}\right) + U\left(T_{20}\right) = 2U\left(\sqrt{T_{10}T_{20}}\right)$$

A solução dessa relação funcional é:

$$U(T) = A + B\ln T$$
$$\therefore C(T) = \frac{dU}{dT} = \frac{B}{T}$$

4.4.6 A series of $N+1$ large vats of water have temperatures $\mathbf{T_0, T_1, T_2, ..., T_N}$ (with $\mathbf{T_n > T_{n-1}}$). A small body with heat capacity C ... [SUMÁRIO]

SOLUÇÃO:

a)

$$\Delta S_{body}^{(n)} = C\int_{T_{n-1}}^{T_n}\frac{dT}{T} = c\ln\frac{T_n}{T_{n-1}} = \frac{C}{N}\ln\left(T_N/T_0\right)$$

$$\Delta S_{vat}^{(n)} = C\frac{T_{n-1}-T_n}{T_n} = C\left[\left(T_N/T_0\right)^{-1/N}-1\right]$$

$$\therefore \Delta S_{up} = C\ln\frac{T_N}{T_0} + NC\left(T_N/T_0\right)^{-1/N} - NC$$

b)

$$\Delta S_{body}^{(n)} = -\frac{C}{N}\ln\left(T_N/T_0\right)$$

$$\Delta S_{vat}^{(n)} = C\frac{T_n-T_{n-1}}{T_{n-1}} = C\left[\left(\frac{T_N}{T_0}\right)^{1/N}-1\right]$$

$$\therefore \Delta S_{down} = -C\ln\frac{T_N}{T_0} + NC\left(\frac{T_N}{T_0}\right)^{1/N} - NC$$

Então

$$\Delta S = \Delta S_{up} + \Delta S_{down} = NC\left[\left(\frac{T_N}{T_0}\right)^{1/N} + \left(\frac{T_0}{T_N}\right)^{1/N} - 2C\right]$$

Para $N \to \infty$ nós aplicamos a relação $N\left(x^{1/N}-1\right) \simeq \ln x + \frac{1}{2N}(\ln x)^2 + \cdots$

$$\therefore \Delta S \simeq C\left[\ln \frac{T_N}{T_0} + \frac{1}{2N}\left(\ln \frac{T_N}{T_0}\right)^2 + \cdots + \ln \frac{T_0}{T_N} + \frac{1}{2N}\left(\ln \frac{T_0}{T_N}\right)^2 + \cdots\right]$$
$$\simeq \frac{C}{N}\left(\ln \frac{T_N}{T_0}\right)^2$$

4.5 THE MAXIMUM WORK THEOREM [SUMÁRIO]

4.5.1 One mole of a monatomic ideal gas is contained in a cylinder of volume 10^{-3}m^3 at temperature of 400 K ... [SUMÁRIO]

SOLUÇÃO:

$$U = \frac{3}{2}RT \text{ e } S = S_0 + R\ln\left[\left(\frac{T}{T_0}\right)^{3/2}\frac{V}{V_0}\right]$$

$\therefore S$ aumenta, mas U permanece constante, para um gás.

$$\Delta S_{\text{gas}} + \Delta S_{\text{res}} = R\ln\left(\frac{V_f}{V_i}\right) + \Delta S_{\text{res}} = 0$$
$$\therefore \Delta S_{res} = -R\ln 2$$

Conservação da energia:

$$\Delta U_{gas} + \Delta U_{res} + W_{\text{Rws}} = 0 + T_{res}\Delta S_{\text{res}} + W_{\text{Rws}} = 0 \text{ Ou } \boxed{W_{\text{Rws}} = 300R\ln 2}$$

4.5.2 Consider the following process for the system of Problem 4.5-1. The ideal gas is first expanded adiabatically ... [SUMÁRIO]

SOLUÇÃO:

a)
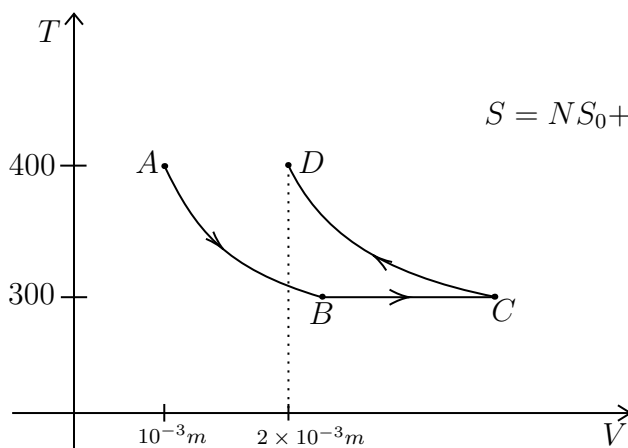
$$S = NS_0 + NR\ln\left[\left(\frac{U}{U_0}\right)^{5/2}\frac{V}{V_0}\left(\frac{N_0}{N}\right)^{5/2}\right] \text{ e ainda } U = \frac{3}{2}NRT$$

Variação	ΔS	ΔU
Subsistema	$NR \ln (V_f/V_i) = NR \ln 2$	0
Total	0	0
RHS	$-NR \ln 2$	$-NR 300 \ln 2$
RWS	0	$+NR 300 \ln 2$

$$\therefore \boxed{W = 300R \ln 2}$$

b) Em um processo adiabático $T^{3/2} V = const$

$$\therefore V_B = V_A \left(\frac{T_A}{T_B}\right)^{3/2} = 10^{-3} \left(\frac{4}{3}\right)^{3/2} = 1,54 \times 10^{-3} \text{ m}^3$$

$$V_C = V_D \left(\frac{T_D}{T_C}\right)^{3/2} = 2 \times 10^{-3} \left(\frac{4}{3}\right)^{3/2} = 3.08 \times 10^{-3} \text{ m}^3$$

$$W = \int P dV = \int \frac{NRT}{V} dV = NRT_A \int_A^B \left(\frac{V_A}{V}\right)^{2/3} \frac{dV}{V} + NRT_B \int_B^C \frac{dV}{V} + NRT_D \int_C^D \left(\frac{V_D}{V}\right)^{2/3} \frac{dV}{V}$$

$$= -\frac{3}{2} NRT_A V_A^{2/3} \left[V_B^{-2/3} - V_A^{-2/3}\right] + NRT_B \ln \frac{V_C}{V_B} - \frac{3}{2} NRT_D V_D^{2/3} \left[V_D^{-2/3} - V_c^{-2/3}\right] = \boxed{300R \ln 2}$$

4.5.3 Describe how the gas of the preceding two problems could be brought to the desired final state by a free expansion. ... [SUMÁRIO]

SOLUÇÃO:

Desde que T não mude, U não muda (para um gás ideal). Ambos W e Q são zero.

Isso é consistente com o teorema do trabalho máximo, para W é menos do que aquela entregue em um processo reversível, como calculado acima.

4.5.4 The gasous system of Problem 4.5-1 is to be restored to its initial state. Both states have temperature 400 K ... [SUMÁRIO]

SOLUÇÃO:

$$\boxed{W' = 300R \ln 2}$$

4.5.5 If the thermal reservoir of Problem 4.5-1 were to be replaced by a reversible heat source having a heat capacity of ... [SUMÁRIO]

SOLUÇÃO:

Como no problema $4.5-1$, para o subsistema $\Delta S = R ln 2$ e $\Delta U = 0$. Para uma fonte reversível de calor,

$$\Delta S_{RHS} = \int_{300}^{T_f} \frac{C(T)}{T} dT = R \int_{300}^{T_f} \left(\frac{2}{T} + \frac{1}{150}\right) dT = 2R \ln \frac{T_f}{300} + R \frac{T_f - 300}{150}$$

A condição de reversibilidade é

$$\Delta S + \Delta S_{RHS} = R \left[\ln 2 + 2 \ln \frac{T_f}{300} + \frac{T_f - 300}{150} \right] = 0$$

A solução numérica dessa equação dada é

$$T_f \approx 250K$$

Então

$$\Delta U + \Delta U_{RHS} + W = 0 \quad \text{ou} \quad 0 + \int_{300}^{T_f} C(T)dT + W = 0$$

$$\therefore W = -\int_{300}^{T_F} C(T)dT = \int_{250}^{300} \left(2 + \frac{T}{150} \right) RdT = \boxed{192R}$$

Que, como o esperado, é menor do que no problema $4.5 - 1$

4.5.6 A system can be taken from state A to state B (where $S_B = S_A$) either (a) directly along the adiabat S = constant, or (b) along the isochore AC ... [SUMÁRIO]

SOLUÇÃO:
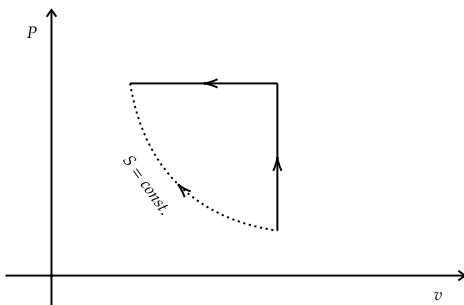
Não. No caminho superior algum calor é ejetado, a uma temperatura maior do que a do reservatório. Se esse calor for colocado em um processo reversível, pode ser parcialmente convertido em trabalho.

4.5.7 Consider the maximum work theorem in the case in which the specified final state of the subsystem has lower... [SUMÁRIO]

SOLUÇÃO:

O aumento na entropia do sistema pode ser compensado pela remoção de calor da fonte reversível de calor(diminuindo a entropia da fonte de calor). este calor pode fornecer o aumento de energia necessário do sistema (tanto no todo como em parte, a diferença sendo entregue para ou tirada da fonte reversível de calor).

4.5.8 If $S_B < S_A$ and $U_B > U_A$ does this imply that the delivered work is negative ? Prove your assertion ... [SUMÁRIO]

SOLUÇÃO:

a) Sim.

$$\Delta S^c + \Delta S \geqslant 0 \quad , \text{ mas } \Delta S < 0, \quad \therefore \Delta S^c > 0 \text{ ou } \Delta Q^c > 0$$

$$\text{Mas } \Delta U + \Delta Q^c + \Delta W^{RWS} = 0 \quad \text{e} \quad \Delta U > 0 \quad (\text{dado})$$

$$\therefore \Delta W^{\text{Rws}} < 0$$

b) As condições dadas não violam o postulado III

4.5.9 Two identical bodies each have constant and equal heat capacities ($C_1 = C_2 = C$, a constant). In addition a reversible work source is available ... [SUMÁRIO]

SOLUÇÃO:

$$U_1 = CT_1 \quad , \quad S_1 = C\ln T_1 \quad , \quad U_2 = CT_2, \quad S_2 = C\ln T_2$$

$$\Delta U_1 + \Delta U_2 + W = 0 \quad , \text{ou} \quad C\left(T_f - T_{10}\right) + C\left(T_f - T_{20}\right) + W = 0$$

$$\therefore \quad W = C\left[T_{10} + T_{20} - 2T_f\right]$$

Então

$$\Delta S = c\ln\frac{T_f}{T_{10}} + C\ln\frac{T_f}{T_{20}} = 0$$

$$T_f = \sqrt{T_{10}T_{20}}$$

donde

$$W = C\left[T_{10} + T_{20} - 2\sqrt{T_{10}T_{20}}\right] = C\left[\sqrt{T_{20}} - \sqrt{T_{10}}\right]^2$$

$$\text{Se} \quad C = 8 \text{ J/k}, \quad T_{10} = 373 \text{ K} \quad \text{e} \quad T_{20} = 273 \text{ K}$$

$$W = 62,3 \text{ J} \quad \text{e} \quad T_f^{\min} = 319 \text{ K} = 46°\text{C}$$

$$\text{enquanto} \quad T_f^{\max} = \tfrac{1}{2}\left(T_{10} + T_{20}\right) = 50°\text{C}$$

4.5.10 Two identical bodies eqch have heat capacities (at constant volume) of $C(T) = a/T$ ... [SUMÁRIO]

SOLUÇÃO:

$$\Delta S_1 = a\left(\frac{1}{T_{10}} - \frac{1}{T_f}\right) \quad , \Delta S_2 = a\left(\frac{1}{T_{20}} - \frac{1}{T_f}\right), \Delta U_1 = a\ln\frac{T_f}{T_{10}}, \Delta U_2 = a\ln\frac{T_f}{T_{20}}$$

$$\text{de } \Delta S = 0, \quad a\left[\frac{1}{T_0} - \frac{1}{T_f}\right] + a\left[\frac{1}{T_{20}} - \frac{1}{T_f}\right] = 0 \quad \text{ou} \quad T_f = \left[\frac{2T_{10}T_{20}}{(T_{10} + T_{20})}\right].$$

$$W = 0 \text{ se } T_{10} = T_{20}$$

$$W = a\ln\frac{9}{8} \text{ se } T_{20} = 2T_{10}$$

4.5.11 Two bodies have heat capacities (at constant volume) of $C_1 = aT$ and $C_2 = 2bT$ ... [SUMÁRIO]

SOLUÇÃO:

$$\Delta U_1 = \tfrac{1}{2}a\left(T_f^2 - T_{10}^2\right), \Delta U_2 = \tfrac{2}{3}b\left(T_f^3 - T_{20}^3\right)$$

$$\Delta S_1 = \int_{T_{10}}^{T_f}\frac{C_1}{T}dT = a\left(T_f - T_{10}\right) \quad , \Delta S_2 = b\left(T_f^2 - T_{20}^2\right)$$

$$\text{mas} \quad \Delta S_1 + \Delta S_2 = 0, \text{ ou} \quad bT_f^2 + aT_f - \left(bT_{20}^2 + aT_{10}\right) = 0$$

$$T_f = -\frac{a}{2b} + \frac{1}{2b}\sqrt{a^2 + 4b^2 T_{20}^2 + 4abT_{10}}$$

Então

$$W + \Delta U_1 + \Delta U_2 = 0$$

Ou ainda

$$W = -\frac{1}{2}a\left(T_f^2 - T_{10}^2\right) - \frac{2}{3}b\left(T_f^3 - T_{20}^3\right)$$

4.5.12 One mole of an ideal Van der Waals fluid is contained in a cylinder fitted with a piston. The initial temperature of the gas... [SUMÁRIO]

SOLUÇÃO:

Das equações 3.49 e 3.51,

$$u = cRT - a/v$$
$$s = s_0 + R\ln\left[(v - b)(cRT)^c\right]$$

Então, da Conservação da energia,

$$cR\left(T_f - T_i\right) - a\left(\frac{1}{v_f} - \frac{1}{v_i}\right) + C\left(T_f - T_0\right) + W = 0$$

E da condição de reversibilidade,

$$R\ln\frac{(v_f - b)\,T_f^c}{(v_i - b)\,T_i^c} + C\ln\frac{T_f}{T_0} = 0.$$

$$\therefore T_f = \left[\left(\frac{v_i - b}{v_f - b}\right)^R T_i^{cR} T_0^C\right]^{\left(\frac{1}{cR + C}\right)}$$

E

$$W = cR\left[T_i - T_f\right] + a\left(\frac{1}{v_f} - \frac{1}{v_i}\right) + C\left(T_0 - T_f\right)$$

4.5.13 A system has a temperature-independent heat capacity C. The system is initially at temperature T$_i$ and a heat reservoir ... [SUMÁRIO]

SOLUÇÃO:

$$\Delta S_{corpo} = C\ln\frac{T_c}{T_i}, \quad \Delta U_{\text{corpo}} = C\left(T_c - T_i\right), \quad \Delta S_{res} = Q_{res}/T_c$$

$$\Delta S_{\text{corpo}} + \Delta S_{\text{res}} = C\ln\frac{T_c}{T_i} + \frac{Q_{res}}{T_c} = 0 \quad \text{ou} \quad Q_{\text{res}} = -CT_c\ln\frac{T_c}{T_i}$$

$$W + \Delta U_{\text{corpo}} + Q_{\text{res}} = 0 \quad, \text{ ou} \quad W = -C\left(T_c - T_i\right) + CT_c\ln\left(T_c/T_i\right)$$

4.5.14 If the temperature of the atmosphere is 5°C on a winter day and if 1 Kg of water at 90 °C is ... [SUMÁRIO]

SOLUÇÃO:

O número de mols é $N = 10^3 gramas/18 gramas/mol = 55,5 mol$

$$\therefore C = Nc_v = 4167 \text{ J/K}$$

$$\Delta U = C\left(T_f - T_i\right) = 4167 \times (-85) = -354.2 \times 10^3 J.$$
$$\Delta S = C \ln\left(T_f/T_i\right) = 4167 \ln(278/363) = -1112 J/K$$
$$\therefore \Delta S_{\text{res}} = +1112 \text{ J/K}$$

$$\therefore \boxed{W = -\Delta U - T_{\text{res}}\,\Delta S_{res} = 45 \times 10^3 \text{ J}}$$

4.5.15 A rigid cylinder contains an internal adiabatic piston separating it into two chambers, of volume V_{10} and V_{20}. ... [SUMÁRIO]

SOLUÇÃO:

$$\frac{S}{R} = \tfrac{3}{2}\ln T_1 + \ln V_1 + \tfrac{5}{2}\ln T_2 + \ln V_2 + const.$$

$$\frac{U}{R} = \tfrac{3}{2}T_1 + \tfrac{5}{2}T_2$$

No estado final

$$V_1 = V_2 = \left(V_{10} + V_{20}\right)/2 \quad \text{e} \quad T_1 = T_2 = T_c$$

Então

$$\Delta S_{\text{gas}} = \frac{3}{2}\ln\frac{T_c}{T_{10}} + \frac{5}{2}\ln\frac{T_c}{T_{20}} + \ln\frac{\left(V_{10}+V_{20}\right)^2}{4V_{10}V_{20}}$$

$$\Delta U_{\text{gas}} = \frac{3}{2}\left(T_c - T_{10}\right) + \frac{5}{2}\left(T_c - T_{20}\right)$$

Então Q_c é determinado a partir de $\boxed{\Delta S_{gas} + Q_c/T_c = 0}$ e $\boxed{W = -\Delta U_{\text{gas}} - Q_c = -\Delta U_{gas} + T_c\Delta S_{gas}}$
Ou

$$\boxed{W = -\frac{3}{2}R\left(T_c - T_{10}\right) - \frac{5}{2}R\left(T_c - T_{20}\right) + \frac{3}{2}RT_c\ln\frac{T_c}{T_{10}} + \frac{5}{2}RT_c\ln\frac{T_c}{T_{20}} + RT_c\ln\left[\frac{\left(V_{10}+V_{20}\right)^2}{4V_{10}V_{20}}\right]}$$

4.5.16 Each of three identical bodies has a temperature-independent heat capacity C. The three bodies ... [SUMÁRIO]

SOLUÇÃO:

$$\Delta S = C\ln\frac{T_f}{T_1} + C\ln\frac{T_f}{T_2} + C\ln\frac{T_f}{T_3} = C\ln\frac{T_f^3}{T_1 T_2 T_3} = 0$$
$$\therefore T_f = \left(T_1 T_2 T_3\right)^{1/3}$$

$$(-W) = U_i - U_f = C \left[T_1 + T_2 + T_3 - 3 \left(T_1 T_2 T_3 \right)^{1/3} \right]$$

4.5.17 Each of two bodies has a heat capacity given by C = A + 2BT ... [SUMÁRIO]

SOLUÇÃO:

$$\Delta S_1 = \int_{T_i}^{T_f} \frac{A + 2BT}{T} dT = A \ln \frac{T_f}{T_i} + 2B \left(T_f - T_i \right)$$

$$\Delta U_1 = \int_{T_i}^{T_f} (A + 2BT) dT = A \left(T_f - T_i \right) + B \left(T_f^2 - T_i^2 \right)$$

De $\Delta S = 0$, $A \ln \frac{T_f^2}{T_{1i} T_{2i}} + 2B \left(2T_f - T_{1i} - T_{2i} \right) = 0$

Ou fazendo $\tau \equiv 10^{-2} T_f$

$$2 \ln \tau + \tau - 3 - \ln 8 = 0, \quad \tau \simeq 2,885$$

$$\therefore \boxed{T_f = 288,5 \text{ K}}$$

Para encontrar a temperatura máxima, $\Delta U = 0$

$$A \left(T_f - 200 \right) + B \left(T_f^2 - 200^2 \right) + A \left(T_f - 400 \right) + B \left(T_f^2 - 400^2 \right) = 0$$

$$\text{ou} \quad 2T_f^2 - 20 \times 10^4 + 400 \left(2T_f - 600 \right) = 0$$

$$\text{ou} \quad \boxed{T_f = 329K} \quad \text{Temperatura máxima}$$

Para encontrar o trabalho máximo:

$$W_{max} = A(T - 200) + B \left(T^2 - 200^2 \right) + A(T - 400) + B \left(T^2 - 400 \right), \quad T = 288,5K$$

$$\boxed{W_{max} = 2,22 \times 10^3 J}$$

4.5.18 A particular system has the equations of state T = As/v$^{1/2}$ and P = T^2/4Av$^{1/2}$ ... [SUMÁRIO]

SOLUÇÃO:

$$\frac{\partial U}{\partial S} = A \frac{S}{\sqrt{NV}} \quad \therefore U = \frac{A}{2} \frac{S^2}{\sqrt{NV}} + f(V)$$

$f(V)$ é uma função desconhecida.

$$\text{Mas} \quad -P = \frac{\partial U}{\partial V} = -\frac{1}{4} A \frac{S^2}{N^{1/2} V^{3/2}} + f'(V) = -\frac{T^2}{4A} \left(\frac{N}{V} \right)^{1/2} + f'(V)$$

Então $f'(V) = 0$, ou $f(V) = $ const. e $U = \frac{A}{2} \frac{S^2}{\sqrt{NV}}$ (tomando $const = 0$)

Então

$$U = TS/2 \quad ; \quad U = \frac{T^2}{2A} \sqrt{NV}; \quad S = T\sqrt{NV}/A$$

Na medida em que o sistema vai de T_1, V_1 para T_2, V_2, $\Delta S = A^{-1} N^{1/2} \left[T_2 \sqrt{V_2} - T_1 \sqrt{V_1} \right]$ e ainda $\Delta U = \frac{1}{2} A^{-1} N^{1/2} \left[T_2^2 \sqrt{V_2} - T_1^2 \sqrt{V_1} \right]$

Para o segundo sistema,

$$\Delta S' = \int_{T_0}^{T_f} \frac{c(T)}{T} dT = 2B \left[T_f^{1/2} - T_2^{1/2} \right]$$

$$\Delta U' = \int_{T_c}^{T_s} \frac{c(T)}{T} dT = \frac{2}{3} B \left[T_f^{3/2} - T_c^{3/2} \right]$$

Para determinar T_f, impomos a condição de reversibilidade $\Delta S + \Delta S' = 0$, ou

$$\boxed{2B \left[T_f^{1/2} - T_c^{1/2} \right] + A^{-1} \sqrt{N} \left[T_2 \sqrt{V_2} - T_1 \sqrt{V_1} \right] = 0}$$

Essa última equação determina T_f.

E da conservação da energia,

$$\boxed{W = -\Delta U - \Delta U' = -A^{-1} \sqrt{N} \left[T_2^2 \sqrt{V_2} - T_1^2 \sqrt{V_1} \right] - \frac{2}{3} B \left[T_f^{3/2} - T_c^{3/2} \right]}$$

4.5.19 A particular type of system obeys the equations $\mathbf{T = \frac{u}{b}}$ and $\mathbf{P = avT}$ ... [SUMÁRIO]

SOLUÇÃO:

$$\frac{1}{T} = b/u \quad \text{e} \quad P/T = av \quad \therefore \delta s = \frac{b}{u} du + av \delta v$$

$$\therefore A = b \ln(bT) + \frac{1}{2} av^2 + const. \quad \text{e} \quad u = bT$$

$$\Delta S = b \ln \frac{T_f}{T_1} + b \ln \frac{T_f}{T_2} + \frac{1}{2} a \left(2v_f^2 - 2v_0^2 \right) = 0$$

$$\therefore T_f = \sqrt{T_1 T_2} \exp \left[\frac{a}{2b} \left(v_0^2 - v_f^2 \right) \right]$$

$$W = -2b T_f + b T_1 + b T_2$$

$$\therefore W = -2b \sqrt{T_1 T_2} \exp \left[\frac{a}{2b} \left(v_0^2 - v_f^2 \right) \right] + b \left(T_1 + T_2 \right)$$

4.5.20 Suppose that we have a system in some initial state (we may think of a tank of hot, compressed gas as an example) and ... [SUMÁRIO]

SOLUÇÃO:

Reversibilidade:

$$S_f - S_0 + \frac{Q_{atm}}{T_{atm}} = 0$$

Conservação da energia:

$$U_f - U_0 + Q_{atm} + W_{RWS} + P_{atm} \left(V_f - V_0 \right) = 0$$

$$\therefore W_{RWS} = U_0 - U_f + P_{atm} \left(V_0 - V_f \right) - T_{atm} \left(S_f - S_0 \right)$$

Ou disponibilidade $= [U_0 + P_{atm}V_0 - T_{atm}S_0] - [U_f + P_{atm}V_f - T_{atm}S_f]$

(*Reações químicas* não *invalidam esse resultado*)

4.5.21 An antartic meteorological station suddenly loses all of its fuel. It has N moles of an inert "ideal Van der Waals fluid"at ... [SUMÁRIO]

SOLUÇÃO:

$$s = s_0 + R\ln\left[\left(u + \frac{a}{v}\right)^c (v - b)\right], \frac{1}{T} = \frac{\partial s}{\partial u} = \frac{cR}{u + a/v}, \frac{P}{T} = \frac{R}{v - b} - \frac{acR}{uv + a}\frac{1}{v}$$

Sejam v_h e v_0 soluções da equação acima, correspondendo a $(P_h, T_h) + (P_0, T_0)$ respectivamente.

$$s = s_0 + R\ln\left[(cRT)^c (v - b)\right]$$
$$\therefore \Delta s = R\ln\left[\left(\frac{T_0}{T_h}\right)^c \frac{v_0 - b}{v_h - b}\right]$$

Onde $v_0 \equiv v(P_0, T_0) + v_h = v(P_h, T_h)$. Também $\Delta u = cR(T_0 - T_h) - \frac{a}{v_0} + \frac{a}{v_h}$

$$W_{RWS} = -N[\Delta u + T_0 \Delta s] = -N\left\{cR(T_0 - T_h) - \frac{a}{v_0} + \frac{a}{v_h} - RT_0\ln\left[\left(\frac{T_0}{T_h}\right)^c \frac{v_0 - b}{v_h - b}\right]\right\}$$

$$\text{E} \quad t_{max} = W_{RWS}/\mathscr{P}$$

4.5.22 A "geothermal"power source is available to drive an oxygen production plant. The geothermal source is simply a ... [SUMÁRIO]

SOLUÇÃO:

$$\Delta_S = -NR\sum_i x_i \ln x_i = -NR\left(\frac{1}{5}\ln\frac{1}{5} + \frac{4}{5}\ln\frac{4}{5}\right) = -N \times (2cal/k) \times (-0,5004) \approx N \quad (cal/k)$$

$$\text{Ou} \quad N_{0_2} = \frac{1}{5}N \simeq \frac{1}{5}\Delta S \quad, \Delta S \quad em \quad cal/k$$

Considere o poço: capacidade térmica=vol. em $cm^3 \times \dfrac{1cal}{cm^3 K} \approx 10^9 cal/K$

$$dS_{\text{poço}} = \frac{\text{đ}Q}{T} = 10^9 \frac{dT}{T} cal/K$$

$$\Delta S_{\text{poço}} = 10^9 \ln(T_f/T_i) = 10^9 \ln\frac{293}{373} = -0,29 \times 10^7 cal/K$$

$$\Delta S_{\text{lago}} = 10^6 \frac{95°}{T_{\text{cold}}} = 0,34 \times 10^9 cal/K$$

$$\therefore \Delta S_{\text{poço}} + \Delta S_{\text{lago}} = 0,05 \times 10^9 = 5 \times 10^7 cal/k$$

$$N_{0_2} = \frac{1}{5}\Delta S = 10^7 \text{ mols}$$

4.6 COEFFICIENTS OF ENGINE, REFRIGERATOR, AND HEAT PUMP PERFORMANCE [SUMÁRIO]

4.6.1 A temperature of 0.001 K is accessible in low temperature laboratories with moderate effort. If the price ... [SUMÁRIO]

SOLUÇÃO:

$$-W = \frac{T_h - T_c}{T_c} Q_c = \frac{300}{10^{-3}} \times 1 = 3 \times 10^5 \text{ watt-horas } = 300 \text{kwh.}$$

$$\text{Custo} = \$45$$

4.6.2 A home is to be maintained at 70°F, and the external temperature is 50°F. One method of heating ... [SUMÁRIO]

SOLUÇÃO:

$$\epsilon_p = \frac{T_h}{T_h - T_c} = \frac{330}{330 - 319} \simeq 30 \quad \therefore \text{razão de custos } \simeq 30$$

4.6.3 A household refrigerator is maintained at a temperature of 35°F. Every time the door is opened, warm material ... [SUMÁRIO]

SOLUÇÃO:

$$\varepsilon_r = \frac{-dQ_c}{-dW_{rws}} = \frac{T_c}{T_h - T_c} = \frac{495}{35} = 14$$

$$\varepsilon_r' = 0,15 \times 14 = 2,1$$

$$(-dW_{\text{rws}}) = \frac{(-dQ_c)}{\varepsilon_r'} = \frac{50 \times 10^3}{2,1} \times 15 = 3.6 \times 10^5 \text{ cal / dia } = 0,43 \text{kwh/dia}$$

O custo mensal será 13kwh/mês ou \$1,95/mês

4.6.4 Heat is extracted from a bath of liquid helium at a temperature of 4.2 K. The high-temperature reservoir is a ... [SUMÁRIO]

SOLUÇÃO:

$$\Delta S_{cold} = \frac{-1}{4,2} J/K \quad \therefore \Delta S_{\text{hot}} = \frac{-\Delta Q_h}{77,3} = +\frac{1}{4,2}$$

$$\Delta Q_h = 18,4 \text{ Joules}$$

4.6.5 Assume that a particular body has the equation of state U = NCT with NC = 10 J/K and assume that this equation ... [SUMÁRIO]

SOLUÇÃO:

$$\Delta U = NC\Delta T = 10(0,5 - 300) = -299.5 \text{ Joules } \simeq -3000 \text{ Joules}$$

$$\Delta S_{body} = +NC \ln \frac{T_f}{T_i} = +10 \ln \frac{0,5}{300} = -64 \text{J/K}$$

$$\Delta S_{res} = \frac{W - \Delta U_{body}}{T_{res}} = \frac{2995 + W}{300} = 10 + \frac{W}{300}$$

$$\Delta S = \Delta S_{body} + \Delta S_{res} = -64 + 10 + \frac{W}{300} = 0$$

$$\boxed{W = 16,2KJ}$$

4.6.6 One mole of a monatomic ideal gas is allowed to expand isothermally from an initial volume of 10 liter to a final ... [SUMÁRIO]

SOLUÇÃO:

$$W = \int_{v_i}^{v_f} Pdv = RT \int_{v_i}^{v_f} \frac{dv}{v} = RT \ln \frac{15}{10} = 400R \ln 1,5$$

$$\varepsilon_r = \frac{-dQ_c}{-dW_{rws}} = \frac{T_c}{T_h - T_c}. \quad \text{ou} \frac{-Q_c}{400 \ln 1,5} = \frac{200}{100}$$

$$(-Q_c) = 800R \ln 1.5 = 2.7 \times 10^3 \text{Jonlos}$$

4.6.7 Give a "constructive solution"of Example 2 of Section 4.1. Your solution may be based on the following procedure ... [SUMÁRIO]

SOLUÇÃO:

Considere os dois corpos mais frios, com temperaturas T_1 e T_2. Faça-os chegar em uma temperatura comum, extraindo trabalho:

$$\Delta S = C \ln \frac{T'}{T_1} + C \ln \frac{T'}{T_2} = C \ln \frac{T'^2}{T_1 T_2} = 0 \quad \therefore T' = \sqrt{T_1 T_2}$$

$$W = CT_1 + CT_2 - 2CT' = C\left[T_1 + T_2 - 2\sqrt{T_1 T_2}\right]$$

Com esse trabalho disponível podemos extrair calor do par frio, para aumentar a temperatura do terceiro corpo: Faça a temperatura resultante do par frio ser T_f. Então, o calor extraído é $2C(T'-T_f)$ e a variação de entropia é

$$\Delta S_{12} = 2C\ln\left(T_f\right) = 2C\ln\left(T_f/\sqrt{T_1 T_2}\right)$$

Enquanto o corpo quente tem esse calor extraído inserido nele, bem como o trabalho extraído. Isto é, a energia inserida no corpo quente é

$$Q_3 = 2C\left(T'-T_f\right) + C\left[T_1 + T_2 - 2\sqrt{T_1 T_2}\right]$$

e esse calor inserido eleva o corpo quente a uma temperatura T_h, onde

$$T_h = T_3 + Q_3/C = T_3 + 2\left(T'-T_f\right) + \left[T_1 + T_2 - 2\sqrt{T_1 T_2}\right] = T_1 + T_2 + T_3 - 2T_f$$

A variação de entropia correspondente é

$$\Delta S_3 = C\ln\left[\left(T_3 + T_1 + T_2 - 2T_f\right)/T_3\right]$$

A temperatura ainda desconhecida T_f é determinada pela condição de reversibilidade:

$$\Delta S_{12} + \Delta S_3 = 2C\ln\frac{T_f}{\sqrt{T_1 T_2}} + C\ln\left[1 + \frac{T_1 + T_2 - 2T_f}{T_3}\right] = 0$$

ou ainda

$$2T_f^3 - T_f^2\left[T_1 + T_2 + T_3\right] + T_1 T_2 T_3 = 0$$

Essa é a equação para T_f encontrada no exemplo da seção 4.8 (note que a solução para T_f também determina T_h $(= T_1 + T_2 + T_3 - 2T_f)$

4.6.8 Assume that 1 mole of an ideal Van der Waals fluid is expanded isothermally, at temperature T_h, from an initial ... [SUMÁRIO]

SOLUÇÃO:

(a)

$$u = cRT - \frac{a}{v} \quad s = s_0 + R\ln\left[(v-b)\left(u + \frac{a}{v}\right)^c\right]$$

$$\therefore \quad s = s_0 + R\ln(v-b) + cR\ln(cRT)$$

Faça o gás sofrer uma expansão δv, a T constante

$$-\delta W = P\delta v = \left(\frac{RT}{v-b} - \frac{a}{v^2}\right)\delta v$$

$$-\delta Q = -T\delta s = -\frac{RT}{v-b}\delta v$$

A equação 4.9 é

$$\delta W_{\text{rws}} = \left(1 - \frac{T_c}{T}\right)(-\delta Q) + (-\delta W)$$

$$= \left(1 - \frac{T_c}{T}\right)\left(-\frac{RT}{v-b}\right)\delta v + \left(\frac{RT}{v-b} - \frac{a}{v^2}\right)\delta v$$

$$= \left(\frac{RT_c}{v-b} - \frac{a}{v^2}\right)\delta v$$

Integrando:

$$\boxed{W_{rws} = RT_c \ln\frac{v_f - b}{v_i - b} + \frac{a}{v_f} - \frac{a}{v_i}}$$

(b) Pela conservação da energia e da entropia:

$$u = cRT - \frac{a}{v} \quad \therefore \Delta u = -\frac{a}{v_f} + \frac{a}{v_i}$$

$$\Delta = s_0 + R\ln(v-b) + cR\ln(cRT) \quad \therefore \Delta s = R\ln\frac{v_f - b}{v_i - b}$$

$$Q_{rhs} = -T_c\Delta s = -RT_c\ln\frac{v_f - b}{v_i - b}$$

$$\therefore \boxed{W_{Rws} = -\Delta u - Q_{rhs} = \frac{a}{v_f} - \frac{a}{v_i} + RT_c\ln\frac{v_f - b}{v_i - b}}$$

corroborando o resultado da parte (a)

4.6.9 Two moles of a monatomic ideal gas are to be taken from an initial state $(\mathbf{P_i}, \mathbf{V_i})$ to a final state... [SUMÁRIO]

$\boxed{\textsc{Solução:}}$

Expressando S como função de P e V:

$$S = Ns_0 + \frac{3}{2}NR\ln(P/P_0) + \frac{5}{2}NR\ln(V/V_0) - \frac{5}{2}NR\ln(N/N_0)$$

donde

$$S_f - S_i = \tfrac{3}{2}NR\ln B^2 + \tfrac{5}{2}NR\ln B^{-1} = \tfrac{1}{2}NR\ln B$$
$$U_f - U_i = \tfrac{3}{2}P_fV_f - \tfrac{3}{2}P_iV_i = \tfrac{3}{2}NRT_i(B-1)$$

da condição de reversibilidade:

$$S_f - S_i + \frac{Q_c}{T_c} = \frac{1}{2}NR\ln B + \frac{Q_C}{T_C} = 0$$

ou

$$-Q_c = \frac{1}{2}NRT_c\ln B$$

Da conservação de energia

$$W_{\text{Rws}} = -(U_f - U_i) - Q_c = -\frac{3}{2}NRT_i(B-1) + \frac{1}{2}NRT_c\ln B$$
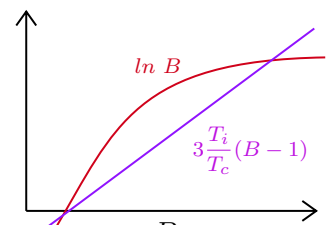
ou

$$W^{\text{Rws}} = \frac{1}{2}NRT_c \left[\ln B - 3\frac{T_1}{T_c}(B-1) \right]$$

Note que $\ln B$ e $3\frac{T_i}{T_c}(B-1)$ são ambos zero em $B = 1$, e eles têm inclinações de 1 e de $3T_i/T_c$ respectivamente. O trabalho entregue é positivo se $T_i < \frac{T_c}{3}\frac{\ln B}{B-1}$ ou $P_i V_i < \frac{2}{3}RT_c\frac{\ln B}{B-1}$

4.6.10   Assume the process in Problem 4.6-9 to occur along the locus $P = B/V^2$, where $B = P_i V_i^2$. Apply the ...

SOLUÇÃO:

$$S = S_0 + \frac{3}{2}NR\ln\frac{P}{P_0} + \frac{5}{2}NR\ln\frac{V}{V_0} - \frac{5}{2}NR\ln\frac{N}{N_0}$$

$$dQ = TdS = \frac{PV}{NR}dS = \frac{3}{2}VdP + \frac{5}{2}PdV$$

$$dW = -PdV$$

O trabalho (-dW) pode ser transferido diretamente para a fonte reversível de trabalho. O calor (-dQ) pode ser parcialmente convertido em trabalho, fornecendo a transferência de trabalho adicional dW'.

$$dw' = \left[1 - \frac{T_c}{T} \right](-dQ)$$

$$= \left[1 - \frac{NRT_c}{PV} \right]\left(-\frac{3}{2}VdP - \frac{5}{2}PdV \right)$$

$$dW_{\text{Rws}} = -dW - dW' = PdV + \left[1 - \frac{NRT_c}{PV} \right]\left(-\frac{3}{2}Vc'P - \frac{5}{2}PdV \right)$$

Integrando ao longo do caminho $P = B/V^2$

$$dW_{Rws} = B\frac{dV}{V^2} + \left[1 - \frac{NRT_c}{B}V \right]\left[+\frac{3B}{V^2}dV - \frac{5}{2}\frac{B}{V^2}dV \right]$$

$$= B\frac{dV}{V^2} + \left[1 - \frac{NRT_c}{B}V \right]\left[+\frac{B}{2V^2}dV \right]$$

$$= \frac{3}{2}B\frac{dV}{V^2} - \frac{NRT_c}{2V}dV$$

$$W_{Rws} = \frac{3}{2}B\left(\frac{1}{V_i} - \frac{1}{V_f} \right) - \frac{NRT_c}{2}\ln\frac{V_f}{V_i}$$

$$= \frac{3}{2}\left(P_i V_i - P_f V_f \right) + \frac{1}{2}NRT_c\ln B$$

O que é idêntico ao resultado do problema 4.6-9

4.6.11 Assume the process in Problem 4.6-9 to occur along a straight-line locus in the T − V plane. Integrate along ...

> **Solução:**

$$\text{Como } PV = NRT \quad \text{temos} \quad T_f/T_i = P_f V_f / P_i V_i = B$$

O *"lugar de linha reta** é $T = T_i + D \cdot (V - V_i)$, onde encontramos que $D = B(1-B)T_i/V_i$. Ao longo desse *lugar*,

$$P = NRT/V = NRD + NR\left(T_i - DV_i\right)/V$$

Uma expansão infinitesimal dV, o calor absorvido pelos gases é

$$đQ = TdS = \frac{3}{2}NRdT + PdV$$

e a fração desse calor transferida para as fontes reversíveis de calor é

$$đw_1^{Rws} = \left(1 - \frac{T_c}{T}\right)(-đQ) = NR\left(T_c - T\right)\left[\frac{3}{2}\frac{dT}{T} + \frac{dV}{V}\right]$$

A isso deve ser adicionado o trabalho PdV, então

$$đ^{Rws} = \frac{3}{2}NR\left(T_c - T\right)\frac{dT}{T} + NRT_c\frac{dV}{V}$$

ao longo do caminho linear isso se torna

$$đw^{\text{Rws}} = \frac{3}{2}NR\left[-1 + \frac{T_c}{T_i + D\left(V - V_i\right)}\right]DdV + NRT_c\frac{dV}{V}$$

Integrando

$$
\begin{aligned}
W^{R\omega s} &= -\frac{3}{2}NRD\left(V_f - V_i\right) + \frac{3}{2}NRT_c \ln \frac{T_i + D\left(V_i - V_i\right)}{T_i} + NRT_c \ln \frac{V_f}{V_i}\\
&= -\frac{3}{2}NRT_i(B-1) + \frac{1}{2}NRT_c \ln B\\
&= \frac{3}{2}\left(P_iV_i - P_fV_f\right) + \frac{1}{2}NRT_c \ln B
\end{aligned}
$$

o que novamente é idêntico ao resultado do problema 4.6-10.

4.7 THE CARNOT CYCLE

4.7.1 Repeat the calculation of Example 5 assuming the "working substance"of the auxiliary system to be 1 mole. ...

> **Solução:**

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*Straight-line locus - a tradução está correta?"
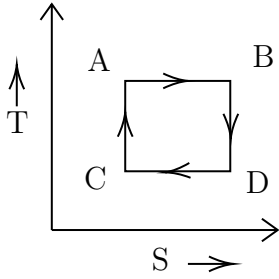
$$S = Ns_0 + NR \ln \left[(v-b)(u+a/v)^c \right] \quad \text{Eq. 3.51}$$

$$\text{mas} \quad u + \frac{a}{v} = cRT \quad \text{(Eq. 3.49)}$$

$$\therefore S = NR \ln[(v-b)cRT] + Ns_0$$

$$Q_{AB} = RT_h \ln \frac{v_B - b}{v_A - b}$$

$$\Delta U_{AB} = -\frac{a}{v_B} + \frac{a}{v_A}$$

$$W_{AB} = \Delta U_{AB} - Q_{AB} = \frac{a}{v_A} - \frac{a}{v_b} - RT_h \ln \frac{v_B - b}{v_A - b}$$

De B até C:

$$(v-b)T = const$$

$$\therefore (v_B - b)T_h = (v_C - b)T_c$$

$$W_{BC} = \Delta u_{BC} = cR(T_c - T_h) - \frac{a}{v_c} + \frac{a}{v_B} = cR(T_c - T_h) + \frac{a}{v_B} - \frac{a}{(v_B - b)T_h + bT_C}$$

$$\therefore Q_{BC} = 0$$

De C até D:

$$Q_{CD} = T_c R \ln \frac{v_D - b}{v_c - b} = T_c R \ln \frac{(v_A - b)T_h/T_c}{(v_B - b)T_n/T_c} = T_c R \ln \frac{v_A - b}{v_B - b}$$

$$\Delta U_{CD} = -\frac{a}{v_D} + \frac{a}{v_C}$$

$$W_{CD} = \Delta U_{CD} - Q_{CD} = -\frac{a}{v_D} + \frac{a}{v_C} - RT_c \ln \frac{v_A - b}{v_B - b}$$

De D até A:

$$Q_{DA} = 0$$

$$W_{DA} = \Delta U_{DA} = cR(T_h - T_c) - \frac{a}{v_A} + \frac{a}{v_D}$$

Então, temos que

$$W = \frac{a}{v_A} - \frac{a}{v_B} - RT_h \ln \frac{v_B - b}{v_A - b} + cR(T_c - T_h) - \frac{a}{v_C} + \frac{a}{v_B} - \frac{a}{v_D} + \frac{a}{v_C} - RT_c \ln \frac{v_A - b}{v_B - b} + cR(T_h - T_c) - \frac{a}{v_A} + \frac{a}{v_D}$$

$$\therefore W = R(T_h - T_c) \ln \frac{v_B - b}{v_A - b} \Rightarrow Q_{AB} = -RT_h \ln \frac{v_A - b}{v_B - b}$$

$$\therefore \boxed{\frac{W}{|Q_{AB}|} = \frac{T_h - T_c}{T_h}}$$

4.7.2 Calculate the work and the heat transfers in each stage of the carnot cycle for the auxiliary system being an ... [SUMÁRIO]

SOLUÇÃO:

$$U = bVT^4 \quad \text{e também} \quad S = \frac{4}{3}bVT^3 = \frac{4}{3}b^{1/4}U^{3/4}V^{1/4}$$

$$\Delta U_{AB} = bT_h^4 \left(V_B - V_A\right), \quad \Delta S_{AB} = \frac{4}{3}bT_h^3 \left(V_B - V_A\right)$$

$$\therefore Q_{AB} = \frac{4}{3}bT_h^4 \left(V_B - V_A\right), \quad W_{AB} = \Delta U_{AB} - Q_{AB} = -\frac{1}{3}bT_h^4 \left(V_B - V_A\right)$$

$$Q_{BC} = \Delta S_{BC} = 0 \quad \text{e} \quad VT^3 = const.$$

$$\therefore V_c = V_B \left(\frac{T_h}{T_c}\right)^3$$

$$W_{BC} = b\left(V_c T_c^4 - V_B T_h^4\right) = -b\left[V_B T_h^4 - V_B \left(\frac{T_h}{T_c}\right)^3 T_c^4\right] = -bV_B T_h^3 \left(T_h - T_c\right)$$

$$Q_{CD} = \frac{4}{3}bT_c^4 \left(V_D - V_c\right) = \frac{4}{3}bT_c^4 \left[V_A \left(\frac{T_h}{T_c}\right)^3 - V_B \left(\frac{T_h}{T_c}\right)^3\right] = \frac{4}{3}bT_h^3 T_c \left(V_A - V_B\right)$$

$$\Delta U_{CD} = bT_c^4 \left(V_D - V_C\right) = bT_h^3 T_c \left(V_A - V_B\right)$$

$$W_{CD} = \Delta U_{CD} - Q_{CD} = -\frac{1}{3}bT_h^3 T_c \left(V_A - V_B\right)$$

$$Q_{DA} = \Delta S_{DA} = 0 \quad ; \quad W_{DA} = -b\left(V_D T_c^4 - V_A T_h^4\right) = -bV_A T_h^3 \left(T_c - T_h\right)$$

$$\text{Então } W = W_{AB} + W_{BC} + W_{CD} + W_{DA} = -\frac{4}{3}bT_h^3 \left(T_h - T_c\right)\left(V_B - V_A\right)$$

$$\boxed{\varepsilon \equiv \frac{|W|}{|Q_{AB}|} = \frac{T_h - T_c}{T_h}}$$

4.7.3 A "primary subsystem" in the initial state A is to be brought reversibly to a specified final state B. A reversible ... [SUMÁRIO]

SOLUÇÃO:

Pode ser feito em três passos:
1) Levar o sistema ao longo de uma adiabata até a temperatura T_r.
2) Levar o sistema isotermicamente até a interseção da isoterma com o adiabata que contém o estado B.
3) Levar o sistema ao longo da adiabata até o estado B.

4.7.4 The fundamental equation of a particular fluid is $UN^{1/2}V^{1/2} = A(S-R)^3$ where A... [SUMÁRIO]

SOLUÇÃO:
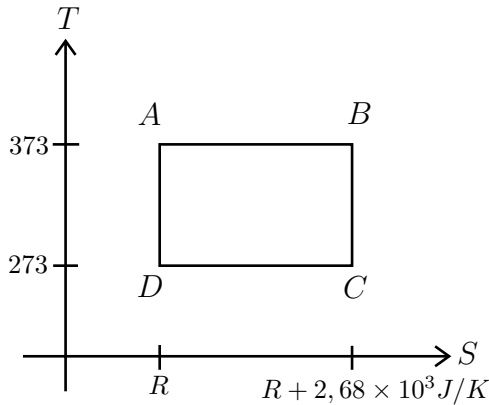
Seja $\quad \hat{S} \equiv S - R.$ Então $T = 3A\hat{S}^2 V^{-3/2} N^{-1/2}$

ou $\quad \hat{S} = (3A)^{-1/2} T^{1/2} V^{3/4} N^{1/4}$

$\therefore U = 3^{-3/2} A^{-1/2} T^{3/2} V^{3/4} N^{1/4} \quad$ e $\quad U = \dfrac{1}{3} T\hat{S}$

$Q_{AB} = T_h \Delta S_{AB} = 10^6$ Joules

$\therefore \Delta S_{AB} = 2,68 \times 10^3$ J/K

$$\Delta U_{AB} = \frac{1}{3} T_h \left(S_B - S_A \right) = W_{AB} + Q_{AB}$$

$$\therefore W_{AB} = -\frac{2}{3} T_h \left(S_B - S_A \right) = -0,667 \times 10^6 \text{ J}$$

$$Q_{BC} = 0$$

$$W_{BC} = \Delta U = \Delta \left(\frac{1}{3} T\hat{S} \right) = \frac{1}{3}(-100)\left(R + 2.68 \times 10^3 \right) = -0,366 \times 10^6 J$$

$$Q_{CD} = 273 \times \left(-2.68 \times 10^3 \right) = -0,732 \times 10^6 \text{ J}$$

$$\Delta U_{CD} = \frac{1}{3} T \Delta S_{CD} = \frac{1}{3} \times 273 \times \left(-2,68 \times 10^3 \right) = -0,243 \times 10^6 \text{ J}$$

$$W_{CD} = \Delta U_{CD} - Q_{CD} = 0,489 \times 10^6 \text{ J}$$

$$Q_{DA} = 0$$

$$W_{DA} = \Delta U_{DA} = \frac{1}{3} \Delta T \times S = \frac{1}{3} \times 100 \times 8,314 \times 10^3 = 0,277 \times 10^6 \text{ J}$$

$$Q \equiv Q_{AB} + Q_{BC} + Q_{CD} + Q_{DA} = 0,267 \times 10^6 \text{ J}$$

$$W = W_{AB} + W_{BC} + W_{CD} + W_{DA} = -0,267 \times 10^6 \text{ J}$$

$$\varepsilon = \frac{-W}{Q_{AB}} = \frac{0,267 \times 10^6}{10^6} \Longrightarrow \boxed{\varepsilon = 0,267..} \quad \text{e} \quad \boxed{\varepsilon_{\text{theor}} = 1 - \frac{T_D}{T_A} = .268}$$

4.7.5 One mole of the "simple paramagnetic model system"of equation 3.66 is to be used as the auxiliary system of ... [SUMÁRIO]

SOLUÇÃO:

$$Q_1 = Q_{AB} = T_h \Delta S \quad \text{é dado}$$

$$\text{da equação 3.66} \quad U = NRT_0 \exp\left[\frac{S}{NR} + \frac{\mu_0 I^2}{2\chi_1 R N^2} \right]$$

$$\therefore T = \frac{\partial U}{\partial S} = \frac{U}{NR} \quad \text{ou} \quad U = NRT$$

$$\text{Consequentemente} \quad U_{AB} = 0 \quad \text{ou} \quad W_{AB} + Q_{AB} = 0$$

$$W_{AB} = -Q_1$$

$$B \to C:$$

$$\Delta U_{BC} = R\left(T_c - T_h\right) \quad, Q_{BC} = 0 \quad, \quad \therefore W_{BC} = R\left(T_c - T_h\right)$$

$$C \to D:$$

$$Q_{CD} = T_c\left(S_D - S_C\right) = T_c\left(S_A - S_B\right) = -\frac{T_c}{T_h}Q_1$$

$$D \to A:$$

$$\Delta U_{CD} = 0 \quad \therefore W_{CD} = -Q_{CD} = \frac{T_c}{T_h}Q_1$$

$$Q_{DA} = 0, \quad W_{DA} = \Delta U_{DA} = R\left(T_h - T_c\right)$$

$$\text{Consequentemente} \quad W = -\left(W_{AB} + W_{BC} + W_{CD} + W_{DA}\right) = Q_1 + R\left(T_h - T_c\right) - \frac{T_c}{T_h}Q_1 - R\left(T_h - T_c\right)$$

$$\therefore \boxed{W = \left(1 - \frac{T_c}{T_h}\right)Q_1}$$

O que é o resultado de Carnot.

4.7.6 Repeat Problem 4.7-4 using the "rubber band" model of section 3.7 as the auxiliary system. [SUMÁRIO]

SOLUÇÃO:

Para o elástico de borracha $U = cL_cT$ (equação 3.58)

Essa equação é isomorfica à equação $U = NRT$ do problema 4.7-5 (com cL_0 substituindo NR). Como $U = NRT$ era a única equação na solução do problema 4.7-5, a solução deste problema (4.7-6) é obtida daquela do problema 4.7-5 pela substituição $NR \to cL_0$.

4.7.7 (Supplementary Problem) Repeat Problem 4.7-4 if the working substance is one mole of an ideal Van der Waals fluid. For analytic convenience, take b = 0. [SUMÁRIO]

SOLUÇÃO:

$$\Delta - \Delta_0 = R\ln\left[v\left(u + \frac{a}{v}\right)^c\right]$$

$$\text{ou} \quad u = -\frac{a}{v} + v^{-1/c}\exp\left[\frac{s - s_0}{cR}\right]$$

$$T = \frac{\partial u}{\partial s} = \frac{1}{cRv^{1/c}}\exp\left[\frac{s - s_0}{cR}\right]$$

$$\therefore v = (cRT)^{-c}\exp\left[\frac{s - s_0}{R}\right]$$
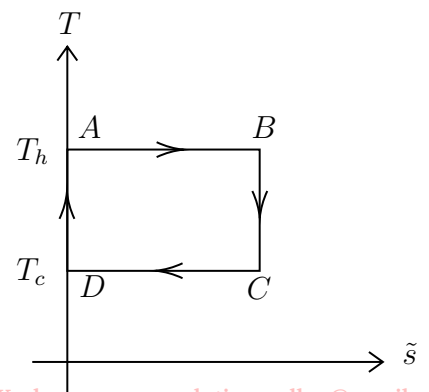
$$\text{e} \quad u = -a(cRT)^c e^{-\tilde{s}^2/R} + cRT,$$

$$\text{onde} \quad \tilde{s}^2 = s - s_0$$

$A \to B:$

$$Q_{AB} = T_h \Delta\tilde{s} \equiv Q_1$$

$$\Delta u_{AB} = -a\left(cRT_h\right)^c e^{-\tilde{s}_B/R} + cRT_h + a\left(cRT_h\right)^c - cRT_h$$

$$\Delta u_{AB} = a\left(cRT_h\right)^c \left(1 - e^{-s_B^2/R}\right) = a\left(cRT_h\right)^c \left(1 - e^{-Q_1/RT_h}\right)$$

$$\therefore W_{AB} = \Delta U_{AB} - Q_{AB} = a\left(cRT_h\right)^c \left[1 - e^{-Q_1/RT_h}\right] - Q_1$$

$B \to C:$

$$Q_{BC} = 0$$

$$W_{BC} = -a(cR)^c \left[T_c^c - T_h^c\right] e^{-Q_1/RT_h} + cR\left(T_c - T_h\right)$$

$C \to D:$

$$Q_{CD} = -T_c \Delta\tilde{s}$$

$$W_{CD} = \Delta u_{CD} - Q_{CD} = a\left(cRT_c\right)^c \left[e^{-Q_i/RT_c} - 1\right] + \frac{T_c}{T_h}Q_1$$

$D \to A:$

$$Q_{DA} = 0$$

$$W_{DA} = \Delta u_{DA} = -a\left(cRT_h\right)^c + cRT_h + a\left(cRT_c\right)^c - cRT_c$$

$$-W = -\left(W_{AB} + W_{BC} + W_{CD} + W_{DA}\right) \implies \boxed{-W = \frac{T_h - T_c}{T_n}Q_1}$$

O que é o resultado de Carnot.

4.8 MEASURABILITY OF THE TEMPERATURE AND OF THE ENTROPY [SUMÁRIO]

4.8.1 To corroborate equation 4.22 show that $\left(\frac{\partial P}{\partial s}\right)_T = -\left(\frac{\partial T}{\partial v}\right)_P$ ... [SUMÁRIO]

SOLUÇÃO:

$$dT = u_{ss}ds + u_{vs}dv$$

$$\therefore \left(\frac{\partial T}{\partial v}\right)_p = u_{ss}\left(\frac{\partial s}{\partial v}\right)_p + u_{vs} = -u_{ss}\frac{u_{vv}}{u_{ss}} + u_{vs}$$

$$\delta P = \frac{\partial P}{\partial s}\delta s + \frac{\partial P}{\partial v}\delta v = -u_{sv}\delta s - u_{vv}\delta v$$

$$\therefore \left(\frac{\partial P}{\partial s}\right)_T = -u_{sv} - u_{vv}\left(\frac{\partial v}{\partial s}\right)_T = -u_{sv} + u_{vv}\frac{u_{ss}}{u_{vs}}$$

$$\therefore \boxed{\left(\frac{\partial P}{\partial s}\right)_T = -\left(\frac{\partial T}{\partial v}\right)_P}$$

4.9 OTHER CRITERIA OF ENGINE PERFORMANCE; POWER OUTPUT AND "ENDOREVERSIBLE ENGINES " [SUMÁRIO]

4.9.1 Show that the efficiency of an endoreversible engine, maximized for power output, is always less than $\varepsilon_{\text{Carnot}}$ ... [SUMÁRIO]

SOLUÇÃO:

$$\varepsilon_{\text{erp}} = 1 - \left(\frac{T_c}{T_h}\right)^{1/2} \qquad \varepsilon = 1 - \left(\frac{T_c}{T_h}\right)$$

$$\therefore \frac{T_c}{T_h} = (1 - \varepsilon_{erp})^2 = 1 - \varepsilon$$

$$\text{De} \quad \left(\frac{T_c}{T_h}\right)^{1/2} > \frac{T_c}{T_h}$$

$$1 - \left(\frac{T_c}{T_h}\right)^{1/2} > 1 - \frac{T_c}{T_h}$$

$$\varepsilon_{erp} < \varepsilon$$
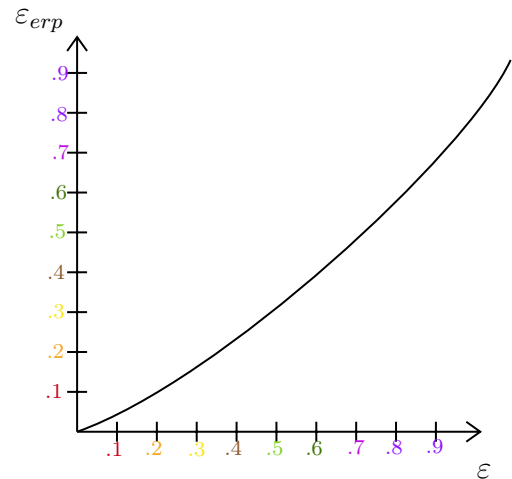
4.9.2 Suppose the conductance σ_{h} ($= \sigma_{\text{c}}$) to be such that 1 KW is transfered to the system (as heat flux) if its ... [SUMÁRIO]

SOLUÇÃO:

$$\sigma_h = \sigma_c = \frac{Q_h}{t_h\,(T_h - T_w)} = \frac{10^3}{50}\,\frac{\text{J}}{segundos\ \ K} = 20 \text{ J/segundos } K$$

$$c = \frac{1}{2}\left(T_h^{1/2} + T_c^{1/2}\right) = 22.4 \quad \text{(equação 4.27)}$$

$$T_w = c\sqrt{T_h} = 645 \text{ K} \quad \text{(equação 4.26)}$$

$$T_t = c\sqrt{T_c} = 395 \text{ K}$$

$$\text{Power } = \sigma_h \sigma_c \frac{T_h^{1/2} - T_c^{1/2}}{\sigma_h^{1/2} + \sigma_c^{1/2}} = \frac{\sigma^{3/2}}{2}\left(T_h^{1/2} - T_c^{1/2}\right) = 490 \text{ watts}$$

4.9.3 Consider an endoreversible engine for which the high temperature reservoir is boiling water (100℃) and... [SUMÁRIO]

SOLUÇÃO:

$$\varepsilon_{erp} = 1 - \sqrt{\frac{293}{373}} = 0,114 \quad (= W/Q_h)$$

$$\varepsilon_{\text{carnot}} = 1 - \frac{293}{373} = 0,214 \quad (= W/Q_h)$$

$$Q_H - Q_{\text{H carnot}} = W\left[\frac{1}{0,114} - \frac{1}{0,214}\right] = [8,77 - 4,67]\text{w} = 4,1\ \text{W}$$

$\therefore$ O motor de Carnot extrai $8,77$ kwh de calor por kwh de trabalho entregue e o motor endo-reversível extrai $4,67$ kwh de calor por kwh de trabalho entregue. $\boxed{\text{Razão} = 1,9}$

4.9.4 **Assume that on cycle of the engine of Problem 4.9-3 takes 20 s and that the condutance $\sigma_{\text{h}} = \sigma_{\text{c}} = 100\ \text{W/K}$ ...** [SUMÁRIO]

$\boxed{\textsc{Solução:}}$

$Area = trabalho/ciclo$
$= \Delta S \times \Delta T$
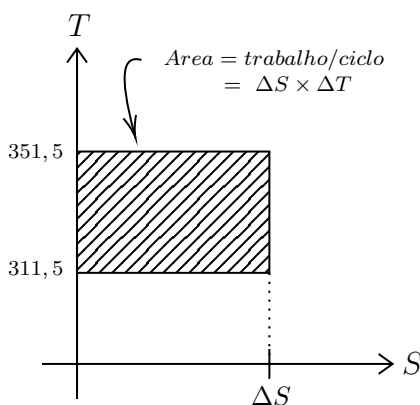
$$c = \frac{1}{2}\left[\sqrt{T_h} + \sqrt{T_c}\right] = 18.2\ \text{K}^{1/2} \quad \text{(equação 4.27)}$$

$$T_w = cT_h^{1/2} = 18,2\sqrt{373} = 351,5\ \text{K} \quad \text{(equação 4.26)}$$

$$T_t = cT_c^{1/2} = 18,2\sqrt{293} = 311,5\ \text{K} \quad \text{(equação 4.26)}$$

$$\Delta T \times \Delta S = \frac{1}{4}\sigma\left[\sqrt{T_h} - \sqrt{T_c}\right]^2 \times t = \frac{100}{4}\left[\sqrt{373} - \sqrt{293}\right]^2 \times 20$$

$$\Delta T \times \Delta S = 2411\text{watt/segundo} = 0,67\text{watt-hora/ciclo}$$

$$\Delta S = 0,67\ \text{watt-hora}/40\text{K} = 0,167\ \text{watt-hora/K}$$

4.10 OTHER CYCLIC PROCESSES [SUMÁRIO]

4.10.1 **Assuming that the working gas is a monatomic ideal gas, plot a $T - S$ diagram for the Otto cycle.** [SUMÁRIO]

$\boxed{\textsc{Solução:}}$

$\boxed{\text{NENHUMA SOLUÇÃO PARA ESSE PROBLEMA NO MOMENTO}}$

4.10.2 **Assuming that the working gas is a simple ideal gas (with temperature-independent heat capacities), show that the engine efficiency of the Otto cycle...** [SUMÁRIO]

$\boxed{\textsc{Solução:}}$

$\boxed{\text{NENHUMA SOLUÇÃO PARA ESSE PROBLEMA NO MOMENTO}}$

4.10.3 Assuming that the working gas is a simples ideal gas(with temperature-independent heat capacities), show that the engine efficiency of the Brayton cycle ...

Solução:

NENHUMA SOLUÇÃO PARA ESSE PROBLEMA NO MOMENTO

4.10.4 Assuming that the working gas is a monatomic ideal gas, plot a $T - S$ diagram of the Brayton cycle.

Solução:

NENHUMA SOLUÇÃO PARA ESSE PROBLEMA NO MOMENTO

4.10.5 Assuming that the working gas is a monatomic ideal gas, plot a $T - S$ diagram of the air-standart diesel cycle.

Solução:

NENHUMA SOLUÇÃO PARA ESSE PROBLEMA NO MOMENTO

5 ALTERNATIVE FORMULATIONS AND LEGENDRE TRANSFORMATIONS

5.1 THE ENERGY MINIMUM PRINCIPLE

5.1.1 Formulate a proof that the energy minimum principle implies the entropy maximum ...

Solução:

A prova é parcialmente fornecida como uma dica no texto. Para completar é somente necessario observar que a fonte de calor reversivel resfriada pode ser usada para extrair o calor do sistema original, restaurando-o para sua entropia inicial porém a uma menor energia.

5.1.2 An adiabatic, impermeable and fixed piston separates a cylinder into two chambers ... [SUMÁRIO]

SOLUÇÃO:

(a)

$$U_{inicial} = U_{final} \quad \text{ou} \quad \frac{3}{2}RT_s + \frac{3}{2}RT_l = \frac{3}{2}RT_f \quad \therefore T_f = \frac{1}{2}(T_s + T_l)$$

$$\text{e} \quad P_s = P_l \quad \text{ou} \quad RT_f/V_s = RT_f/V_l \quad \therefore V_s = V_l = V_0/2$$

(b)

A pressão em cada lado do pistão é igual, mas a diferença de pressão é gerada em oposição à força aplicada $\left[\left(\dfrac{\partial P}{\partial V}\right)_s = -c_p/c_v V0 < 0\right]$ Portanto esse trabalho deve ser feito contra essa diferença de pressão. Então a energia é mínima.

(c)

Relacionando o pistao quase-estaticamente até $P_s = P_l$:

$$PV^{5/3} = \text{constante} \quad \text{e} \quad P_s = P_l$$

ou

$$\begin{cases} P_{0s}\left(V_{0s}/V_s\right)^{5/3} = P_{0l}\left(V_{0l}/V_l\right)^{5/3} \\ V_s + V_l = 0 \end{cases}$$

Duas equações determinam V_s e V_l.

(d)

Se o cilindro agora está adiabaticamente isolado e o pistao liberado, nenhum movimento ocorre ($P_s = P_l$). Portanto, por (a) a energia é mínima a S constante.

5.2 LEGENDRE TRANSFORMATIONS [SUMÁRIO]

5.2.1 The equation y = x²/10 describes a parabola. ... [SUMÁRIO]

SOLUÇÃO:

$$y = \frac{1}{10}x^2, \quad P = \frac{1}{5}x, \quad \psi = y - Px = \frac{(5P)^2}{10} - 5P^2 = -\frac{5}{2}P^2$$

5.2.2 Let y = Ae^{Bx} ... [SUMÁRIO]
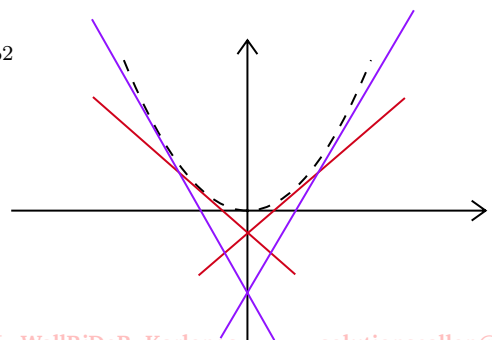
5.2.2 Let $y = Ae^{Bx}$ ... [SUMÁRIO]

> **SOLUÇÃO:**

(a)

$$P = ABe^{Bx} = BY$$

$$\psi = y - Px = Y\left[1 - Bx\right] = \frac{P}{B}\left[1 - \ln\frac{P}{AB}\right]$$

(b)

$$-x = \frac{\partial \psi}{\partial P} = \frac{1}{B}\left[1 - \ln\frac{P}{AB}\right] - \frac{1}{B} = -\frac{1}{B}\ln\frac{P}{AB}$$

$$y = \psi + Px = \frac{P}{B}\left[1 - \ln\frac{P}{AB}\right] + P\left[\frac{1}{B}\ln\frac{P}{AB}\right] = P/B = Ae^{Bx}$$

5.3   THERMODINAMIC POTENTIALS [SUMÁRIO]

5.3.1   Find the fundamental equation of a monatomic ideal gas in the Helmholtz representation, ... [SUMÁRIO]

> **SOLUÇÃO:**

$F_{repres.}$:

$$U = \frac{U_0 V_0^{2/3}}{N_0^{5/3}}\frac{N^{5/3}}{V^{2/3}}e^{\frac{2}{3R}\left(\frac{3}{N}-s_0\right)}, \quad T = \frac{2U}{3NR}, \quad P = \frac{2U}{3V}, \mu = \frac{5U}{3N}$$

$$F = U - TS = \left(\frac{3}{2}NR - Ns_0\right)T - \frac{3}{2}NRT\ln\left[\frac{T}{T_0}\frac{V^{2/3}}{V_0^{2/3}}\frac{N_0^{2/3}}{N^{2/3}}\right]$$

Então:

$$-S = \frac{\partial F}{\partial T} = -Ns_0 - \frac{3}{2}NR\ln\left[\frac{T}{T_0}\frac{V^{2/3}}{V_0^{2/3}}\frac{N_0^{2/3}}{N^{2/3}}\right]$$

$$-P = \frac{\partial F}{\partial V} = -\frac{NRT}{V} \quad \text{e} \quad \mu = \frac{\partial F}{\partial N} = \frac{F}{N} + RT$$

$H_{repres.}$:

$$H = U + PV = \frac{5}{3}U$$

$$\text{e} \quad H = \frac{5}{3^{3/5}2^{2/5}}\frac{U_0^{3/5}V_0^{2/5}}{N_0}NP^{2/5}e^{\frac{2}{5R}\left(\frac{5}{N}-s_0\right)}$$

$$\text{etc...}$$

$G_{repres.}$:

$$G = F + PV = F + NRT$$

$$\text{e} \quad G = \left(\frac{5}{2}NR - Ns_0\right)T - NRT\ln\left[\left(\frac{T}{T_0}\right)^{5/2}\frac{P_0}{P}\right]$$

5.3.2   Find the fundamental equation of the ideal van der Waals fluid (Section 3.5) in the Helmholtz representation ... [SUMÁRIO]

SOLUÇÃO:

$$u = -\frac{a}{v} + (v-b)^{1/c}\exp\left(\frac{s-s_0}{cR}\right) \quad \therefore T = \frac{\partial u}{\partial s} = \frac{1}{cR}(v-b)^{1/c}\exp\left(\frac{s-s_0}{cR}\right)$$

$$F = u - Ts = -\frac{a}{v} + (v-b)^{-1/c}e^{\frac{s-s_0}{cR}} - Ts = -\frac{a}{v} + cRT - Ts$$

$$= -\frac{a}{v} + cRT - Ts_0 - cRT\ln(cRT) - RT\ln(v-b)$$

5.3.3   Find the fundamental equation of electromagnetic radiation in the Helmholtz representation ... [SUMÁRIO]

SOLUÇÃO:

Da equação 3.57 $\quad S = \frac{4}{3}b^{1/4}U^{3/4}V^{1/4}$

Ou invertendo $\quad U = \left(\frac{3}{4}\right)^{4/3}b^{-1/3}S^{4/3}V^{-1/3}$

Diferenciando $\quad \therefore \; T = \left(\frac{3}{4}\right)^{1/3}b^{-1/3}S^{1/3}V^{-1/3}$

Ou invertendo $\quad S = \frac{4}{3}bT^{1/3}V$

$$\therefore \quad \boxed{F \equiv U - TS = -\frac{1}{3}bT^4V}$$

As equações de estado são:

$$\boxed{S = -\frac{\partial F}{\partial T} = \frac{4}{3}bT^3V}$$

$$\boxed{-P = \frac{\partial F}{\partial V} = -\frac{1}{3}bT^4}$$

Substituindo na equação para U, $U = bT^4V$, que é a equação 3.52. E tambem $T^4 = 3P/b$, substituindo isso em $U = bT^4V$ temos $p = \frac{U}{3V}$, ou equação. 3.53.

5.3.4 Justify the following recipe for obtaining a plot of F(V) from a plot of G(P) ... [SUMÁRIO]
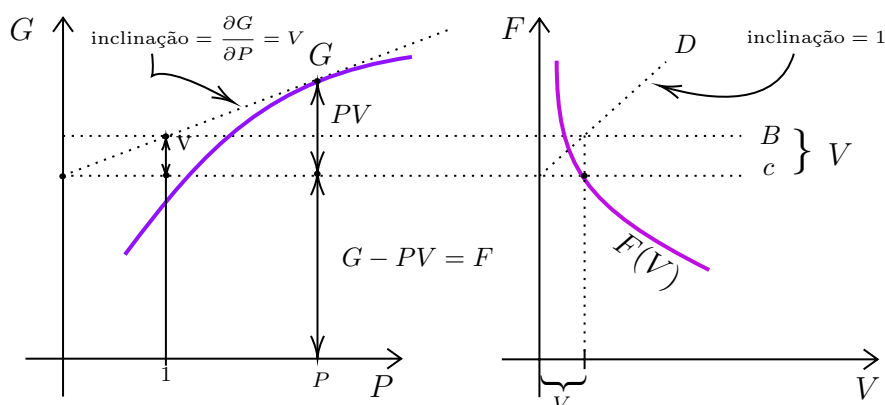
Note que as unidades de F são iguais às unidades de G que são iguais ao produto de unidades de P e V.

$$\left.\frac{\partial^2 G}{\partial P^2}\right)_{T,N} = \left.\frac{\partial V}{\partial P}\right)_{T,N} = -V\kappa_T$$

$$\therefore \frac{\partial^2 G}{\partial P^2} < 0 \text{ se } \kappa_T > 0$$

5.3.5 From the first acceptable fundamental equation in Problem 1.10-1 calculate the fundamental equation ... [SUMÁRIO]

$$S = (R^2/v_0\theta)^{1/3}(NVU)^{1/3} \quad \text{ou} \quad U = \left(\frac{v_0\theta}{R^2}\right)S^3/NV$$

$$\therefore T = 3\left(\frac{v_0\theta}{R^2}\right)S^2/NV, \quad -P = (v_0\theta/R^2)S^3/NV^2 \quad \text{Faça} \quad v_0\theta/R^2 \equiv A$$

$$\therefore G = U + PV - TS = A\frac{S^3}{NV} + A\frac{S^3}{NV} - 3A\frac{S^3}{NV} = -A\frac{S^3}{NV}$$

$$\text{Mas} \quad S = \frac{NT^2}{9AP} \quad \text{e} \quad Y = \frac{1}{27}\frac{N}{A}\frac{T^3}{P^2}$$

$$\boxed{\therefore G = -\frac{N}{27A}\frac{T^3}{P^2}}$$

$$\boxed{c_p = \frac{T}{N}\left(-\frac{\partial^2 G}{\partial T^2}\right)_p = \frac{2R^2}{9N_0 s}\frac{T}{P}}$$

$$\boxed{\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p = \left(\frac{\partial G}{\partial p}\right)^{-1}\left(\frac{\partial^2 G}{\partial T \partial P}\right) = \frac{3}{T}}$$

5.3.6 From the second acceptable fundamental equation in Problem 1.10-1 calculate the ... [SUMÁRIO]

> **SOLUÇÃO:**

invertendo

$$U = -\frac{R\theta}{v_0^2}\frac{V^2}{N} + \frac{\theta}{R}\frac{S^2}{N}$$

$$P = -\frac{\partial U}{\partial V} = \frac{2R\theta}{v_0^2}\frac{V}{N}$$

$$\boxed{H = U + PV = -\frac{R\theta}{v_0^2}\frac{V^2}{N} + \frac{\theta}{R}\frac{S^2}{N} + \frac{2R\theta}{v_0^2}\frac{V^2}{N} = \frac{Nv_0^2}{4R\theta}P^2 + \frac{\theta}{R}\frac{S^2}{N}}$$

$$V = \frac{\partial H}{\partial P} = \frac{Nv_0^2}{2R\theta}P \quad \text{O que confere.}$$

5.3.7 The enthalpy of a particular system is $H = AS^2N^{-1}\ln(P/P_0)$... [SUMÁRIO]

> **SOLUÇÃO:**

$$T = \frac{\partial H}{\partial S} = 2\frac{AS}{N}\ln(P/P_0)$$

$$\text{e} \quad V = \frac{\partial H}{\partial P} = AS^2/NP$$

$$\therefore P = AS^2/NV \quad \text{e} \quad T = \frac{2AS}{N}\ln\left(\frac{AS^2}{NVP_0}\right)$$

$$\therefore \left(\frac{\partial T}{\partial S}\right)_v = \frac{2A}{N}\ln\frac{AS^2}{NVP_0} + 4\frac{A}{N} = -\frac{2A}{N}\ln\frac{P}{P_0} + 4\frac{A}{N}$$

$$c_v = \frac{T}{N}\left(\frac{\partial S}{\partial T}\right)_V = \frac{T}{2A}(2 + \ln p/p_0)^{-1}$$

5.3.8 In Chapter 15 it is shown by a statistical mechanical calculation that the fundamental equation ... [SUMÁRIO]

> **SOLUÇÃO:**

$$S = \frac{1}{T}U - \frac{1}{T}F \quad \text{ou} \quad S/k_B = \beta U - \beta F \quad , \beta \equiv \frac{1}{k_B T}$$

$$U = F - TS = F - T\frac{\partial F}{\partial T} = F + \beta\frac{\partial F}{\partial \beta} = \frac{\partial}{\partial \beta}(\beta F)$$

$$\therefore U = -\tilde{N}\frac{\partial}{\partial \beta}\ln\left(e^{-\beta\epsilon_u} + e^{-\beta\epsilon_d}\right) = \tilde{N}\left(\epsilon_u e^{-\beta\epsilon_u} + \epsilon_d e^{-\beta\epsilon_d}\right)/\left(e^{-\beta\epsilon_u} + e^{-\beta\epsilon_d}\right)$$

$$\xi \equiv e^{-\beta(\epsilon_u - \epsilon_d)}, \quad \tilde{u} \equiv U/\tilde{N} = \frac{\epsilon_u \xi + \epsilon_d}{\xi + 1}, \quad \text{e inversamente} \quad \xi = \frac{\epsilon_d - \tilde{u}}{\tilde{u} - \epsilon_u}$$

$$\therefore \beta = \frac{1}{\epsilon_d - \epsilon u} \ln \frac{\epsilon_d - \tilde{u}}{\tilde{u} - \epsilon_u}$$

$$e^{-\beta \epsilon_u} = \left(\frac{\tilde{u} - \epsilon_u}{\epsilon_d - \tilde{u}}\right)^{\frac{\epsilon_u}{\epsilon_d - \epsilon_u}} \qquad e^{-\beta \epsilon_d} = \left(\frac{\tilde{u} - \epsilon_u}{\epsilon_d - \tilde{u}}\right)^{\frac{\epsilon_d}{\epsilon_d - \epsilon_u}}$$

$$\frac{1}{k_B} \tilde{s} = \frac{\tilde{u}}{\epsilon_d - \epsilon_u} \ln \frac{\epsilon_d - \tilde{u}}{\tilde{u} - \epsilon_u} + \ln \left[\left(\frac{\tilde{u} - \epsilon_u}{\epsilon_d - \tilde{u}}\right)^{\frac{\epsilon_u}{\epsilon_d - \epsilon_u}} + \left(\frac{\tilde{u} - \epsilon_u}{\epsilon_d - \tilde{u}}\right)^{\frac{\epsilon_d}{\epsilon_d - \epsilon_u}} \right]$$

$$\Rightarrow \frac{1}{k_B} \tilde{s} = \frac{\tilde{u} - \epsilon_u}{\epsilon_d - \epsilon_u} \ln \frac{\epsilon_d - \tilde{u}}{\tilde{u} - \epsilon_u} + \ln \left[1 + \left(\frac{\tilde{u} - \epsilon_u}{\epsilon_d - \tilde{u}}\right)^{\epsilon_d / \epsilon_u} \right]$$

$$= -Y \ln Y + \ln \left(1 + Y^{\epsilon_d / \epsilon_u}\right) \quad , \quad Y \equiv \frac{\tilde{u} - \epsilon_u}{\epsilon_d - \tilde{u}}$$

$$= \ln \left(\frac{1 + Y^{\epsilon_d / \epsilon_u}}{Y^Y}\right)$$

5.3.9   Show, for the two-level system of Problem 5.3-8, that as the temperature increases from zero... [SUMÁRIO]

SOLUÇÃO:

(a) No problema 5.3-8 nós temos

$$U/\tilde{N} = \frac{\epsilon_u e^{-\beta \epsilon_u} + \epsilon_d e^{-\beta \epsilon_d}}{e^{-\beta \epsilon_u} + e^{-\beta \epsilon_d}} = \frac{\epsilon_u + \epsilon_d e^{-\beta (\epsilon_d - \epsilon_u)}}{1 + e^{-\beta (\epsilon_d - \epsilon_u)}} \quad \text{com } \epsilon_d - \epsilon_u > 0$$

$$\therefore \quad \text{em} T = 0 (\text{ou} \quad \beta \to \infty), \quad U/\tilde{N} \Rightarrow \epsilon_u$$

$$\text{na medida em que} \quad T \to \infty (\text{ou} \quad \beta \to 0), \quad U/\tilde{N} \longrightarrow \frac{1}{2}(\epsilon_u + \epsilon_d)$$

(b)

$$e^{-\beta (\epsilon_d - \epsilon_u)} = (\epsilon_u - U/\tilde{N})/(U/\tilde{N} - \epsilon_d)$$

$$\text{e faça} \quad U/\tilde{N} = \frac{\epsilon_u + \epsilon_d}{2}(1 + \xi)$$

$$\text{Então} \quad \beta = \frac{1}{\epsilon_d - \epsilon_u} \ln \frac{1 - \xi}{1 + \xi}$$

$$\text{Que é negativo se } \xi > 0$$

5.3.10   Show that the Helmholtz potential of a mixture of simple ideal gases is the. ... [SUMÁRIO]

SOLUÇÃO:

Relembrando a equação 3.39: $U = \sum_j (N_j c_j) RT$

$\therefore \quad S(T, V, N)$ e $U(T, V, N)$ são aditivas, e consequentemente $F(T, V, N) \equiv U - TS$ é aditiva.

5.3.11 A mixture of two monatomic ideal gases is contained in a volume V at temperature T ... [SUMÁRIO]

SOLUÇÃO:

$$F = \left(\frac{3}{2}R - s_0\right) T (N_1 + N_2) - \frac{3}{2}N_1 RT \ln\left[\frac{T}{T_0}\left(\frac{V}{V_0}\right)^{2/3}\left(\frac{N_0}{N_1}\right)^{2/3}\right] - \frac{3}{2}N_2 RT \ln\left[\frac{T}{T_0}\left(\frac{V}{V_0}\right)^{2/3}\left(\frac{N_0}{N_2}\right)^{2/3}\right]$$

$$\therefore \mu_1 = \frac{\partial F}{\partial N_1} = \left(\frac{3}{2}R - s_0\right) T - \frac{3}{2}RT \ln\left[\frac{T}{T_0}\left(\frac{V}{V_0}\right)^{2/3}\left(\frac{N_0}{N_1}\right)^{2/3}\right] + RT$$

$$\text{de onde} \quad \frac{N_1}{N_0} = \frac{V}{V_0}\left(\frac{T}{T_0}\right)^{3/2} \exp\left[\frac{\mu_1 - \frac{5}{2}RT + Ts_0}{RT}\right]$$

$$\text{Então} \quad P = \frac{NRT}{V} = \frac{(N_2 + N_1) RT}{V} = \frac{N_2 RT}{V} + \frac{N_0 RT^{5/2}}{V_0 T_0^{3/2}} \exp\left[\frac{\mu_1 - \frac{5}{2}RT + Ts_0}{RT}\right]$$

5.3.12 A system obeys the fundamental relation $(s - s_0)^4 = avu^2$... [SUMÁRIO]

SOLUÇÃO:

$$u = A^{-1/2}(S - Ns_0)^2 N^{-1/2} V^{-1/2}$$

$$T = \frac{2}{\sqrt{AN}}(S - Ns_0)^2 V^{1/2} \quad , P = -\frac{\partial U}{\partial V} = \frac{1}{2\sqrt{AN}}(S - Ns_0)^2/V^{3/2} = \frac{1}{8}\sqrt{AN}T^2/V^{1/2}$$

$$\therefore G = U + PV - TS = \frac{ANT^4}{2^6 P} - NTs_0$$

5.3.13 For a particular system it is found that $u = (\frac{3}{2})Pv$ and $P = AvT^4$... [SUMÁRIO]

SOLUÇÃO:

$$\frac{1}{T} = \left(\frac{3A}{2}\right)^{1/4} v^{1/2}u^{-1/4} \text{ and } \frac{P}{T} = \left(\frac{2}{3}\right)^{3/4} A^{1/4}v^{-1/2}u^{3/4}$$

$$\therefore \delta s = \frac{1}{T}\delta u + \frac{P}{T}\delta v = \left(\frac{3}{2}A\right)^{1/4} v^{1/2}u^{-1/4}du + \left(\frac{3}{2}\right)^{-3/4} A^{1/4}v^{-1/2}u^{3/4}dv = C\delta\left(v^{1/2}u^{3/4}\right), \quad c \equiv \frac{2^{3/4}}{3^{3/4}}A^{1/4}$$

$$S = cV^{1/2}U^{3/4}N^{-1/4}$$

$$\frac{\mu}{T} = -\frac{\partial S}{\partial N} = +\frac{1}{4}\frac{S}{N} = A^{-1}2^{-5/4}P^2/T^5 \quad \text{ou} \quad \mu = P^2/2^{5/4}AT^4$$

$$\text{Para encontrar } F(T, V, N): \quad U = \left(\frac{3^3}{2^7 A}\right)^{1/3} S^{4/3}V^{-2/3}N^{1/3}$$

$$T = \frac{\partial U}{\partial S} = 2^{-1/3}A^{-1/3}S^{1/3}V^{-2/3}N^{1/3}$$

$$F = U - TS = -2^{-7/3}A^{-1/3}S^{4/3}V^{-2/3}N^{1/3} = -\frac{A}{2}T^4V^2/N$$

5.3.14 **For a particular system (of 1 mole) the quantity $(v+a)f$ is known to be a function of...**

SOLUÇÃO:

$$-s = (\partial f/\partial T)_v \quad \text{e} \therefore \quad c_v = \left(T\frac{\partial s}{\partial T}\right)_v = -T\left(\frac{\partial^2 f}{\partial T}\right)_v = -T\frac{d^2 Y}{dT^2}/(v+a) = b(v)T^{1/2}$$

$$\therefore b(v) = A/(v+a), A = \text{const}$$

$$\text{e} \quad c_v = \frac{A}{v+a}T^{1/2} = -T\frac{d^2 Y}{dT^2}/(v+a) \quad \text{ou} \quad \frac{d^2 Y}{dT^2} = -\frac{A}{T^{1/2}}$$

$$\therefore Y(T) = -\frac{4}{3}AT^{3/2} + DT + E$$

$$\text{e} \quad f = Y(T)/(v+a) = \left(-\frac{4}{3}AT^{3/2} + DT + E\right)/(v+a)$$

$$\therefore s = -\left(\frac{\partial f}{\partial T}\right)_v = \left[2AT^{1/2} - D\right]/(v+a)$$

$$\text{No processo considerado} \quad \Delta s = \frac{2AT_f^{1/2} - D}{v_f + a} - \frac{2AT_0^{1/2} - D}{v_0 + a}$$

$$\text{e} \quad \Delta u = \Delta(f + Ts) = \Delta\left[\frac{\frac{2}{3}AT^{3/2} + E}{v+a}\right] = \frac{\frac{2}{3}AT_f^{3/2} + E}{v_f + a} - \frac{\frac{2}{3}AT_0^{3/2} + E}{v_0 + a}$$

A transferência de calor para o reservatório é

$$Q^{(r)} = T^{(r)}[-\Delta s]$$

$$\text{e} \quad W^{(Rws)} = -\Delta u - Q^{(r)}$$

$$\therefore W^{(Rws)} = \left[-\frac{\frac{2}{3}AT_f^{3/2} + E}{v_f + a} + \frac{\frac{2}{3}AT_c^{3/2} + E}{v_0 + a}\right] + T^{(r)}\left[\frac{2AT_f^{1/2} - D}{v_f + a} - \frac{2AT_0^{1/2} - D}{v_0 + a}\right]$$

5.4 GENERALIZED MASSIEU FUNCTIONS

5.4.1 **Find the fundamental equation of a monatomic ideal gas in the representation ...**

SOLUÇÃO:

$$S = Ns_0 + NR\ln\left[\left(\frac{U}{U_0}\right)^{3/2}\frac{V}{V_0}\left(\frac{N_0}{N}\right)^{5/2}\right]$$

$$P/T = \frac{NR}{V} \quad \text{e} \quad -\frac{\mu}{T} = \frac{\partial S}{\partial N} = \frac{S}{N} - \frac{5}{2}R$$

$$\therefore S\left[\frac{P}{T}, \frac{\mu}{T}\right] = S - \frac{P}{T}V + \frac{\mu}{T}N = \frac{3}{2}NR \quad \text{e isso deve ser expresso em termos de} \quad U, \frac{P}{T}, \frac{\mu}{T}.$$

$$\text{Mas} \quad -\frac{\mu}{T} = s_0 - \frac{5}{2}R + R\ln\left[\left(\frac{U}{U_0}\right)^{3/2}\frac{P_0/T_0}{P/T}\left(\frac{N_0}{N}\right)^{5/2}\right]$$

$$\text{ou} \quad N = N_0 \left(\frac{P_0/T_0}{P/T} \right)^{2/3} \frac{U}{U_0} \exp\left[\frac{2}{3}\frac{s_0}{R} - \frac{5}{3} + \frac{2}{3}\frac{\mu}{RT} \right]$$

$$\therefore S\left[\frac{P}{T}, \frac{\mu}{T} \right] = \frac{3}{2}N_0 R \left(\frac{P_0}{T_0}\frac{T}{P} \right)^{2/3} \frac{U}{U_0} e^{\frac{2}{3}\frac{s_0}{R} - \frac{5}{3}} e^{2\mu/3RT}$$

Para corroborar as equações de estado:

$$-V = \frac{\partial S\left[P/T, \mu/T\right]}{\partial(P/T)} == -\frac{2}{3}\frac{S\left[\frac{P}{T}, \frac{\mu}{T}\right]}{P/T} = -\frac{2}{3}\frac{\frac{3}{2}NR}{P/T} = -\frac{NRT}{P}$$

O que está correto!

5.4.2 Find the fundamental equation of electromagnetic radiation (Section 3.6) ... [SUMÁRIO]

> **Solução:**

$$U = \frac{3}{4}C^{1/3}S^{4/3}/V^{1/3} \text{e} T = (CS/V)^{1/3} \text{ (equações 3.45 e 3.39)}$$

$$\therefore S = VT^3/C \quad \text{e} \quad U = \frac{3}{4}\frac{V}{C}T^4$$

$$\boxed{S\left[\frac{1}{T} \right] = S - \frac{1}{T}U = \frac{1}{4C}VT^3}$$

$$\text{Também} \quad P = \frac{1}{4}(CS^4/V^4)^{1/3} = \frac{1}{4}S/V$$

$$S\left[\frac{P}{T} \right] = S - \frac{P}{T}V = \frac{3}{4}S$$

$$\text{Mas} \quad U = \frac{3}{4}C^{1/3}S\left(\frac{S}{V} \right)^{1/3} = \frac{3}{4}C^{1/3}S\left(\frac{4P}{T} \right)^{1/3}$$

$$\text{ou} \quad S = \frac{4}{3}C^3\left(4\frac{P}{T} \right)^{-1/3}U$$

$$\therefore S\left[\frac{P}{T} \right] = C^3\left(\frac{4P}{T} \right)^{-1/3}U$$

5.4.3 Find the fundamental equation of the ideal van der Waals fluid in the representation S[1/T]. ... [SUMÁRIO]

> **Solução:**

$$S = Ns_0 + NR\ln\left[\left(\frac{V}{N} - b \right)\left(\frac{U}{N} + \frac{aN}{V} \right)^c \right]$$

$$\text{ou} \quad s - s_0 = R\ln\left[(v-b)(u + \frac{a}{v})^c \right]$$

$$\therefore \frac{1}{T} = \frac{\partial s}{\partial u} = \frac{cR}{u + a/v} \quad \text{e} \quad u = -\frac{a}{v} = cRT$$

$$s\left[\frac{1}{T}\right] = s - \frac{1}{T}u = s_0 + R\ln\left[(v - b)(u + \frac{a}{v})^c\right] + \frac{a}{vT} - cR$$

$$\text{Então} \quad s\left[\frac{1}{T}\right] = s_0 + R\ln\left[(v - b)(cRT)^c\right] + \frac{a}{vT} - cR$$

E isso é igual a $-f/T$, onde f é calculado no problema 5.3-2

6 THE EXTREMUM PRINCIPLE IN THE LEGEN-DRE TRANSFORMED REPRESENTATIONS [SUMÁRIO]

6.2 THE HELMHOLTZ POTENTIAL [SUMÁRIO]

6.2.1 Calculate the pressure on each side of the internal piston in Example 1, for ... [SUMÁRIO]

SOLUÇÃO:

Volume total = 11 litros $\equiv V_0$

No lado esquerdo : $P^{(1)} = RT/V^{(1)}$, No lado direito : $P^{(2)} = \dfrac{RT}{V^{(2)}} = \dfrac{RT}{V_0 - V^{(1)}}$

$$\therefore P^{(1)} - P^{(2)} = RT\left[\frac{1}{V^{(1)}} - \frac{1}{V_0 - V^{(1)}}\right]$$

$$W = \int\left[P^{(1)} - P^{(2)}\right]dV^{(1)} = RT\ln(V_f^{(1)}/V_i^{(1)}) - RT\ln(V_f^{(2)}/V_i^{(2)}) = RT\ln\frac{V_f^{(1)}V_i^{(2)}}{V_i^{(1)}V_f^{(2)}}$$

$$= RT\ln\left(\frac{6}{10}\frac{5}{1}\right) = RT\ln 3$$

6.2.2 Two ideal van der Waals fluids are contained in a cylinder, separated by an internal ... [SUMÁRIO]

SOLUÇÃO:

$$f = -\frac{a}{v} + cRT - Ts_0 - cRT\ln(cRT) - RT\ln(v - b) \quad \text{(equação 5.3-2)}$$

$$\therefore P = -\frac{\partial f}{\partial v} = \frac{a}{v^2} + \frac{RT}{v - b}$$

Isso é especificado que $v_1 + v_2 = V$ e $P_1 = P_2$

$$\therefore \frac{a_1}{v_1^2} = \frac{a_2}{v_2^2} \quad \text{,ou} \quad v_1/\sqrt{a_1} = v_2/\sqrt{a_2}$$

$$\text{e} \quad v_1 + v_2 = V$$

$$\therefore v_1 = V \frac{\sqrt{a_1}}{\sqrt{a_1} + \sqrt{a_2}} \quad , v_2 = V \frac{\sqrt{a_2}}{\sqrt{a_1} + \sqrt{a_2}}$$

$$\therefore F = -\frac{a_1}{V}\frac{\sqrt{a_1}\sqrt{a_2}}{\sqrt{a_1}} - \frac{a_2}{V}\frac{\sqrt{a_1}\sqrt{a_2}}{\sqrt{a_2}} + 2cRT - 2Ts_0 - 2cRT\ln(cRT) - RT\ln\left[\frac{V\sqrt{a_1}}{\sqrt{a_1} + \sqrt{a_2}} - b\right]$$
$$-RT\ln\left[\frac{V\sqrt{a_2}}{\sqrt{a_1}\sqrt{a_2}} - b\right]$$

$$\text{ou} \quad F = -\frac{1}{V}(\sqrt{a_1} + \sqrt{a_2})^2 + 2cRT - 2Ts_0 - 2cRT\ln(cRT) - RT\ln\left[V^2\frac{\sqrt{a_1 a_2}}{(\sqrt{a_1} + \sqrt{a_2})^2} - bV + b^2\right]$$

$$(-W) = F(2V) - F(V) = \frac{(\sqrt{a_1} + \sqrt{a_2})^2}{2V} + RT\ln\frac{V^2 d - bV + b^2}{4V^2 d - 2bV + b^2} \quad \text{Onde} \quad d \equiv \frac{\sqrt{a_1 a_2}}{(\sqrt{a_1} + \sqrt{a_2})^2}$$

6.2.3 Two subsystems are contained within a cylinder and are separated by an internal piston ... [SUMÁRIO]

SOLUÇÃO:

Metodo elementar: Há um equilíbrio do He (Hélio) e portanto nenhuma contribuição na diferença de pressão

$$\text{Portanto} \quad \Delta P = \frac{RT}{V^{(1)}} - \frac{RT}{V^{(2)}} = \frac{RT}{V^{(1)}} - \frac{RT}{V - V^{(1)}}, \quad \text{e} \quad \int \Delta P dV^{(1)} = RT\ln\frac{10 \times 10}{5 \times 15} = RT\ln\frac{4}{3}$$

Metodo Formal: Para cada subsistema:

$$F = (N + N_2)\frac{T}{T_0}f_0 - N_1 RT\ln\left[\left(\frac{T}{T_0}\right)^{3/2}\frac{V}{V_0}\frac{N_0}{N_1}\right] - N_2 R\ln\left[\left(\frac{T}{T_0}\right)^{3/2}\frac{V}{V_0}\frac{N_0}{N_2}\right]$$

$$\therefore \mu_1^{(1)} = \left(\frac{f_0}{T_0} + R\right)T - RT\ln\left[\left(\frac{T}{T_0}\right)^{3/2}\frac{V^{(1)}}{V_0}\frac{N_0}{N_1^{(1)}}\right]$$

$$\text{e} \quad \mu_1^{(2)} = \left(\frac{f_0}{T_0} + R\right)T - RT\ln\left[\left(\frac{T}{T_0}\right)^{3/2}\frac{V^{(2)}}{V_0}\frac{N_0}{N_2}\right]$$

$$\text{De} \quad \mu_1^{(1)} = \mu_1^{(2)} \quad \text{concluímos que} \quad V^{(1)}/N_1^{(1)} = V^{(2)}/N_1^{(2)} \quad , \text{Ou} \quad N_1^{(2)} = N_1 V^{(2)}/V$$

$$\therefore F = F_1 + F_2 = N\frac{T}{T_0}f_0 - \frac{3}{2}NRT\ln\frac{T}{T_0} - N_1 RT\ln\left(\frac{V}{V_0}\frac{N_0}{N_1}\right) - N_2^{(1)}RT\ln\frac{V^{(1)}N_0}{V_0 N_2^{(1)}} - N_2^{(2)}RT\ln\frac{V^{(2)}N_0}{V_0 N_2^{(2)}}$$

$$\Delta F = -RT\Delta\left\{N_2^{(1)}\ln\frac{V^{(1)}N_0}{V_0 N_2^{(1)}} + N_2^{(2)}\ln\frac{V^{(2)}N_0}{V_0 N_2^{(2)}}\right\} = -RTN_2^{(1)}\ln\frac{V_f^{(1)}}{V_l^{(1)}} - RTN_2^{(2)}\ln\frac{V_f^{(2)}}{V_f^{(2)}}$$

$$= -RT\ln\left\{\frac{5}{10} + \ln\frac{15}{10}\right\} = RT\ln\frac{4}{3} = 893 \ J$$

6.3 THE ENTHALPY: THE JOULE-THOMSOM OR"THROTTLING "PROCESS

6.3.1 A hole is opened in the wall separating two chemically identical single-component subsystems ...

SOLUÇÃO:

$$\delta H = T^{(1)}dS^{(1)} + T^{(2)}dS^{(2)} + \mu^{(1)}dN^{(1)} + \mu^{(2)}dN^{(2)}$$

$$\text{Mas} \qquad N^{(1)} + N^{(2)} = N \qquad \text{Uma constante}$$

Além disso, como a entalpia não é uma transformação de Legendre com respeito à entropia, ela herda da energia a condição de ser mínima sobre o ensemble de estados de entropia total constante.

$$\therefore \qquad S^{(1)} + S^{(2)} = S \qquad \text{Uma constante}$$

$$\text{E} \qquad \delta H = \left[T^{(1)} - T^{(2)}\right]\delta S^{(1)} + [\mu^{(1)} - \mu^{(2)}]dN^{(1)}$$

para $\delta s^{(1)}$ e $\delta N^{(1)}$ arbitrários

$$\therefore T^{(1)} = T^{(2)} \qquad \text{e} \qquad \mu^{(1)} = \mu^{(2)}$$

6.3.2 A gas has the following equations of state ...

SOLUÇÃO:

$$\frac{1}{T} = \frac{1}{3B}\frac{N^{1/3}V^{1/3}}{U^{2/3}} \qquad , \qquad \frac{P}{T} = \frac{1}{3B}\frac{N^{1/3}U^{1/3}}{V^{2/3}}$$

$$dS = \frac{1}{T}dU + \frac{P}{T}dV = \frac{1}{3B}\left[\frac{N^{1/3}V^{1/3}}{U^{2/3}}dU + \frac{N^{1/3}U^{1/3}}{V^{2/3}}dV\right] \qquad \therefore S = \frac{1}{3}[NVU]^{1/3}$$

$$\text{Ou} \qquad U = B^3S^3/NV$$

$$H = U + PV = B^3S^3/NV + (B^3S^3/NV^2)V = 2B^3S^3/NV = 2U$$

Com isso nós conseguimos encontrar

$$H = 2NT^3/3^3B^3P$$

Portanto, na expansão Joule-Thomson ($H =$constante)

$$T^3/P = \text{constante}$$

$$\text{Ou} \qquad T_f = T_i(P_f/P_i)^{1/3}$$

6.3.3 Show that for an ideal van der Waals fluid ...

SOLUÇÃO:

$$\text{Nós temos} \quad S = NR\ln\left[(v-b)(u+\frac{a}{v})^c\right] + Ns_0$$

$$\therefore u = -\frac{a}{v} + (v-b)^{-1/c} exp\left(\frac{s-s_0}{cR}\right)$$

$$P = -\frac{\partial u}{\partial v} = -\frac{a}{v^2} + \frac{1}{c}(v-b)^{-\frac{1}{c}-1} exp\left(\frac{s-s_0}{cR}\right) \quad ; \quad T = \frac{\partial u}{\partial s} = \frac{1}{cR}(v-b)^{-1/c} exp\left(\frac{s-s_0}{cR}\right)$$

$$\therefore h = u + Pv = -\frac{2a}{v} + RT\left[c + \frac{v}{v-b}\right]$$

Para achar ΔT; $\qquad \dfrac{dT}{dP} = \dfrac{v}{c_p}(T\alpha - 1),$ $\qquad$ e do problema 3 9-3:

$$\alpha = \frac{R}{Pv + \frac{2ab}{v^2} - \frac{a}{v}} \simeq \frac{R}{Pv - a/v}$$

Também $\quad \dfrac{Pv}{RT} = \dfrac{1}{1-b/v} - \dfrac{a}{RTv} \simeq 1 + \dfrac{b}{v} - \dfrac{a}{RTv} + \cdots$

$$\therefore \qquad \alpha = \frac{R}{RT\left[1 - \frac{b}{v} - \frac{2a}{RTv} + \cdots\right]} = \frac{1}{T}\left[1 - \frac{b}{v} - \frac{2a}{RTv} + \cdots\right]$$

Então $\quad \dfrac{dT}{dP} = \dfrac{v}{c_p}(T\alpha - 1) = \dfrac{v}{c_p}\left[-\dfrac{b}{v} + \dfrac{2a}{RTv}\right] = \dfrac{1}{c_p}\left[\dfrac{2a}{RT} - b\right]$

Para $\quad CO_2 \quad$, $\quad a = 401$ Pa$m^6 \quad$, $\quad b = 42,7 \times 10^{-6}m^3$

$$\frac{dT}{dP} \simeq 1,2 \times 10^{-5}\text{K/Pa} \qquad e \quad \Delta P \simeq 10^6\text{Pa}, \qquad \Delta T \simeq 12 \text{ K}$$

6.3.4 One mole of a monatomic ideal gas is in a cylinder with a movable piston on the other ... [SUMÁRIO]

SOLUÇÃO:

$$\Delta H = Q, \quad \text{Mas} \quad \Delta H = \Delta(U+PV) = \Delta\left(\frac{5}{2}PV\right) = \frac{5}{2}P\Delta V = \frac{5}{2}\times 10^7 \text{ Pa}\times 30\times 10^{-3}m^3 = 75\times 10^4 \text{ J}$$

6.3.5 Assume that the gas of Problem 6.3-4 is an ideal van der Waals fluid with the van der Waals ... [SUMÁRIO]

SOLUÇÃO:

$$h = -\frac{2a}{v} + RT\left(c + \frac{v}{v-b}\right) \qquad e \qquad \left(P + \frac{a}{v^2}\right)(v-b) = RT$$

$$\therefore h = -\frac{2a}{v} + \left(P + \frac{a}{v^2}\right)\left(cv - bc + \frac{v}{v-b}\right)$$

E com os valores dados o último termo é desprezado

$$\therefore \Delta h = 2a\left(\frac{1}{v_i} - \frac{1}{v_f}\right) = 2 \times 0,132 \times \left(\frac{1}{0,02} - \frac{1}{0,05}\right) = 7,92 \text{ Joules}$$

6.4 THE GIBBS POTENTIAL; CHEMICAL REACTIONS [SUMÁRIO]

6.4.1 One half mole of H₂S, $\frac{3}{4}$ mole of H₂O, 2 moles of H₂, and ... [SUMÁRIO]

> **Solução:**

(a) $3\mu_{H_2} + \mu_{SO_2} = \mu_{H_2S} + 2\mu_{H_2O}$

(b) $N_{H2} = 2 - 3\Delta\tilde{N}$, $N_{SO2} = 1 - \Delta\tilde{N}$, $N_{H2S} = \frac{1}{2} + \Delta\tilde{N}$, $N_{H20} = \frac{3}{4} + 2\Delta\tilde{N}$

$N_H2 = 0@\Delta\tilde{N} = \frac{2}{3}$, $N_{SO2} - 0@\Delta\tilde{N} = 1$, $N_{H2S} = O@\Delta\tilde{N} = -\frac{1}{2}$, $N_{H2O} = O@\Delta\tilde{N} = -3/8$

(c)

$$\Delta\tilde{N}_{max} = \frac{2}{3} \qquad \text{com esgotamento de } H_2$$

$$\Delta\tilde{N}_{min} = -3/8 \qquad \text{com esgotamento de } H_2O$$

(d)

$$\epsilon = \frac{\Delta\tilde{N} - \Delta\tilde{N}_{min}}{\Delta\tilde{N}_{max} - \Delta\tilde{N}_{min}} = \frac{\Delta\tilde{N} + \frac{3}{8}}{\frac{2}{3} + \frac{3}{8}} = \frac{24}{25}\Delta\tilde{N} + \frac{9}{25}$$

$$\text{Se} \qquad \Delta\tilde{N} = 1/4 \quad , \quad \epsilon = 3/5$$

$$\text{Então} \qquad N_{H_2} = 2 - \frac{3}{4} = \frac{5}{4} \quad , \quad N_{SO_2} = 0,75 \quad , \quad N_{H_2O} = \frac{5}{4} \qquad \text{e} \quad N = 4$$

$$\therefore X_{H_2} = \frac{5}{16} \quad , \quad X_{SO_2} = \frac{3}{16} \quad , \quad X_{H_2S} = \frac{3}{16} \quad , \quad X_{H_2O} = \frac{5}{16}$$

(e)

Se $\Delta\tilde{N}$ é nominalmente igual a 0,8 a solução deve ser rejeitada e trocada por $\Delta N_{max} = 2/3$

$$\text{Então} \quad N_{H_2} = 0 \quad , \quad N_{SO_2} = 1 - \frac{2}{3} = \frac{1}{3} \quad , \quad N_{H_2S} = \frac{1}{2} + \frac{4}{5} = 1,3 \quad , \quad N_{H_2O} = 2,35$$

$$\therefore N_{total} = 3,98$$

$$X_{H_2} = 0 \quad , \quad X_{SO_2} = 0,0837 \quad , \quad X_{H_2S} = 0,326 \quad , \quad X_{H_2O} = 0,590$$

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7 MAXWELL RELATIONS [SUMÁRIO]

7.2 A THERMODYNAMIC MNEMONIC DIAGRAM [SUMÁRIO]

7.2.1 In the immediate vicinity of the state T₀, v₀ the volume of a particular ... [SUMÁRIO]

> **Solução:**

7.2.2 For a particular system of 1 mole, in the vicinity of a particular state ... [SUMÁRIO]

SOLUÇÃO:

$$\alpha = \frac{1}{v}\left(\frac{\partial v}{\partial T}\right)_P = -\frac{1}{v}\left(\frac{\partial s}{\partial P}\right)_T = -\frac{A}{Tv}$$

7.2.3 Show that the relation $\alpha = \frac{1}{T}$ implies ... [SUMÁRIO]

SOLUÇÃO:

$$\left(\frac{\partial C_p}{\partial P}\right)_T = \frac{\partial}{\partial P}\left[\frac{T}{N}\left(\frac{\partial S}{\partial T}\right)_P\right]_T = \frac{T}{N}\frac{\partial^2 S}{\partial P \partial T} = -\frac{T}{N}\frac{\partial}{\partial T}\left(\frac{\partial V}{\partial T}\right)_P = -\frac{T}{N}\left(\frac{\partial(V_\alpha)}{\partial T}\right)_P$$

Então $\quad \left(\frac{\partial C_p}{\partial P}\right)_T = -\frac{T}{N}\frac{\partial}{\partial T}\left(\frac{V}{T}\right)_P = -\frac{T}{N}\left[\frac{1}{T}\left(\frac{\partial V}{\partial T}\right)_P - \frac{V}{T^2}\right] = -\frac{T}{N}\left[\frac{V}{T^2} - \frac{V}{T^2}\right] = 0$

7.3 A PROCEDURE FOR THE REDUCTION OF DERIVATIVES IN SINGLE-COMPONENT SYSTEMS [SUMÁRIO]

7.3.1 Thermodynamicists sometimes refer to the "first TdS equation"and ... [SUMÁRIO]

SOLUÇÃO:

a) Se $S = S(T,V)$:
$$dS = \left(\frac{\partial S}{\partial T}\right)_V dT + \left(\frac{\partial S}{\partial V}\right)_T dV$$

$$\text{Ou}\quad TdS = Nc_v dT + T\left(\frac{\partial P}{\partial T}\right)_V dV = Nc_v dT - T\left[\left(\frac{\partial V}{\partial T}\right)_P \Big/ \left(\frac{\partial V}{\partial P}\right)_T\right] dV$$
$$= Nc_v dT + T\frac{\alpha}{\kappa_T} dV$$

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

$$\text{ou}\quad TdS = Nc_p dT - T\left(\frac{\partial V}{\partial T}\right)_P dP$$
$$= Nc_p dT - TV\alpha dP$$

7.3.2 **Show that the second equation in the preceding problem leads directly ...** [SUMÁRIO]

SOLUÇÃO:

$$TdS = Nc_p dT - TV\alpha dP$$

$$T\left(\frac{\partial S}{\partial T}\right)_v = Nc_p - TV\alpha \left(\frac{\partial P}{\partial T}\right)_v = Nc_p - TNv\alpha \left[-\left(\frac{\partial v}{\partial T}\right)_P \middle/ \left(\frac{\partial v}{\partial P}\right)_T\right]$$

$$c_v = c_p - Tv\alpha\left[\alpha/\kappa_T\right] \quad \text{ou} \quad c_p - c_v = Tv\alpha^2/\kappa_T$$

7.3.3 **Calculate $(\partial H/\partial V)_{T,N}$ in terms of the standart quantities ...** [SUMÁRIO]

SOLUÇÃO:

$$dH = TdS + VdP$$

$$\left(\frac{\partial H}{\partial V}\right)_T = T\left(\frac{\partial S}{\partial V}\right)_T + V\left(\frac{\partial P}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V - \frac{1}{\kappa_T} = -T\frac{\left(\frac{\partial V}{\partial T}\right)_P}{\left(\frac{\partial V}{\partial P}\right)_T} - \frac{1}{\kappa_T}$$

$$= T\frac{\alpha}{\kappa_T} - \frac{1}{\kappa_T} = \frac{T\alpha - 1}{\kappa_T}$$

7.3.4 **Reduce the derivative $(\partial v/\partial s)_P$ ...** [SUMÁRIO]

SOLUÇÃO:

$$\left(\frac{\partial v}{\partial s}\right)_P = 1 \middle/ \left(\frac{\partial s}{\partial v}\right)_P = \left(\frac{\partial v}{\partial T}\right)_P \middle/ \left(\frac{\partial \alpha}{\partial T}\right)_p = v\alpha/\left(c_p/T\right) = Tv\alpha/c_p$$

7.3.5 **Reduce the derivative $(\partial s/\partial f)_v$ ...** [SUMÁRIO]

SOLUÇÃO:

$$\left(\frac{\partial s}{\partial F}\right)_v = \left[\left(\frac{\partial F}{\partial s}\right)_v\right]^{-1} = \left[-S\left(\frac{\partial T}{\partial s}\right)_v\right]^{-1} = \left[-S\frac{T}{c_v}\right]^{-1} = -c_v/TS$$

7.3.6 Reduce the derivative $(\partial s/\partial f)_P$ ... [SUMÁRIO]

SOLUÇÃO:

$$
\left(\frac{\partial s}{\partial F}\right)_P = \left[\left(\frac{\partial F}{\partial s}\right)_P\right]^{-1} = \left[-Ns\left(\frac{\partial T}{\partial s}\right)_P - NP\left(\frac{\partial N}{\partial s}\right)_P\right]^{-1} = \frac{-1}{N}\left[\frac{sT}{c_p} + P\left(\frac{\partial v}{\partial T}\right)_P \Big/ \left(\frac{\partial s}{\partial T}\right)_P\right]^{-1}
$$

$$
= -\frac{1}{N}\left[\frac{sT}{c_p} + P\frac{v\alpha}{c_p/T}\right]^{-1} = -\frac{1}{N}\left[\frac{T}{c_p}(s + Pv\alpha)\right]^{-1}
$$

$$
= -\frac{c_p}{NT}[s + Pv\alpha]^{-1}
$$

7.3.7 Reduce the derivative $(\partial s/\partial v)_h$ ... [SUMÁRIO]

SOLUÇÃO:

$$
\left(\frac{\partial s}{\partial v}\right)_H = -\left(\frac{\partial H}{\partial v}\right)_s \Big/ \left(\frac{\partial H}{\partial s}\right)_v = -V\left(\frac{\partial P}{\partial v}\right)_s \Big/ \left[TN + V\left(\frac{\partial P}{\partial s}\right)_v\right]
$$

Então
$$
\left(\frac{\partial s}{\partial v}\right)_H = v\frac{(\partial s/\partial v)_P}{(\partial s/\partial P)_v}\left[T + v\frac{(\partial P/\partial T)_v}{(\partial s/\partial T)_v}\right]^{-1}
$$

$$
= v\frac{\left(\frac{\partial s}{\partial T}\right)_P \Big/ \left(\frac{\partial v}{\partial T}\right)_P}{\left(\frac{\partial s}{\partial T}\right)_v \Big/ \left(\frac{\partial P}{\partial T}\right)_v}\left[T + v\frac{-\left(\frac{\partial v}{\partial T}\right)_P \Big/ \left(\frac{\partial v}{\partial P}\right)_T}{c_v/T}\right]^{-1}
$$

$$
= v\frac{c_P}{c_v}\frac{(\partial T/\partial v)_P}{(\partial T/\partial P)_v}\left[T + Tv\frac{v\alpha/vk_T}{c_v}\right]^{-1}
$$

$$
= -v\frac{c_P}{c_v}\left(\frac{\partial P}{\partial v}\right)_T[T + Tv\alpha/c_v\kappa_T]^{-1}
$$

$$
= -v\frac{c_p}{c_v}\left(\frac{1}{v}\kappa_T\right)\frac{1}{T}\frac{c_v\kappa_T}{c_v\kappa_T + v\alpha}
$$

$$
= \frac{c_p}{T}\frac{1}{c_v\kappa_T + v\alpha} \quad \text{com} \quad c_p - c_v - Tv\alpha^2/\kappa_T
$$

7.4 SOME SIMPLE APPLICATIONS [SUMÁRIO]

7.4.1 In the analysis of a Joule-Thomson experiment we may be given the initial ... [SUMÁRIO]

SOLUÇÃO:

$$
\left(\frac{\partial T}{\partial v}\right)_h = -\left(\frac{\partial h}{\partial v}\right)_T \Big/ \left(\frac{\partial h}{\partial T}\right)_v = -\frac{v\left(\frac{\partial P}{\partial v}\right)_T + T\left(\frac{\partial s}{\partial v}\right)_T}{v\left(\frac{\partial P}{\partial T}\right)_v + T\left(\frac{\partial s}{\partial T}\right)_v} = -\frac{-\frac{1}{\kappa_T} + T\left(\frac{\partial P}{\partial T}\right)_v}{v\left(\frac{\partial P}{\partial T}\right)_v + c_v}
$$

$$\text{Então} \quad \left(\frac{\partial T}{\partial v}\right)_h = \frac{-\frac{1}{\kappa_T} + T\alpha/\kappa_T}{v\alpha/\kappa_T + c_v} = \frac{T\alpha - 1}{v\alpha + c_v\kappa_T} \qquad (\text{e} \quad c_v = c_p - Tv\alpha^2/\kappa_T)$$

7.4.2 The adiabatic bulk modulus is defined by ... [SUMÁRIO]

SOLUÇÃO:

$$\beta_S \equiv -V\left(\frac{\partial P}{\partial V}\right)_S = V\frac{\left(\frac{\partial S}{\partial V}\right)_P}{\left(\frac{\partial S}{\partial P}\right)_V} = V\frac{\left[\left(\frac{\partial S}{\partial T}\right)_P / \left(\frac{\partial V}{\partial T}\right)_P\right]}{\left[\left(\frac{\partial S}{\partial T}\right)_V / \left(\frac{\partial P}{\partial T}\right)_V\right]}$$

$$\beta_S = V\frac{c_p}{c_v}\frac{(\partial T/\partial V)_p}{(\partial T/\partial P)_V} = -V\frac{c_p}{c_v}\left(\frac{\partial P}{\partial V}\right)_T = \frac{c_p}{c_v\kappa_T}$$

7.4.3 Evaluate the change in temperature in an infinitesimal free expansion of ... [SUMÁRIO]

SOLUÇÃO:

Da equação 7.51 $\quad dT = \left[\frac{P}{Nc_v} - \frac{T\alpha}{Nc_v\kappa_T}\right]dV, \qquad$ mas$\alpha = 1/T \quad$ e $\quad \kappa_T = 1/P \quad$ para um gás ideal

$$\therefore dT = 0$$

de forma mais geral, para um gás ideal $U = U(T, N)$, e se U é constante então T é constante.

7.4.4 Show that equation 7.46 can be written as ... [SUMÁRIO]

SOLUÇÃO:

NENHUMA SOLUÇÃO PARA ESSE PROBLEMA NO MOMENTO

7.4.5 A 1% decrease in volume of a system is carried out adiabatically. Find ... [SUMÁRIO]

SOLUÇÃO:

$$\left(\frac{\partial \mu}{\partial V}\right)_S = v\left(\frac{\partial P}{\partial V}\right)_S - s\left(\frac{\partial T}{\partial V}\right)_S = -v\frac{(\partial S/\partial V)_P}{(\partial S/\partial P)_V} + s\frac{(\partial S/\partial v)_T}{(\partial S/\partial T)_v}$$

$$\text{Então} \quad \left(\frac{\partial \mu}{\partial V}\right)_S = -v\frac{c_p/\left(\frac{\partial V}{\partial T}\right)_P}{c_v/\left(\frac{\partial P}{\partial T}\right)_V} + s\frac{(\partial P/\partial T)_V}{Nc_v/T} = v\frac{c_p}{c_v}\left(\frac{\partial P}{\partial V}\right)_T + \frac{TS}{N^2 c_v}\left(\frac{-\left(\frac{\partial V}{\partial T}\right)_P}{\left(\frac{\partial V}{\partial P}\right)_T}\right)$$

$$= -\frac{c_p}{Nc_v\kappa_T} - \frac{Ts}{Nc_v}\frac{\alpha}{\kappa_T} = -\frac{N}{c_v\kappa_T}\left[c_p + T\alpha s\right]$$

$$\text{ou} \quad V\left(\frac{\partial \mu}{\partial V}\right)_S = -\frac{v}{c_v\kappa_T}\left(c_p + T\alpha s\right) \qquad (\text{com} \quad c_p = c_v + Tv\alpha^2/\kappa_T)$$

7.4.6 Two moles of an imperfect gas occupy a volume of 1 liter and are at ... [SUMÁRIO]

SOLUÇÃO:

$$\Delta H = \left[T\left(\frac{\partial S}{\partial V}\right)_U + V\left(\frac{\partial P}{\partial V}\right)_U \right]\Delta V = \left[-T\frac{(\partial U/\partial V)_S}{(\partial U/\partial S)_V} - v\frac{(\partial U/\partial V)_P}{(\partial U/\partial P)_V} \right]\Delta V$$

$$\Delta H = \left[-T\frac{(-P)}{T} - V\frac{T\left(\frac{\partial S}{\partial V}\right)_P - P}{T\left(\frac{\partial S}{\partial P}\right)_V} \right]\Delta V = \left[P - V\frac{Nc_p/\left(\frac{\partial V}{\partial T}\right)_P - P}{Nc_v/\left(\frac{\partial P}{\partial T}\right)_V} \right]\Delta V$$

$$\frac{\Delta H}{\Delta V} = P - V\frac{Nc_p/V\alpha - P}{Nc_v\kappa_T/\alpha} = P - \frac{c_p - Pv\alpha}{c_v\kappa_T} = P - \frac{c_p - Pv\alpha}{c_p\kappa_T - Tv\alpha^2}$$

$$\therefore \boxed{\Delta H = 15 \text{ Joules}}$$

7.4.7 Show that $(\partial c_v/\partial v)_T = T(\partial^2 P/\partial T^2)_v$ and evaluate this ... [SUMÁRIO]

SOLUÇÃO:

$$\left(\frac{\partial c_v}{\partial v}\right)_T = T\frac{\partial}{\partial T}\left(\left(\frac{\partial s}{\partial v}\right)_T\right)_v$$

$$\frac{\partial}{\partial T_v}\frac{\partial s}{\partial v_T} = T\frac{\partial}{\partial T_v}\left(\frac{\partial P}{\partial T}\right)_v = T\left(\frac{\partial^2 P}{\partial T^2}\right)_v$$

As equações de Van der Waals são $\qquad \left(P + \frac{a}{v^2}\right)(v - b) = RT \qquad$ ou $\qquad P = -\frac{a}{v^2} + \frac{RT}{v - b}$

$$\therefore \left(\frac{\partial P}{\partial T}\right)_v = \frac{R}{v - b} \quad \text{e} \quad \left(\frac{\partial^2 P}{\partial T^2}\right)_v = 0$$

$$\therefore \boxed{\left(\frac{\partial c_v}{\partial v}\right)_T = 0} \quad \text{para a equação de estado de Van der Waals}$$

7.4.8 Show that ... [SUMÁRIO]

SOLUÇÃO:

$$\left(\frac{\partial c_p}{\partial P}\right)_T = \frac{\partial}{\partial P_T}\left(T\frac{\partial s}{\partial T_P}\right) = T\frac{\partial^2 s}{\partial P \partial T} = T\frac{\partial^2 s}{\partial T \partial T} = -T\frac{\partial}{\partial T_p}\frac{\partial v}{\partial T_p} = -T\left(\frac{\partial^2 v}{\partial T^2}\right)_P$$

Então $\qquad \left(\frac{\partial c_p}{\partial P}\right)_T = -T\left(\frac{\partial}{\partial T}v\alpha\right)_p = -Tv\left(\frac{\partial \alpha}{\partial T}\right)_p - T\alpha^2 v = -Tv\left[\alpha^2 + \left(\frac{\partial \alpha}{\partial T}\right)_p\right]$

Se $\quad P\left(c + A/T^2\right) = RT \quad$ então $\quad v = RT/P - A/T^2$

$$\therefore \left(\frac{\partial v}{\partial T}\right)_P = \frac{R}{p} + \frac{2A}{T^3} \quad \text{e} \quad \left(\frac{\partial^2 v}{\partial T^2}\right)_P = -\frac{6A}{T^4}$$

$$\therefore \boxed{\left(\frac{\partial c_p}{\partial P}\right)_T = \frac{6A}{T^3}}$$

7.4.9   One mole of the system of Problem 7.4-8 is expanded isothermally ...   [SUMÁRIO]

Solução:

$$Q = \int T ds = T \int \left(\frac{\partial s}{\partial P}\right)_T dP = -T \int \left(\frac{\partial v}{\partial T}\right)_P dP = -T \int \left(\frac{R}{P} + \frac{2A}{T^3}\right) dP$$

$$\therefore \boxed{Q = -RT \ln \frac{P_f}{P_0} - 2 \frac{A}{T^2} \left(P_f - P_0\right)}$$

7.4.10   A system obeys the van der Waals equation of state.   One mole...   [SUMÁRIO]

Solução:

$$Q = T \int \left(\frac{\partial s}{\partial v}\right)_T dv = T \int \left(\frac{\partial P}{\partial T}\right)_v dv = T \int \frac{1}{v - b} dv = T \ln \frac{v_f - b}{v_i - b}$$

7.4.11   Two moles of O_2 are initially at a pressure of 10^5 Pa and a temperature... [SUMÁRIO]

Solução:

$$\left(\frac{\partial P}{\partial T}\right)_S = \frac{c_p}{Tv\alpha} = Pc_p/RT^2\alpha \quad \text{and} \quad \alpha = \frac{1}{v}\left(\frac{\partial v}{\partial T}\right)_P = \frac{1}{v}\left(\frac{R}{P}\right) = \frac{1}{T}$$

$$\therefore \left(\frac{\partial P}{\partial T}\right)_S = \frac{Pc_P}{RT} \quad \text{e} \quad R\frac{dP}{P} = \left[\frac{26,2}{T} + 11,5 \times 10^{-3} - 3,22 \times 10^{-6}T\right] dT$$

$$R \ln \frac{P_f}{P_i} = 26,2 \ln \frac{T_f}{T_i} + 11,5 \times 10^{-3}\left(T_f - T_i\right) - 1.61 \times 10^{-6}\left(T_f^2 - T_i^2\right)$$

$$\ln \frac{P_f}{P_i} = 2,33 + 0,414 - 0,049 = 2,695$$

$$\therefore \boxed{P_f = 14,8 P_i = 14,8 \times 10^5 P_a}$$

7.4.12   A ball bearing of mass 10g just fits in a vertical glass tube of ...   [SUMÁRIO]

Solução:

Primeiro encontramos $\quad \left(\frac{\partial P}{\partial V}\right)_S = -\left(\frac{\partial S}{\partial V}\right)_P \Big/ \left(\frac{\partial S}{\partial P}\right)_V = -\frac{\left[\left(\frac{\partial S}{\partial T}\right)_P \Big/ \left(\frac{\partial V}{\partial T}\right)_P\right]}{\left[\left(\frac{\partial S}{\partial T}\right)_V \Big/ \left(\frac{\partial P}{\partial T}\right)_V\right]} = -\frac{c_p}{V \kappa_T c_v}$

Da lei de Hooke : $\quad K_{mola} = -\frac{F}{X} = -\frac{\partial(PA)}{\partial(V/A)} = -(A)^2 \left(\frac{\partial P}{\partial V}\right)_S = A^2 \frac{c_p}{c_v} \frac{1}{V \kappa_T} \qquad (A \quad \text{é a área})$

Em $\quad T = 303$ K; $\quad c_p = 29,39$ J/ K $\quad$ e $\quad c_v = c_p - R = 21.08$ J/ K $\quad$ e $\quad \kappa_T = 1/P = 10^{-5}$ Pa^{-1}

$$\therefore K_{mola} = \left[2 \times 10^{-2} \text{ m}^2\right]^2 \times \frac{29,39}{21,08} \times \frac{1}{5 \times 10^{-3} \text{ m}^3} \frac{1}{10^{-5} \text{ Pa}^{-1}} = 1,11 \times 10^4 \text{ newton/metro}$$

$$\omega = \sqrt{\frac{K_{mola}}{massa}} = \left(\frac{1,11 \times 10^4}{10^{-2}}\right)^{1/2} \simeq 10^3 \text{ segundo}^{-1} \qquad (freq = 159 \text{ ciclos/segundo})$$

A frequência é muito alta pois a massa é muit pequena e a área muito grande. _____

7.4.13 Calculate the change in the molar internal energy in a throttling ... [SUMÁRIO]

SOLUÇÃO:

$$\left(\frac{\partial u}{\partial P}\right)_H = T\left(\frac{\partial s}{\partial P}\right)_H - P\left(\frac{\partial v}{\partial P}\right)_H = -T\left(\frac{\partial H}{\partial P}\right)_S \bigg/ \left(\frac{\partial H}{\partial s}\right)_P + P\left(\frac{\partial H}{\partial P}\right)_v \bigg/ \left(\frac{\partial H}{\partial v}\right)_P$$

Então $\qquad \left(\frac{\partial u}{\partial P}\right)_H = -T\frac{v}{T} + P\frac{V + T\left(\frac{\partial S}{\partial P}\right)_V}{T\left(\frac{\partial S}{\partial v}\right)_p} = -v + P\frac{V + Nc_v\kappa_T/\alpha}{Nc_p/v\alpha} = -v + Pv\frac{\alpha v + c_v\kappa_T}{c_p}$

$$\therefore du = v\left[\frac{p}{c_p}(\alpha v + c_v\kappa_T) - 1\right]dP \qquad \text{com} \qquad c_v = c_p - Tv\alpha^2/\kappa_T$$

_____

7.4.14 Assuming that a gas undergoes a free expansion and that the ... [SUMÁRIO]

SOLUÇÃO:

$$\left(\frac{\partial P}{\partial T}\right)_U = -\left(\frac{\partial U}{\partial T}\right)_P \bigg/ \left(\frac{\partial U}{\partial P}\right)_T = \frac{T\left(\frac{\partial s}{\partial T}\right)_P - P\left(\frac{\partial U}{\partial T}\right)_P}{T\left(\frac{\partial s}{\partial P}\right)_T - P\left(\frac{\partial v}{\partial P}\right)_T} = \frac{c_p - Pv\alpha}{-T\left(\frac{\partial v}{\partial T}\right)_P - P\left(\frac{\partial v}{\partial P}\right)_T}$$

$$= \frac{c_p - Pv\alpha}{-Tv\alpha + Pv\kappa_T}$$

$$\therefore \quad dP = \frac{(c_p/v) - P_\alpha}{T\alpha - P\kappa_T}dT$$

_____

7.4.15 One mole of an ideal van der Waals fluid is contained in a vessel ... [SUMÁRIO]

SOLUÇÃO:

$$S = Ns_0 + NR\ln\left[\left(u + \frac{a}{v}\right)^c (v - b)\right]$$

$$\text{e} \quad \frac{1}{T} = \frac{\partial s}{\partial u} = cR/(u + a/v) \quad \text{ou} \quad u = cRT - \frac{a}{v} = \text{const.}$$

$$\therefore cR\Delta T = a\Delta\left(\frac{1}{v}\right) \quad \text{or} \quad \Delta T = \frac{a}{cR}\Delta\left(\frac{1}{v}\right)$$

As constante de Van der Waals para o argônio são $a = 0,132$ Pam^6, $b = 30,2 \times 10^{-6}m^3$, $c = 1,5$

$$\therefore \quad \Delta T = \frac{0,132}{1,5 \times 8,314}\left[\frac{10^3}{5} - \frac{10^3}{2}\right] = -3,2 \text{ K} \quad \text{e} \quad \boxed{T_f = 296.8 \text{ K}}$$

7.4.16 Assuming the expansion of the ideal van der Waals fluid of ... [SUMÁRIO]

Solução:

$$S = Ns_0 + NR \ln \left[(cRT)^c (v - b) \right]$$

$$\therefore T^c (v - b) = const.$$

$$\text{ou} \qquad T_f = T_i \left(\frac{v_i - b}{v_f - b} \right)^{1/c} = 300 \left(\frac{2 - 0,03}{5 - 0,03} \right)^{2/3} = 162 \text{ K}$$

7.4.17 It is observed that an adiabatic decrease in molar volume of 1% ... [SUMÁRIO]

Solução:

$$d\mu = \left(\frac{\partial \mu}{\partial v} \right)_s \times (.01v) = \left(\frac{\partial \mu}{\partial v} \right)_T \times (av)$$

$$\therefore a = 0,01 \left(\frac{\partial \mu}{\partial v} \right)_s \Big/ \left(\frac{\partial \mu}{\partial v} \right)_T$$

$$\text{Mas} \qquad \left(\frac{\partial \mu}{\partial v} \right)_s = v \left(\frac{\partial P}{\partial v} \right)_s - s \left(\frac{\partial T}{\partial v} \right)_s = -v \left(\frac{\partial s}{\partial v} \right)_P \Big/ \left(\frac{\partial s}{\partial P} \right)_v + s \left(\frac{\partial s}{\partial v} \right)_T \Big/ \left(\frac{\partial s}{\partial T} \right)_v$$

$$\text{Então} \qquad \left(\frac{\partial \mu}{\partial v} \right)_s = -v \frac{\left(\frac{\partial s}{\partial T} \right)_P \Big/ \left(\frac{\partial s}{\partial T} \right)_P}{\left(\frac{\partial s}{\partial T} \right)_v \Big/ \left(\frac{\partial P}{\partial T} \right)_v} + s \frac{\left(\frac{\partial P}{\partial T} \right)_v}{c_v / T}$$

$$= -\frac{c_p}{c_v} \frac{1}{\kappa_T} + \frac{Ts}{c_v} \frac{\alpha}{\kappa_T} = \frac{1}{c_v \kappa_T} (Ts\alpha - c_p)$$

$$\text{similarmente} \qquad \left(\frac{\partial \mu}{\partial v} \right)_T = v \left(\frac{\partial P}{\partial v} \right)_T - s = -[\kappa_T^{-1} + s] = -\frac{1 + s\kappa_T}{\kappa_T}$$

$$\therefore a = 0,01 \left(\frac{Ts\alpha - c_p}{c_v \kappa_T} \right) \Big/ \left(-\frac{1 + s\kappa_T}{\kappa_T} \right) \implies \boxed{a = 0,01 \frac{c_p - Ts\alpha}{(1 + s\kappa_T) c_v}}$$

7.4.18 A cylinder is fitted with a piston, and the cylinder contains helium ... [SUMÁRIO]

Solução:

$$K_{\mu,T} = -\frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_{\mu,T} = \frac{1}{V} \left(\frac{\partial \mu}{\partial P} \right)_{T,V} \Big/ \left(\frac{\partial \mu}{\partial V} \right)_{T,P}$$

$$\text{Mas} \quad d\mu = vdP - sdT \quad \text{e} \ \therefore \quad \left(\frac{\partial \mu}{\partial p} \right)_{T,V} = v$$

$$k_{\mu,T} = N \Big/ \left(\frac{\partial \mu}{\partial V} \right)_{T,P} \qquad \text{Mas, pela relação de Gibbs-Duhem} \left(\frac{\partial \mu}{\partial V} \right)_{T,P} = 0 \quad \text{e } k_{\mu,T} \text{ diverge.}$$

Em termos da situação física descrita no texto, H_2 atravessa a barreira na medida em que o volume é alterado, mantendo a pressão constante. Consequentemente $\left(\dfrac{\partial V}{\partial P}\right)_{\mu,T}$ diverge. Alternativamente, note que $\mu = \mu(T,P)$ ou $P = P(T,\mu)$ independem de v.

7.4.19   The cylinder in Problem 7.4-18 is initially filled with $\frac{1}{10}$ mole of ... [SUMÁRIO]

Do problema 5.3-10:

$$F = \left(\frac{3}{2}R - s_0\right)TN - \frac{3}{2}N_1 RT \ln\left[\frac{T}{T_0}\left(\frac{V}{V_0}\right)^{2/3}\left(\frac{N_0}{N_1}\right)^{2/3}\right] - \frac{3}{2}N_2 RT \ln\left[\frac{T}{T_0}\left(\frac{V}{V_0}\right)^{2/3}\left(\frac{N_0}{N_2}\right)^{2/3}\right]$$

$$\mu_1 = \frac{\partial F}{\partial N_1} = \left(\frac{3}{2}R - s_0\right)T - \frac{3}{2}RT \ln\left[\frac{T}{T_0}\left(\frac{V}{V_0}\right)^{2/3}\left(\frac{N_0}{N_1}\right)^{2/3}\right] + RT$$

$$\text{ou} \qquad N_1/N_0 = (V/V_0)\,(T/T_0)^{3/2} \exp\left[\frac{\mu_1 - \frac{5}{2}RT + Ts_0}{RT}\right]$$

$$P = (N_1 + N_2)\frac{RT}{V} = \frac{RT}{V}\left[N_2 + \frac{V}{V_0}N_0\left(\frac{T}{T_0}\right)^{3/2}\exp\left[\frac{\mu_1}{RT} - \frac{5}{2} + \frac{s_0}{R}\right]\right]$$

$$\text{Também} \qquad P = \frac{N_2 RT}{V} + AT^{3/2}e^{\mu_1/RT} \qquad A = const$$

$$\text{E ainda} \qquad \kappa_T = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T = -\frac{1}{V}\left/\left(\frac{\partial P}{\partial V}\right)_T\right. = -\frac{1}{V}\left/\left(-\frac{N_2 RT}{V^2}\right)\right. = \frac{V}{N_2 RT}$$

$$\therefore \boxed{\kappa_T = \frac{1}{\text{Pressão parcial de } N_e}}$$

7.4.20   A system is composed of I mole of a particular substance.   In the ... [SUMÁRIO]
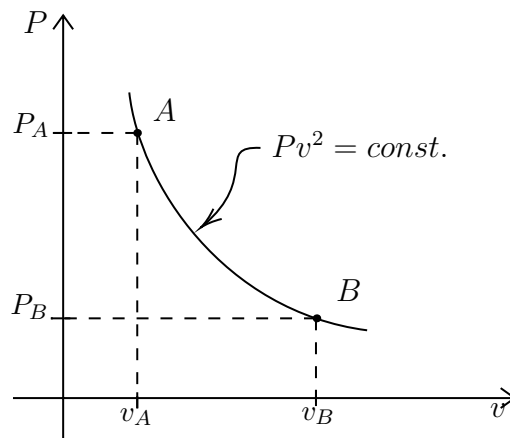
$$\delta T = \left(\frac{\partial T}{\partial v}\right)_P \delta v + \left(\frac{\partial T}{\partial P}\right)_v \delta P = \frac{1}{v\alpha}\delta v + \frac{\kappa_T}{\alpha}\delta P = \left[\frac{1}{v\alpha} + \frac{\kappa_T}{\alpha}\frac{dP}{dv}\right]\delta v$$

$$\text{Mas} \quad P = P_A v_A^2 / v^2 \quad \text{então} \quad \frac{dP}{dv} = -2P_A v_A^2 / v^3$$

$$\therefore \delta T = \left[\frac{1}{v\alpha} - \frac{\kappa_T}{\alpha} \frac{2P_A v_A^2}{v^3} \right] \delta v = \left[\frac{1}{D} + \frac{E}{D} v^2 \frac{2P_A v_A^2}{v^3} \right] \delta v$$

$$\therefore T_B - T_A = \frac{v_B - v_A}{D} + \frac{2}{D} E P_A v_A^2 \ln \frac{v_B}{v_A}$$

7.4.21 A system is composed of I mole of a particular substance. Two ... [SUMÁRIO]

Solução:
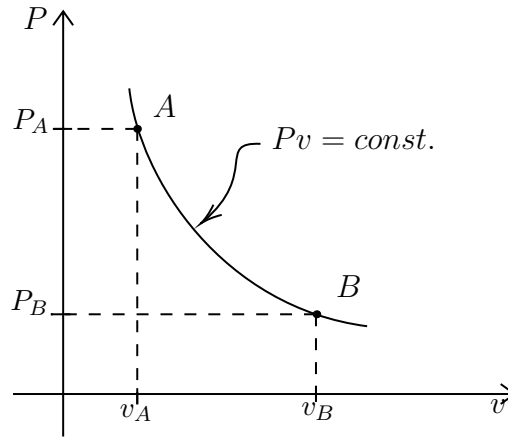
$$du = Tds - Pdv$$

$$= T\left(\frac{\partial s}{\partial v}\right)_P \delta v + T\left(\frac{\partial s}{\partial P}\right)_v \delta P - P\delta v$$

$$= \frac{c_p}{\alpha v} \delta v + \frac{c_v \kappa_T}{\alpha} \delta P - P\delta v$$

$$\therefore \delta u = \left(\frac{c_p}{v\alpha} - P\right)\delta v + \frac{c_v \kappa_T}{\alpha} \frac{dP}{dv} dv = \left[\frac{c_p}{v\alpha} - P + \frac{c_v \kappa_T}{\alpha}\left(-\frac{P_A v_A}{v^2}\right)\right]\delta v$$

$$= \left[\frac{c_p}{v\alpha} - \frac{P_A v_A}{v} - \frac{P_A v_A}{v^2} \frac{c_v \kappa_T}{\alpha}\right]\delta v \quad \text{but} \quad c_v = c_p - Tv\alpha^2/\kappa_T = c_p - \frac{D^2}{E}\frac{T}{v^4}$$

$$= \left[\frac{C}{D}\left(1 - P_A v_A E\right)v^2 - \frac{P_A v_A}{v} + \frac{P_A v_A D T}{v^3}\right]\delta v$$

Para integrar isso, precisamos de $T(v)$. Como no problema 7.4-20 temos

$$\delta T = \left[\frac{1}{v\alpha} + \frac{\kappa_T}{\alpha}\frac{dP}{dv}\right]\delta v$$

$$= \left[\frac{1}{v\alpha} - \frac{\kappa_T}{\alpha}\frac{P_A v_A}{v^2}\right]\delta v = \left[\frac{v}{D} - \frac{E v^3}{D}\frac{P_A v_A}{v^2}\right]\delta v$$

$$T = T_A + \frac{1}{2D}\left(1 - E P_A v_A\right)\left(v^2 - v_A^2\right) \equiv T_A + \left(\frac{v^2}{v_A^2} - 1\right)T_1$$

$$\text{onde} \quad T_1 \equiv \frac{v_A^2}{2D}\left(1 - E P_A v_A\right)$$

$$\text{Então} \quad \delta u = \frac{C}{D}\left(1 - P_A v_A E\right)v^2 - \frac{P_A v_A}{v} + P_A v_A D\left[\frac{T_A - T_1}{v^3} + \frac{T_1}{v_A^2}\frac{1}{v}\right]\delta v$$

E finalmente

$$u_B = u_A + \frac{C}{3D}\left(1 - P_A v_A E\right)\left(v_B^3 - v_A^3\right) - P_A v_A \ln\frac{v_B}{v_A} + P_A v_A D\left[-2\left(T_A - T_1\right)\left(\frac{1}{v_B^2} - \frac{1}{v_A^2}\right) + \frac{T_1}{v_A^2}\ln\frac{v_B}{v_A}\right]$$

7.4.22 The constant-volume heat capacity of a particular simple system is ...
[SUMÁRIO]

SOLUÇÃO:

$$T\left(\frac{\partial s}{\partial T}\right)_v = AT^3 \qquad \therefore s = \frac{1}{3}AT^3 + f(v) \quad f \text{ é desconhecido}$$

Agora, note que $\quad \dfrac{\partial^2 s}{\partial T \partial v} = 0, \quad$ mas $\quad \dfrac{\partial^2 s}{\partial T \partial v} = \dfrac{\partial}{\partial T}\left(\dfrac{\partial P}{\partial T}\right)_v = \left(\dfrac{\partial^2 P}{\partial T^2}\right)_V = 0$

Mas $\quad P = B(T)/\left(v - v_0\right) \quad$ então $\quad \dfrac{d^2 B}{dT^2} = 0, \quad$ ou $\quad B(T) = DT + E \qquad (D \text{ e } E \text{ são constantes})$

$\therefore (v - v_0)P = DT + E \quad$ de onde inferimos $\quad \alpha = \dfrac{1}{v}\left(\dfrac{\partial v}{\partial T}\right)_P = \dfrac{1}{v}\dfrac{T}{P} = \dfrac{T}{v}\dfrac{v - v_0}{DT + E}$

Também $\quad \kappa_T = -\dfrac{1}{v}\left(\dfrac{\partial v}{\partial P}\right)_T = -\dfrac{1}{v}\left(-\dfrac{DT + E}{P^2}\right) = (DT + E)^{-1}\left(v - v_0\right)^2/v$

$$c_p = c_v + \frac{Tv\alpha^2}{\kappa_T} = AT^3 + Tv\left[\frac{T}{v}\frac{v - v_0}{DT + E}\right]^2 \frac{(DT + E)v}{\left(v - v_0\right)^2}$$

$$c_p = AT^3 + \frac{T^3}{DT + E}$$

7.4.23 A system is expanded along a straight line in the $P - v$ plane, from ...
[SUMÁRIO]

SOLUÇÃO:
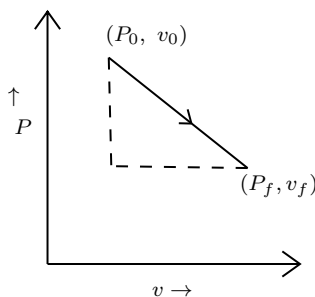
Ao longo da isocórica $v = v_0$:

$$du = \left(\frac{\partial u}{\partial P}\right)_v \delta P = \frac{c_v \kappa_T}{\alpha}dP = APdP$$

Ao longo da isobárica $P = P_f$:

$$du = \left(\frac{\partial u}{\partial v}\right)_P dv = (c_p/v_\alpha - P)\,dv = (Bv - P_f)\,dv$$

Então, em $v = v_0$:

$$\Delta u_1 = \frac{1}{2}A\left(P_f^2 - P_0^2\right)$$

Em $P = P_f$:

$$\Delta u_2 = \frac{1}{2}B\left(v_f^2 - v_0^2\right) - P_f\left(v_f - v_0\right)$$

$$\therefore \quad \Delta u = \frac{1}{2}A\left(P_f^2 - P_0^2\right) + \frac{1}{2}B\left(v_f^2 - v_0^2\right) + \frac{1}{2}\left(P_0 - P_f\right)\left(v_f - v_0\right)$$

Mas o trabalho realizado no processo direto é

$$W = -\int P dv = -\frac{1}{2}\left(P_0 + P_f\right)\left(v_f - v_0\right)$$

$$\therefore \boxed{Q = \Delta u - W = \frac{1}{2}A\left(P_f^2 - P_0^2\right) + \frac{1}{2}B\left(v_f^2 - v_0^2\right) + \frac{1}{2}\left(P_0 - P_f\right)\left(v_f - v_0\right)}$$

7.4.24 A nonideal gas undergoes a throttling process (i.e., a Joule-Thomson expansion) ... [SUMÁRIO]

SOLUÇÃO:
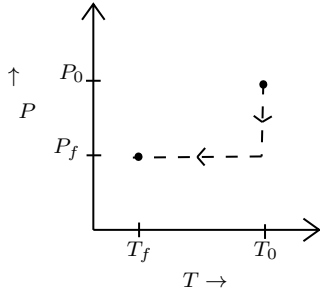
Integre ao longo do caminho mostrado na figura para encontrar Δh:
Ao longo da Isoterma T_0:

$$dh = \left(\frac{\partial h}{\partial P}\right)_T dP = v(1 - T\alpha)dP = v\left(1 - T_0\alpha_0\right)dP$$

Mas para encontrar $v(P)$:

$$\kappa_T = -\frac{1}{v}\frac{\partial v}{\partial P} = A/v^2 \quad \text{or} \quad v^2 = v_0^2 - 2A\left(P - P_0\right)$$

$$\therefore \quad dh = \left[v_0^2 - 2A\left(P - P_0\right)\right]^{1/2}\left(1 - T_0\alpha_0\right)dP$$

$$\text{e} \quad h = \frac{1 - T_0\alpha_0}{-3A}\left[v_0^2 - 2A\left(P - P_0\right)\right]^{3/2} + \text{const.}$$

$$\Delta h_1 = \frac{1 - T_0\alpha_0}{3A}\left\{v_0^3 - \left[v_0^2 - 2A\left(P_f - P_0\right)\right]^{3/2}\right\}$$

Então, ao longo a isobárica P_f:

$$\Delta h_2 = \int_{T_0}^{T_F}\left(\frac{\partial h}{\partial T}\right)_{P_f}dT = \int_{T_0}^{T_f}c_p dT = c_p^0\left(T_f - T_0\right)$$

Mas h é conservado na expansão:

$$\Delta h_1 + \Delta h_2 = 0$$

Assim,

$$T_f = T_0 - \frac{1 - T_0\alpha_0}{3Ac_p^0}\left\{v_0^3 - \left[v_0^2 - 2A\left(P_f - P_0\right)\right]^{3/2}\right\}$$

Note que a quantidade entre as chaves é positiva. Consequentemente $T_f < T_0$ se $T_0\alpha < 1$.

7.5 GENERALIZATIONS: MAGNETIC SYSTEMS [SUMÁRIO]

7.5.1 Calculate the "magnetic Gibbs potential" $U[T, B_e]$ for the paramagnetic ... [SUMÁRIO]

SOLUÇÃO:

$$U = NRT_0 \exp\left[\frac{S}{NR} + \frac{\mu_0}{2\chi_1 R}\frac{I^2}{N^2}\right] \quad \text{and} \quad U[T, B_e] = U - TS - B_e T$$

$$\text{Mas} \quad U = NRT \quad \text{e} \quad I = \frac{\chi_1 N}{\mu_0}\frac{B_e}{T}$$

$$\therefore U[T, B_e] = NRT - TS - \frac{\chi_1 N}{\mu_0 T}B_e^2$$

Ainda devemos eliminar S:

$$\ln\left(\frac{U}{NRT_0}\right) = \frac{S}{NR} + \frac{\mu_0}{2\chi_1 R}\frac{I^2}{N^2} \quad \Longrightarrow \quad \frac{S}{NR} = \ln T - \frac{\chi_1 B_e^2}{2\mu_0 RT^2}$$

$$\therefore U[T, B_e] = NRT\left[1 - \ln T - \frac{\chi_1 B_e^2}{2\mu_0 RT^2}\right]$$

$$\text{Para checar:} \quad \frac{\partial U[T, B_e]}{\partial B_e} = -\frac{N}{T}\chi_1 B_e = -I \quad \boxed{\textbf{OK}}$$

7.5.2 Repeat Problem 7.5-1 for the system with the fundamental equation given ... [SUMÁRIO]

SOLUÇÃO:

$$T = \frac{2\epsilon}{k_B}\exp\left(\frac{2S}{Nk_B}\right) \quad \text{e} \quad B_e = \mu_0 I/N\chi \quad (\text{ou} \quad I = N\chi B_e/\mu_0)$$

$$\therefore \quad U[T, B_e] = U - TS - B_e I = \frac{1}{2}N\chi\mu_0^{-1}B_e^2 - N\chi\mu_0^{-1}B_e^2 - \frac{1}{2}Nk_B T\ln\left(\frac{k_B T}{2\epsilon}\right)$$

$$\therefore \quad \boxed{U[T, B_e] = -\frac{1}{2\mu_0}N\chi B_e^2 - \frac{1}{2}Nk_B T\ln\left(\frac{k_B T}{2\epsilon}\right)}$$

7.5.3 Calculate $(\partial I/\partial T)_s$ for the paramagnetic model of equation 3.66. ... [SUMÁRIO]

SOLUÇÃO:

$$U = NRT_0\exp\left[\frac{S}{NR} + \frac{\mu_0}{2\chi_1 R}\frac{I^2}{N^2}\right] \quad \text{e} \quad U = NRT \quad \text{de onde} \quad \ln\frac{T}{T_0} = \frac{S}{NR} + \frac{\mu_0}{2\chi_1 R}\frac{I^2}{N^2}$$

$$\text{e} \quad \therefore \quad \left(\frac{\partial I}{\partial T}\right)_S = NR/B_e$$

Similarmente $\quad S = -\dfrac{\mu_0}{2\chi_0 N}I^2 + NR\ln\left(\dfrac{N\chi_0 B_e}{IT_0}\right) \quad$ e $\therefore \left(\dfrac{\partial S}{\partial B_e}\right)_I = \dfrac{NR}{B_e}$

Então $\quad \left(\dfrac{\partial I}{\partial T}\right)_S = \left(\dfrac{\partial S}{\partial B_e}\right)_I$
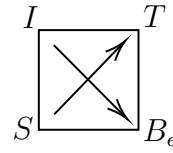
7.5.4 Show that ... [SUMÁRIO]

SOLUÇÃO:

Seja $S = S(I,T,V)$, então $\quad T\left(\dfrac{\partial S}{\partial T}\right)_{B_e} = T\left(\dfrac{\partial S}{\partial I}\right)_T\left(\dfrac{\partial I}{\partial T}\right)_{B_e} + T\left(\dfrac{\partial S}{\partial T}\right)_I$

$$\therefore C_{B_e} - C_I = T\left(\dfrac{\partial S}{\partial I}\right)_T\left(\dfrac{\partial I}{\partial T}\right)_{B_e} = -T\left(\dfrac{\partial B_e}{\partial T}\right)_I\left(\dfrac{\partial I}{\partial T}\right)_{B_e}$$

$$C_{B_e} - C_I = -T\left[\left(\dfrac{\partial I}{\partial T}\right)_{B_E}\middle/\left(\dfrac{\partial I}{\partial B_e}\right)_T\right]\left(\dfrac{\partial I}{\partial T}\right)_{B_e} = \mu_0 T\left(\dfrac{\partial I}{\partial T}\right)^2\middle/\chi_T$$

$$\dfrac{C_{B_e}}{C_I} = \dfrac{\left(\dfrac{\partial S}{\partial T}\right)_{B_e}}{\left(\dfrac{\partial S}{\partial T}\right)_I} = \dfrac{-\left(\dfrac{\partial B_e}{\partial T}\right)_S\middle/\left(\dfrac{\partial B_e}{\partial S}\right)_T}{-\left(\dfrac{\partial I}{\partial T}\right)_S\middle/\left(\dfrac{\partial I}{\partial S}\right)_T} = \left(\dfrac{\partial B_e}{\partial I}\right)_S\middle/\left(\dfrac{\partial B_e}{\partial I}\right)_T = \chi_T\middle/\chi_S$$

$$\therefore \boxed{\dfrac{C_{B_e}}{C_I} = \dfrac{\chi_T}{\chi_S}}$$

8 STABILITY OF THERMODYNAMIC SYSTEMS [SUMÁRIO]

8.1 INTRINSIC STABILITY OF THERMODYNAMIC SYSTEMS [SUMÁRIO]

8.1.1 To establish the inequality 8.6 expand the left-hand side of 8.5 in a Taylor... [SUMÁRIO]

SOLUÇÃO:

Equação 8.5 é $\quad S(U + \Delta U, V + \Delta V, N) + S(U - \Delta U, V - \Delta V, N) \leqslant 2S(U,V,N)$

Até os termos de segunda ordem, temos

$$S(U+\Delta U, V+\Delta V, N) = S(U,V,N) + \dfrac{\partial S}{\partial U}\Delta U + \dfrac{\partial S}{\partial V}\Delta V + \dfrac{1}{2}\left[\dfrac{\partial^2 S}{\partial U^2}(\Delta U)^2 + 2\dfrac{\partial^2 S}{\partial U\partial V}\Delta U\Delta V + \dfrac{\partial^2 S}{\partial V^2}(\Delta V)^2\right]$$

Concluímos que, para ΔU e ΔV arbitrários,

$$S_{UU}(\Delta U)^2 + 2S_{UV}\Delta U\Delta V + S_{VV}(\Delta V)^2 \leq 0$$

multiplicando por S_{UU}, que é negativo, temos

$$S_{UU}^2(\Delta U)^2 + 2S_{UU}S_{UV}\Delta U\Delta V + S_{UU}S_{VV}(\Delta V)^2 \geqslant 0$$

$$S_{_{UU}}^2(\Delta U)^2 + 2S_{_{UU}}S_{_{UV}}\Delta U\Delta V + S_{_{VV}}(\Delta V)^2 + \left(S_{_{UU}}S_{_{UV}} - S_{_{UV}}^2\right)(\Delta V)^2 \geqslant 0$$

$$\left(S_{_{UU}}\Delta U + S_{_{UV}}\Delta V\right)^2 + \left(S_{_{UU}}S_{_{VV}} - S_{_{UV}}^2\right)^2(\Delta V)^2 \geq 0$$

Se tomarmos $\Delta U = -\Delta V$, então

$$\left(S_{_{UU}}S_{_{VV}} - S_{_{UV}}^2\right)^2 \geq 0$$

8.1.2 Consider the fundamental equation of a monatomic ideal gas and show... [SUMÁRIO]

> **SOLUÇÃO:**

$$S = Ns_0 + \frac{3}{2}NR\ln\frac{U}{U_0} + NR\ln\frac{V}{V_0} - \frac{5}{2}NR\ln\frac{N}{N_0}$$

Mas $\ln x$ é côncava em x, então S é côncava em U e em V.

$$\text{também}\qquad \frac{\partial^2 S}{\partial N^2} = -\frac{5}{2}\frac{R}{N} < 0,\quad \text{então } S \text{ é côncava em } N$$

Note que não existem derivadas cruzadas, como $\frac{\partial^2 S}{\partial U\partial V}$, então não precisamos checar a condição da equação 8.6.

8.2 STABILITY CONDITIONS FOR THERMODYNAMIC PO-TENTIALS [SUMÁRIO]

8.2.1 a) Show that in the region $X > 0$ the function $Y = X^n$ is concave... [SUMÁRIO]

> **SOLUÇÃO:**

(a)

Se $\quad y = x^n,\quad \dfrac{d^2y}{dx^2} = n(n-1)x^{n-2} > 0 \quad$ para $n < 0 \quad$ ou $\quad n > 1$
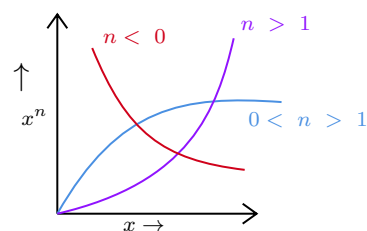
(b)-(c)

O caso (c) é convexo em P e portanto *instável*.

Os casos (b),(d) e (e) são *nominalmente* estáveis, mas ainda devemos checar a "fluting condition"(8.6). Podemos fazer isso diretamente, ou alternativamente podemos "rotacionar as coordenadas"(por exemplo, fazer uma transformação de Legendre) e novamente checar apenas as curvaturas primárias.

Para o caso (b) podemos facilmente encontrar $U = -\frac{1}{4}A^2N^5V^{-3}S^{-1}$, o que é côncavo em S (por causa do sinal de menos). U é côncava em todas as três variáveis. *Instável*.

Para o caso (d) podemos facilmente encontrar $U = \frac{1}{4}CS^4/VN^2$, que é convexa em todas as três variáveis. (é interessante checar que também satisfaz a condição $u_{ss}u_{vv} - u_{sv}^2 \geq 0$). Portanto o caso (d) é *instável*.

Para o caso (e) encontramos $U_{SS} = \frac{3}{4}\frac{U}{S^2}$, $U_{VV} = 2\frac{U}{S^2}$, $U_{SV} = \frac{3}{2}2\frac{U}{SV}$

$$U_{SS}U_{VV} - U_{SV}^2 = \left(\frac{3}{4}\times 2 - 9\right)\frac{U^2}{S^2V^2} = -\frac{15}{2}\left(\frac{U}{SV}\right)^2 < 0 \quad \text{Instável}$$

Em resumo, apenas o caso (d) é estável.

8.2.2 Prove that... [SUMÁRIO]

SOLUÇÃO:

$$\left(\frac{\partial F}{\partial V}\right)_T = -P$$

Diferenciando com respeito a V a T constante, e considerando $P = P(S,V)$

$$\left(\frac{\partial^2 F}{\partial V^2}\right)_T = -\left(\frac{\partial P}{\partial S}\right)_V\left(\frac{\partial S}{\partial V}\right)_T - \left(\frac{\partial P}{\partial V}\right)_S = U_{SV}\left(\frac{\partial S}{\partial V}\right)_T + U_{VV}$$

$$\text{Então} \qquad \left(\frac{\partial^2 F}{\partial V^2}\right)_T = -U_{sv}\left(\frac{\partial T}{\partial V}\right)_S / \left(\frac{\partial T}{\partial S}\right)_V + U_{VV}$$

$$= -\frac{U_{sv}^2}{U_{ss}} + U_{VV}$$

8.2.3 Show that stability requires equations 8.15 and... [SUMÁRIO]

SOLUÇÃO:

$$G(T + \Delta T, P + \Delta P) + G(T - \Delta T, P - \Delta P) - 2G(T,P) \leq 0.$$

Expandindo até a segunda ordem em ΔT e ΔP

$$G + G_T\Delta T + G_P\Delta P + \frac{1}{2}\left[G_{TT}(\Delta T)^2 + 2G_{TP}\Delta T\Delta P + G_{PP}\Delta P)^2\right] +$$

$$+ G - G_T\Delta T - G_P\Delta P + \frac{1}{2}\left[G_{TT}(\Delta T)^2 + 2G_{TP}\Delta T\Delta P + G_{PP}(\Delta P)^2\right] - 2G \leqslant 0$$

$$\therefore \quad G_{TT}(\Delta T)^2 + 2G_{TP}\Delta T\Delta P + G_{PP}(\Delta P)^2 \leq 0 \quad \text{para todo } \Delta T e \Delta P$$

$$\text{Tomando} \quad \Delta P = 0 \quad G_{TT} \leq 0$$
$$\text{Tomando} \quad \Delta T = 0 \quad G_{PP} \leq 0$$

Faça $X = \Delta T/\Delta P$, e dividindo por ΔP

$$G_{TT}x^2 + 2G_{TP}x + G_{PP} \leq 0$$

e a condição de que esta equação quadrática não tenha raízes reais é que o discriminante seja positivo.

8.2.4 (Supplementary Problem) Of the five nominally-acceptable fundamental equations in problem 1.10-1, which are stable?.

> **SOLUÇÃO:**

(a)

$$S = C(NVU)^{1/3}$$

$$U = C^{-3}S^3/NV \quad \therefore U_{SS} = 3 \times 2U/S^2, \quad U_{VV} = 2U/V^2, \quad U_{SV} = -3U/SV$$

$$\therefore U_{SS}U_{VV} - U_{SV}^2 = 3U^2/S^2V^2 > 0 \quad \text{Estável}$$

(c)

$$S = \left(\frac{R}{\theta}\right)^{1/2} \left[NU + R\theta V^2/v_0^2\right]^{1/2} \quad \text{é convexa em } V, \text{ portanto, } \textit{instável}$$

(e)

$$S = C\left[N^2VU^2\right]^{1/5}$$

$$U_{SS} = \frac{5}{2}\frac{3}{2}CV^{-1/2}S^{1/2}/N, U_{VV} = \frac{1}{2}\frac{3}{2}CV^{-5/2}S^{5/2}/N$$

$$U_{SV} = -\frac{1}{2}\frac{5}{2}V^{-3/2}S^{3/2}/N$$

$$U_{SS}U_{VV} - U_{SV}^2 = \left(\frac{45}{16} - \frac{25}{16}\right)V^{-3}S^3/N^2 > 0 \quad \textit{estável}$$

(g)

$$S = A[NU]^{1/2}e^{-V^2B/N^2} \quad \text{convexa em } V, \text{ portanto } \textit{instável}$$

(i)

$$U = AV\left(1 + \frac{S}{NR}\right)e^{-S/NR} \quad \text{não convexa em } S \text{ para valores baixos de } S, \text{ portanto } \textit{instável}$$

c)

g)

i)
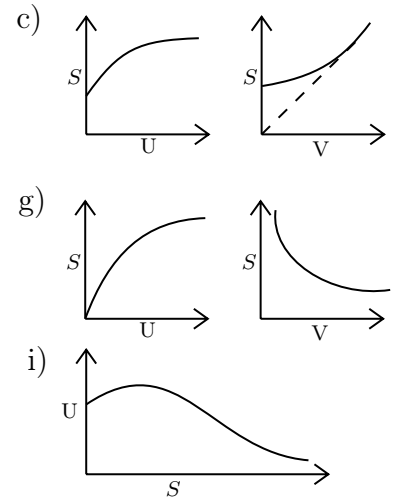
8.3 PHYSICAL CONSEQUENCES OF STABILITY

8.3.1 Explain on intuitive grounds why $c_P \geq c_v$ and $\kappa_T \geq \kappa_S$ ...

> **SOLUÇÃO:**

(a)
Na medida em que os sistema é aquecido em pressão constante ele expande e realiza trabalho "contra a pressão externa". Essa energia adicional deve ser fornecida pela entrada adicional de calor. Portanto $c_p \geq c_v$.

(b)
Considere um incremento na pressão aplicada ao sistema. O decréscimo no volume a uma temperatura constante $(-dV)_T$ excede aquele sob condições adiabáticas $(-dV)_S$ pois o calor

flui do sistema para o reservatório térmico no primeiro caso (tal extração de calor em si tenderia a diminuir o volume). Portanto $(-dV)_T > (-dV)_S$

$$\text{e ainda} \quad -\left(\frac{dV}{dP}\right)_T > -\left(\frac{dV}{dP}\right)_S \quad \text{ou} \quad \kappa_T \geq \kappa_S$$

Esse argumento é o precursor do *princípio de Le Chatelier-Braun*, seção 8.5

8.3.2 Show that the fundamental equation of a monatomic ideal gas satisfies the... [SUMÁRIO]

SOLUÇÃO:

$$S = \frac{3}{2}NR\ln\frac{U}{U_0} + NR\ln\frac{V}{V_0} - \frac{5}{2}NR\ln\frac{N}{N_0}$$

$$\therefore S_{UU} = -\frac{3}{2}\frac{NR}{U^2} < 0, \quad S_{VV} = -\frac{NR}{V^2} < 0, \quad S_{UV} = 0, \quad S_{NN} = -\frac{5}{2}\frac{R}{N} < 0$$

8.3.3 Show that the van der Waals equation of state does not satisfy the criteria... [SUMÁRIO]

SOLUÇÃO:

$$P = \frac{RT}{v-b} - \frac{a}{v^2}$$

$$\kappa_T^{-1} = -v\left(\frac{dP}{\partial v}\right)_T = \frac{RT}{(v-b)^2} - \frac{2a}{v^3}$$

E isso não é positivo em todo lugar no gráfico $P-v$
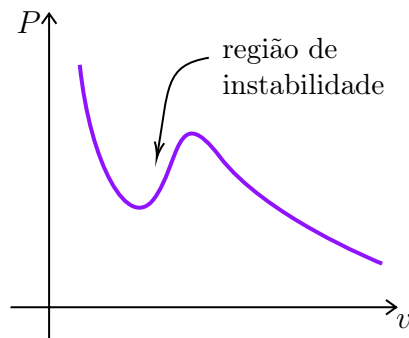
8.3.4 (Supplementary Problem) Show that the stability conditions 8.20-8.21 imply the equations 8.13-8.15. [SUMÁRIO]

SOLUÇÃO:

$$\text{equação 8.20 é} \quad c_p \geqslant c_v \geqslant 0 \quad \text{e} \quad 8.21 \text{ é} \quad \kappa_T \geqslant \kappa_S \geqslant 0$$

$$\frac{\partial^2 F}{\partial T^2} = -\left(\frac{\partial S}{\partial T}\right)_V = -\frac{N}{T}c_v < 0; \quad \frac{\partial^2 F}{\partial V^2} = -\left(\frac{\partial P}{\partial V}\right)_T = \frac{1}{V\kappa_T} > 0$$

$$\frac{\partial^2 H}{\partial S^2} = +\left(\frac{\partial T}{\partial S}\right) = \frac{T}{Nc_p} > 0; \quad \frac{\partial^2 H}{\partial P^2} = \left(\frac{\partial V}{\partial P}\right)_S = -V\kappa_S < 0$$

$$\frac{\partial^2 G}{\partial T^2} = -\left(\frac{\partial S}{\partial T}\right)_P = -\frac{N}{T}c_p < 0; \quad \frac{\partial^2 G}{\partial P^2} = \left(\frac{\partial V}{\partial P}\right)_T = -V\kappa_T < 0$$

8.3.5 (Supplementary Problem) An isochore and an adiabat intersect at a point in the P-T plane. Which has larger slope at the point of intersection?.

SOLUÇÃO:

$$\left(\frac{\partial P}{\partial T}\right)_S = -\left(\frac{\partial S}{\partial T}\right)_P \Big/ \left(\frac{\partial S}{\partial P}\right)_T = -c_p/T \left(\frac{\partial v}{\partial T}\right)_P = -c_p/Tv\alpha$$

$$\left(\frac{\partial P}{\partial T}\right)_V = -\left(\frac{\partial V}{\partial T}\right)_P \Big/ \left(\frac{\partial V}{\partial P}\right)_T = -\frac{\alpha}{\kappa_T}$$

$$\therefore \left(\frac{dP}{dT}\right)_S \Big/ \left(\frac{\partial P}{\partial T}\right)_V = \frac{C_p}{(Tv\alpha^2/\kappa_T)} = \frac{c_p}{c_p - c_v} = \frac{1}{1 - c_v/c_p}$$

Mas $c_p > c_v$, então essa razão é maior que 1
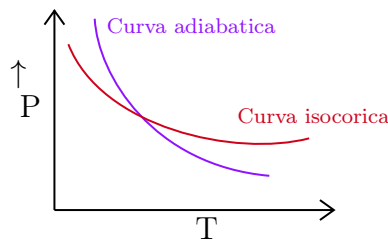
As duas inclinações são negativas. A adiabata tem inclinação maior em magnitude, mas menos inclinação algebricamente.

8.5 THE LE CHATELIER-BRAUN PRINCIPLE

8.5.1 A system is in equilibrium with its environment at a common temperature...

SOLUÇÃO:

O presente problema apenas inverte o papel dos processos primários e secundários como descrito na seção 8-5. Lá o aumento de volume era primário e a resposta primária era a diminuição na pressão. O efeito secundário era uma mudança na temperatura, resultando em um fluxo de calor que por sua vez aumenta a pressão.

Nós temos agora um aumento de entropia dS^f como a flutuação primária. O efeito primário é um incremento na temperatura (levando a um fluxo de calor para fora para diminuir a temperatura: $c_v > 0$). O efeito secundário é aquele em que o aumento na entropia inicial (fluxo de calor para dentro) aumenta a pressão: $dP^{(r)} = \left(\frac{\partial P}{\partial S}\right)_V dS^f = \frac{\alpha}{Tc_v\kappa_T}dS^f$. Esse incremento na

pressão leva a uma expansão ($\partial S/\partial P > 0$), e finalmente essa expansão abaixa a temperatura:
$\left(\frac{\partial T}{\partial V}\right)_s = -\frac{T\alpha}{\kappa_T} < 0$

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9 FIRST-ORDER PHASE TRANSITIONS [SUMÁRIO]

9.1 FIRST-ORDER PHASE TRANSITIONS IN SINGLE COMPONENT SYSTEMS [SUMÁRIO]

9.1.1 The slopes os all three curves in Fig. 9.5 are... [SUMÁRIO]

SOLUÇÃO:
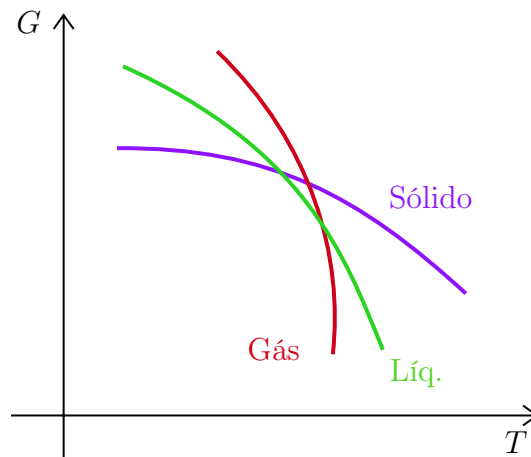
$\left(\frac{\partial \mu}{\partial T}\right)_P = -s \quad < 0 \quad \therefore$ as inclinações são negativas.

$\left(\frac{\partial^2 \mu}{\partial T^2}\right)_P = -\left(\frac{\partial s}{\partial T}\right)_P = -\frac{1}{T}c_p \quad < 0 \quad \therefore$ as curvaturas são negativas.

9.2 THE DISCONTINUITY IN THE ENTROPY - LATENT HEAT [SUMÁRIO]

9.2.1 In a particular solid-liquid phase transition the... [SUMÁRIO]

SOLUÇÃO:

Queremos calcular $l(P_0 + p, T_0 + t)$ dado $l(P_0, T_0)$ de modo que
l é o calor latente de vaporização:

$$s = s_0 + \left(\frac{\partial s}{\partial T}\right)_P dT + \left(\frac{\partial s}{\partial P}\right)_T dP$$

$$= s_0 + \left(\frac{\partial s}{\partial T}\right)_P dT + \left(\frac{\partial U}{\partial T}\right)_P dP$$

$$= s_0 + \frac{1}{T_0}c_p \times t + v\alpha \times p$$

$$\Delta s = \Delta s_0 + \frac{t}{T_0}\Delta c_p + p\Delta(v\alpha)$$
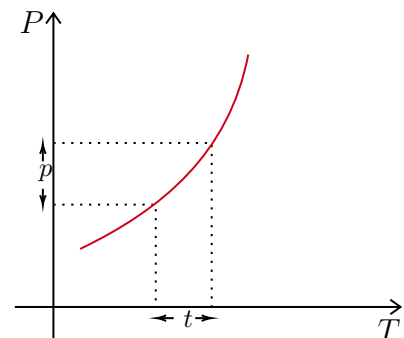
$$T\Delta s = T\Delta s_0 + \frac{T}{T_0}t\Delta c_p + Tp\Delta(v\alpha)$$
$$l = l_0 + t\Delta c_p + pT\Delta(v\alpha)$$

9.2.2 Discuss the equilibrium that eventually results if a solid is... [SUMÁRIO]

SOLUÇÃO:

NENHUMA SOLUÇÃO PARA ESSE PROBLEMA NO MOMENTO

9.3 THE SLOPE OF COEXISTENCE CURVES; THE CLAYPEYRON EQUATION [SUMÁRIO]

9.3.1 A particular liquid boils at 127 °C at a pressure of 800 mmHg ... [SUMÁRIO]

SOLUÇÃO:

O líquido ferve em $T = 127C$ e $P = 800\ mmHg$. O calor de vaporização é $10^3\ cal/mol$. Então, é necessário calcular a temperatura de ebulição á $810\ mmHg$.

$$\frac{dP}{dT} = \frac{l}{T\Delta v}$$

ou

$$\Delta T = \frac{T\Delta v}{l}\Delta P \simeq \frac{T}{l}\frac{RT}{P}\Delta P$$
$$\Delta T = \frac{RT^2}{l}\frac{\Delta P}{P}$$

que ao substituir os valores

$$\Delta T = \frac{2\ cal/mol \cdot K}{10^3} \times (400)^2\frac{10}{800}$$

$$\therefore \quad \boxed{\Delta T = 4\ K \quad ou \quad 4\ °C}$$

9.3.2 A long vertical column is closed at the bottom and open the top ... [SUMÁRIO]

SOLUÇÃO:
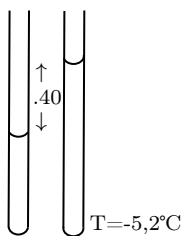
A interface sólido-líquido em um tubo vertical move-se para cima 40 cm se a temperatura T for reduzida de $-5,0°C$ para $-5,2°C$. Encontre a densidade da fase sólida se $l' = 2\ cal/g$ e $\rho_{liquido} = 1\ g/cm^3$.

Dados: $\Delta P = \rho_s gh$; $\Delta T = 0,2\ K$; $l = 2\ cal/g = 8372\ J/Kg$; $\rho_l = 1\ g/cm^3$.

Se M é a massa por mol, então $\rho = M/v$ e $l' = l/M$ o calor latente por unidade de massa. Podemos escrever como:

$$\frac{\Delta P}{\Delta T} = \frac{l'M}{T\Delta v} = \frac{l'}{T}\frac{1}{\Delta(v/M)} = \frac{l'}{T}\frac{1}{\Delta(1/P)}$$

que reescrevendo

$$\frac{1}{\rho_l} - \frac{1}{\rho_s} = \frac{l'}{T}\frac{\Delta T}{\Delta P} = \frac{l'}{T}\frac{\Delta T}{\rho_s gh}$$

$$\frac{\rho_s}{\rho_l} - 1 = \frac{\Delta T}{T}\frac{l'}{gh}$$

$$\frac{\rho_s}{\rho_l} = 1 + \frac{\Delta T}{T}\frac{l'}{gh}$$

$$\frac{\rho_s}{\rho_l} = 1 + \frac{0,2}{268}\frac{8372}{9,8 \times 0,4}$$

$$\therefore \quad \boxed{\rho_s = 2,59\ g/cm^3}$$

9.3.3 It is found that a certain boils at a temperature of 95 °C at the top ... [SUMÁRIO]

$\boxed{\textbf{Solução:}}$

Se $T_{boil} = 99°C$ no topo de uma colina, e $T_{boil} = 101°C$ no final da colina, queremos encontrar qual é a altura da colina, dado que $l = 10^3\ cal/mol$.

$$\frac{\Delta P}{\Delta T} \simeq \frac{l}{Tv_{gas}} \simeq \frac{lP}{RT^2} \quad \text{ou} \quad \frac{\Delta P}{P} \simeq \frac{l}{RT^2}\Delta T_{boil}$$

porém

$$\Delta P = \rho_{ar}gh = \frac{M_{ar}}{v_{ar}}gh = \frac{M_{ar}gh}{RT/P} \quad \therefore \quad \frac{\Delta P}{P} = \frac{M_{ar}gh}{RT}$$

que igualando

$$\frac{l\Delta T_{boil}}{RT^2} = \frac{M_{ar}gh}{RT} \quad ou \quad h = \frac{l}{M_{ar}g} \cdot \frac{\Delta T_{boil}}{T}.$$

Contudo, temos que a massa de ar é dada aproximadamente por:

$$M_{ar} \approx \frac{4}{5}M_{N_2} + \frac{1}{5}M_{O_2} \approx 0,8 \times 28 + 0.2 \times 32 \approx 29\ g/mol \approx 2,9 \times 10^{-3}\ kg/mol.$$

Vale lembrar que:

$$l = 4,2 \times 10^3 J/mol \quad e \quad \frac{l}{M_{ar}g} = \frac{4,2 \times 10^3}{2,9 \times 10^{-3} \times 9,8} = 15 \times 10^3 \; metros$$

logo

$$h = 15 \times 10^3 \frac{\Delta T_{boil}}{T}(metros) = 15 \times 10^3 \cdot \frac{2}{373}$$

$$\therefore \boxed{h = 80,4 \; metros}$$

9.3.4 Two weights are hung on the ends of a wire, which passes ... [SUMÁRIO]

SOLUÇÃO:
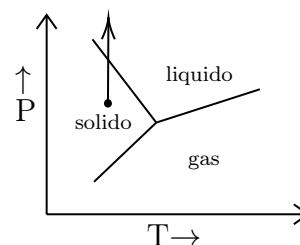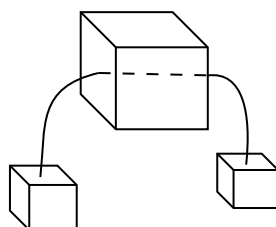
Para resolver esse problema é necessário explicar o fenômeno de *regelation* (em tradução literal para o português significa regelação ou congelar novamente) que é de derreter sob uma dada pressão e recongelar quando a pressão é reduzida. O limite da fase líquido-sólido da água tem uma inclinação negativa P-T, representado no diagrama. A pressão sob o fio desloca os estados verticalmente através do limite da fase, o fio afunda e a água se solidifica acima do fio. Vale lembrar que todo o processo ocorre **com a temperatura constante**.

9.3.5 In the vicinity of the triple point the vapor presure of liquid ammonia... [SUMÁRIO]

SOLUÇÃO:
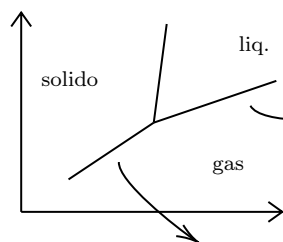
Para a amônia líquida $ln \; P = 15,16 - \frac{3063}{T}$ em atm.

Para a amônia sólida $ln \; P = 18,70 - \frac{3754}{T}$ em atm.

O exercício solicita que encontre P e T e também o calor latente de sublimação, vaporização e de fusão. Para facilitar: sólido, líquido e gasoso serão representadas por s,l e g, respectivamente.

Para a intersecção das curvas no ponto triplo é: $T_{tp} = 195,2\ K$; $P_{tp} = 0,588\ atm$. Diferenciando para curva gás-liquido

$$\frac{dP}{P} = -3063\frac{dT}{T^2} \quad ou \quad \frac{dP}{P} = \frac{3063}{T^2}P = \frac{3063}{T}\frac{R}{v}$$

$$l_{lg} = 3063R \quad \therefore \quad \boxed{l_{lg} = 25,4\times10^3\ J/mol}$$

$$l_{sg} = 3754R \quad \therefore \quad \boxed{l_{sg} = 31,2\times10^3\ J/mol}$$

Além disso, $l_{lg} + l_{gs} + l_{sl} = 0 \Leftrightarrow l_{sl} = l_{sg} - l_{lg}$

$$l_{sl} = 691R \quad \therefore \quad \boxed{l_{sl} = 5,7\times10^3\ J/mol}$$

9.3.6   Let x be the mole fraction of solid phase in a solid-liquid two-phase system...
   [SUMÁRIO]

SOLUÇÃO:

Encontre $\left(\dfrac{dx}{dT}\right)_V$ em termos de v, α, κ_T, c_p para cada fase.

$$v_s x + v_l(1-x) = v \ \ de\ modo\ que\ \ v \equiv \frac{V}{n_s + n_l} \ \ e \ \ x = \frac{v - v_l}{v_s - v_l}, \ sendo\ V\ constante.$$

$$\left(\frac{dx}{dT}\right)_V = -\frac{1}{v_s - v_l}\frac{dv_l}{dT} - \frac{v - v_l}{(v_s - v_l)^2}\left(\frac{dv_s}{dT} - \frac{dv_l}{dT}\right)$$
$$= \left(\frac{v - v_l}{v_s - v_l} - 1\right)\frac{1}{v_s - v_l}\frac{dv_l}{dT} - \frac{v - v_l}{(v_s - v_l)^2}\frac{dv_s}{dT}$$
$$= \frac{v - v_s}{(v_s - v_l)^2}\frac{dv_l}{dT} - \frac{v - v_l}{(v_s - v_l)^2}\frac{dv_s}{dT}$$

Porém

$$\frac{dv_l}{dT} = \left(\frac{\partial v_l}{\partial T}\right)_T\frac{dP}{dT} + \left(\frac{\partial v_l}{\partial T}\right)_P = -v_l\kappa_T^{(l)}\frac{dP}{dT} + v_l\alpha_l$$

e

$$\frac{dP}{dT} = \frac{l_{ls}}{v_l - v_s}$$

$$\therefore \quad \frac{dv_l}{dT} = -v_l\kappa_T^{(l)}\frac{l_{ls}}{v_l - v_s} + v_l\alpha_l = v_l\left[\alpha_l - \frac{\kappa_T^{(l)}l_{ls}}{v_l - v_s}\right]$$

que de maneira análoga

$$\frac{dv_s}{dT} = -v_s\kappa_T^{(s)}\frac{l_{ls}}{v_l - v_s} + v_s\alpha_s = v_s\left[\alpha_s - \frac{\kappa_T^{(s)}l_{ls}}{v_l - v_s}\right]$$

e portanto

$$\boxed{\left(\frac{dx}{dT}\right)_V = \frac{v - v_s}{(v_s - v_l)^2}v_l \left[\alpha_l - \frac{\kappa_T^{(l)} l_{ls}}{v_l - v_s}\right] - \frac{v - v_l}{(v_s - v_l)^2}v_s \left[\alpha_s - \frac{\kappa_T^{(l)} l_{ls}}{v_l - v_s}\right]}$$

9.3.7 A particular material has a latent heat of vaporization of... [SUMÁRIO]

Solução:

Um mol de material com $l = 5 \times 10^3 J/mol$ tem $V = 10^{-2}\ m^3$ a $T = 300\ K$ e $P = 10^5\ Pa$. Em estados de duas fases o material aquecido a volume constante V com $P = 2 \times 10^5\ Pa$. Encontre x_i e x_f. Da equação $PV = NRT$ ou $10^5 \times 10^{-2} = \text{N} \times 8,314\ \times 300$ nós temos $N = 0,401\ mol$ e $x = 0,4$. Então

$$\frac{dP}{dT} = \frac{l}{t\Delta v} \simeq \frac{dP}{P} = \frac{l}{R}\frac{dT}{T^2}$$

de modo que

$$ln\frac{P}{p_i} = \frac{l}{R}\left(\frac{1}{T_i} - \frac{1}{T_f}\right)$$

$$\therefore \quad \boxed{T_f = 458\ K}$$

Para encontrar x_f:

$$P_f V = N_f RT$$
$$2 \times 10^5 \times 10^{-2} = N_f \times 8,314 \times 458$$
$$N_f = 0,52$$

$$\therefore \quad \boxed{x_f = 0,52}$$

9.3.8 Draw the phase diagram, in the $B_e - T$ plane, fora simple ... [SUMÁRIO]

Solução:

A inclinação é dada por:

$$\left(\frac{dB_e}{dT}\right) = \frac{\Delta s}{\Delta I} = \frac{l/T}{\Delta I}$$

a inclinação é negativa pois

$$\Delta s = s_{para} - s_{ferro} > 0$$
$$entretanto \qquad \Delta I = I_{para} - I_{ferro} < 0$$

The figure shows a phase diagram with B_e on the vertical axis and T on the horizontal axis, with a **Ferromagnético** region and a **Paramagnético** region.
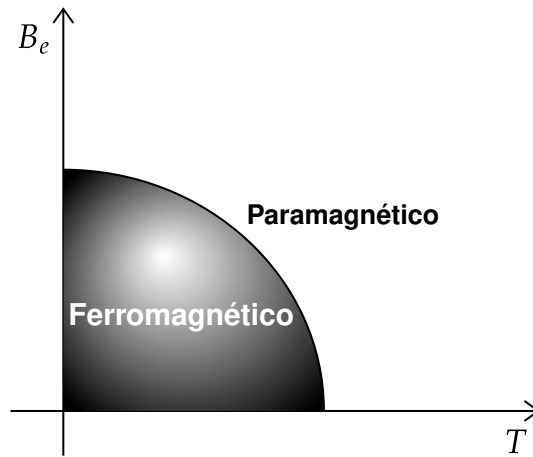
9.3.9 A system has cohexistence curves similar to those shown ...

SOLUÇÃO:

Para o sistema com o diagrama de fase dado por:
esboçar as isotermas no plano P-V para
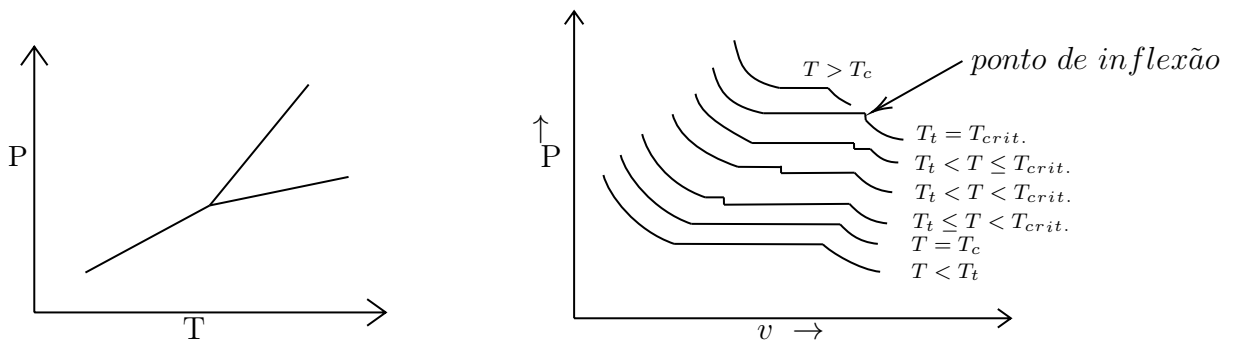
$$(a)\ T < T_b \quad (b)\ T = T_f \quad (c)\ T_f \leq T \leq T_{crit}$$
$$(d)\ T_f < T \leq T_{crit} \quad (e)\ T = T_{crit} \quad (f)\ T = T_{crit}$$

9.4   UNSTABLE ISOTHERMS AND FIRST-ORDER PHASE TRANSITIONS

9.4.1 Show that the difference in molar volumes across a coexistente curve is ...

SOLUÇÃO:

$$\Delta v = -P^{-1}\Delta f$$

$$F = G - PV \quad ou \quad f = \mu - P\Delta v$$

Através da curva de coexistência

$$\Delta f = \Delta \mu - P \Delta v$$

e como $\Delta \mu = 0$

$$\therefore \quad \boxed{\Delta f = -P \Delta v}$$

9.4.2 Derive the expression for v_c, P_c and T_c given in Example 1 ... [SUMÁRIO]

SOLUÇÃO:

$$P = \frac{RT}{v-b} - \frac{a}{v^2} \quad \therefore \quad \frac{dP}{dv} = -\frac{RT}{(v-b)^2} + \frac{2a}{v_3} = 0 \quad e \quad \frac{d^2P}{dv^2} = \frac{2RT}{(v-b)^3} - \frac{6a}{v^4}$$

Dividindo

$$\frac{v-b}{2} = \frac{v}{3} \quad ou \quad \boxed{v_c = 3b}$$

Da derivação temos que

$$RT = \frac{2a(v-b)^2}{v^3} \; ou \; em \; T_c \quad RT_c = \frac{2a(4b^2)}{(3b)^3} \Leftrightarrow \boxed{RT_c = \frac{8}{27}\frac{a}{b}}$$

e então

$$P_c = \frac{RT_c}{v_c - b} - \frac{a}{v_c^2} \; ou \; \boxed{P_c = \frac{a}{27b^2}}$$

9.4.3 Using the van der Waals constants for H_2O as given in table 3.1... [SUMÁRIO]

SOLUÇÃO:

Em resumo, encontre a temperatura e pressão crítica para a água.

Da tabela 3.1, temos que:

$$a = 0,554 \; Pa \; m^6 \quad b = 30,5 \times 10^{-6} \; m^3 \quad c = 3,1$$

$$\therefore \quad RT_c = \frac{8a}{27b} = 5,38 \times 10^3 \quad e T_c = 647,3 \; K$$

$$P_c = \frac{a}{27b^2} = \frac{0,554}{27,0 \times 30,5 \times 10^{-12}}$$

$$P_c = 22,06 \times 10^6$$

$$\boxed{P_c \simeq 22,1 \ MPa}$$

que concorda com o valor listado de $22,1 \ MPa$.

9.4.4 Show that for sufficiently low temperature the van der Waals isoterm... [SUMÁRIO]

SOLUÇÃO:

Mostrar que para um T pequeno, as isotermas de van der Waals se interceptam o eixo P=0.

$$\tilde{P} = \frac{8\tilde{T}}{3\tilde{N} - 1} - \frac{3}{\tilde{N}}$$

que é obtido pelo exemplo e é dado com redução de variáveis. Para $\tilde{P} = 0$ e denotando $\dfrac{1}{\tilde{v}}$ por n_v, temos:

$$0 = \frac{8\tilde{T}}{\dfrac{3}{n_v} - 1} - 3n_v^2 \quad ou \quad 3n_v = \frac{8\tilde{T}}{3 - n_v}$$

$$n_v^2 - 3n_v + \frac{8}{3}\tilde{T} = 0 \Leftrightarrow n_v = \frac{3}{2} \pm \frac{1}{2}\sqrt{9 - \frac{32}{3}\tilde{T}}$$

de modo que as raízes se combinam em $\tilde{T} = \dfrac{27}{32} \simeq 0,84$. Portanto, as isotermas vdw possuem regiões fisicamente não aceitáveis a pressões negativas para:

$$\boxed{\tilde{T} \leq 0,84}$$

9.4.5 Is the fundamental equation of an ideal van der Waals fluid... [SUMÁRIO]

SOLUÇÃO:

Sim, pois a equação fundamental dada é uma ″*relação fundamental subjacente*‵, visto que é intrinsecamente instável. Logo, a construção de Gibbs deve estar correta para produzir uma relação termodinâmica fundamental.

9.4.6 Explicitly derive the relationship among $\tilde{v}_g, \tilde{v}_l$, as given ... [SUMÁRIO]

SOLUÇÃO:

$$\tilde{P} = \frac{8\tilde{T}}{3\tilde{v} - 1} - \frac{3}{\tilde{v}^2} \quad e \quad \int \tilde{P} d\tilde{v} = \frac{3}{3}\tilde{T}\ln(\tilde{v} - \frac{1}{3}) + \frac{3}{\tilde{v}}$$

mas, pela *construção de área igual* requer que

$$\int_{\tilde{v}_l}^{\tilde{v}_g} \tilde{P}d\tilde{v} = \tilde{P}_t = \tilde{P}_t(\tilde{v}_g - \tilde{v}_l)$$

de modo que $\tilde{P}_t$ é a pressão na transição.

$$\therefore \quad \frac{8}{3}\tilde{T}\ln(3\tilde{N} - 1) + \frac{3}{\tilde{v}} - \tilde{P}_t\tilde{v} = constante$$

$$\frac{8}{3}\tilde{T}\ln(3\tilde{N} - 1) + \frac{3}{\tilde{v}} - \left[\frac{8\tilde{T}}{3\tilde{v} - 1} - \frac{3}{\tilde{v}^2}\right]\tilde{v} = constante$$

$$\boxed{\ln(3\tilde{v} - 1) + \frac{9}{4\tilde{T}\tilde{v}} - \frac{1}{3\tilde{v} - 1} = constante}$$

que é a relação dada no exemplo 2.

9.4.7   A particular substance satisfies yhe van der Waals equation of state... [SUMÁRIO]

> **SOLUÇÃO:**

A resposta está descrita na legenda da figura 9.15.

9.4.8   Using the two points as $\tilde{T} = 0,95$ and $\tilde{T} = 1$ on... [SUMÁRIO]

> **SOLUÇÃO:**

Tendo como base o exercício anterior, calcule o calor latente médio da vaporização da água ao longo do intervalo $0,95 < \tilde{T} < 1$.

Temos da figura 9.1

$$T_c = 647,3 \ K \quad e \quad P_c = 22,09 \ MPa$$

da resolução problema 9.4-7 temos que:

$$T = 0,95 \times 647,3 = 614,9 \ K$$
$$P = 0,814 \times 22,09 = 17,98 \ MPa$$

$$\frac{\Delta P}{\Delta T} = \frac{l}{T\Delta v} \Leftrightarrow l = \frac{\Delta P \Delta v}{\left(\frac{\Delta T}{T}\right)}$$

no ponto mais baixo:

$$\Delta v = (1,7 - 0,68)v_{crit},$$
$$v_{crit} = 3b$$
$$= 3 \times 30,5 \times 10^{-5} m^3$$
$$\therefore \quad \Delta v = 9,3 \times 10^{-5} m^3$$

no ponto critico $\Delta v = 0$.

Que consequentemente $\overline{\Delta v} \simeq 4,6 \times 10^{-5} \ m^3$ (que é uma media acima da faixa) e também:

$$\Delta P = 22,09 \ MPa \ - \ 17,98 \ MPa = 4,1 \times 10^6 \ Pa$$

e

$$\frac{\Delta T}{T} \simeq \frac{\Delta T}{T_{\text{médio}}} = \frac{32,4}{631} = 0,05.$$

Logo

$$l = \frac{\Delta P \cdot \Delta v}{\dfrac{\Delta T}{T}} = \frac{4,1 \times 10^6 \times 4,6 \times 10^{-5}}{0,05}$$

$$\boxed{l = 3,8 \times 10^3 \ joules/mol}$$

Observe que à pressão atmosférica $l \simeq 540 \ cal/g \simeq 4,0 \times 10^4 \ joules/mol$. Consequentemente, l é uma ordem de magnitude menor, diminuindo em direção a 0 em T_c, P_c.

9.4.9   Plot the van der Waals isotherm, in reduced variables... [SUMÁRIO]

SOLUÇÃO:

NENHUMA SOLUÇÃO PARA ESSE PROBLEMA NO MOMENTO

9.4.10   Repeat problem 9.4-8 in the range... [SUMÁRIO]

SOLUÇÃO:

NENHUMA SOLUÇÃO PARA ESSE PROBLEMA NO MOMENTO

9.4.11   Two mols of a van der Waals fluid are maintained at ... [SUMÁRIO]

SOLUÇÃO:

Encontre o numero de mols e p volume a cada fase, utilizando as constates de van der Waals do oxigênio.

Da equação 9.27

$$X_g = \frac{v - v_l}{v_g - v_l}$$

e lembrando que para o oxigênio

$$a = 0,138 \ Pa \ m^6$$
$$b = 32,6 \times 10^{-6} m^3$$

$$v = \frac{200 \times 10^{-6}}{2} \frac{m^3}{mol}$$
$$v = 10^{-4} \ m^3/mol$$

$$v_l = 0,68 \times 3b = 66,5 \times 10^{-6} \ m^3/mol \quad e \quad v_g = 1,7 \times 3b = 166 \times 10^{-6} \ m^3/mol$$

então

$$X_g = \frac{10^{-4} - 0,665 \times 10^{-4}}{1,66 \times 10^{-4} - 0,665 \times 10^{-4}}$$

$$\boxed{X_g = 0,337}$$

$$N_g = 2 \times X_g = 2 \times 0,337 = 0,67$$
$$N_l = 2 \times (1 - X_g) = 0,673 = 1,34$$
$$V_g = N_g \times v_g = 0,67 \times 166 \times 10^{-6} = 112 \ cm^3$$
$$V_l = N_l \times n_l = 1,34 \times 6,73 \times 10^{-6} = 88 \ cm^3$$

e portanto:

$$\boxed{N_g = 0,67} \qquad \boxed{N_l = 1,34}$$

$$\boxed{V_g = 112 \ cm^3} \qquad \boxed{V_l = 88 \ cm^3}$$

9.6   FIRST-OERDER PHASE TRANSITIONS IN MULTICOMPO-NENT SYSTEMS - GIBBS PHASE RULE [SUMÁRIO]

9.6.1   In a particular system, solute A and solute B are each dissolved... [SUMÁRIO]

SOLUÇÃO:

$$f = r - M + 2 = 3 - M + 2 = 5 - M$$

(a) Dimensionalidade do espaço $= f$ para $M = 1 \implies \boxed{f = 4}$

(b) $M = 2 \implies \boxed{f = 3}$

(c) $M = 3 \implies \boxed{f = 2}$

(d) $f = 0 \implies \boxed{M = 5}$

9.6.2   If g, the molar Gibbs function, is a convex of x_1, x_2 ...   [SUMÁRIO]

SOLUÇÃO:

Considere apenas uma função x_1. Defina agora uma nova variável dada por $x' = constante \equiv c - x_1$. Então

$$\frac{\partial g}{\partial x_1} = -\frac{\partial g}{\partial x'} \quad e \quad \frac{\partial^2 g}{\partial x_1^2} = +\frac{\partial^2 g}{\partial x_1^2}$$

Porém, em alguns casos de interesse $x' \implies x_r$ e $c \implies \left(1 - \sum_2^{r-1} x_j\right)$. Assim a condição $x' = c - x_1$ é substituída por :

$$\boxed{x_r = \left(1 - \sum_2^{r-1} x_j\right) - x_1} \quad Q.E.D.$$

9.6.3   Show that the conditions of stability in a multicomponent system ...   [SUMÁRIO]

SOLUÇÃO:

Essas alegações são declarações mensuráveis das condições de convexidade nos vários potenciais.
Por exemplo:

$$\left(\frac{\partial^2 G}{\partial N_j^2}\right)_{T,P,N_1,N_2,\dots} = \left(\frac{\partial \mu_j}{\partial N_j}\right)_{T,P,\dots} > 0$$

ou, se impusermos a condição de fechamento(ou completeza) $\sum_j N_j = N$, uma constante,

$$\left(\frac{\partial^2 G}{\partial x_j^2}\right)_{T,P,N_1,N_2,\dots} = \left(\frac{\partial \mu_j}{\partial x_j}\right)_{T,P,N_1,N_2,\dots} > 0$$

que similarmente

$$\left(\frac{\partial^2 U}{\partial N_j^2}\right)_{S,V,N_1,N_2,\dots} = \left(\frac{\partial \mu_j}{\partial N_j}\right)_{S,V,N_1,N_2,\dots} > 0$$

e com a condição citada acima:

$$\boxed{\left(\frac{\partial \mu_j}{\partial x_j}\right)_{S,V,N_1,N_2,...} > 0}$$

9.7 PHASE DIAGRAMS FOR BINARY SYSTEMS [SUMÁRIO]

9.7.1 In a particular system, solute A and solute B are each dissolved... [SUMÁRIO]

SOLUÇÃO:
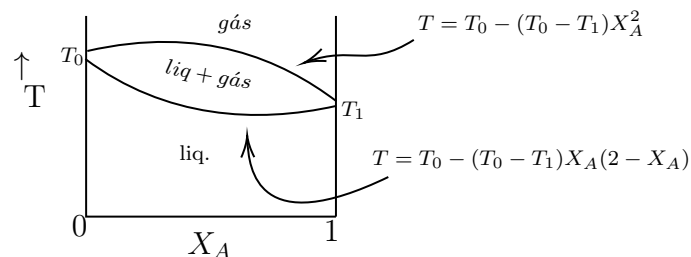
Em $X_A = \dfrac{1}{2}$ a temperatura de ebulição é

$$T = T_0 - (T_0 - T_1)\frac{1}{2} \times \frac{1}{2} \times \frac{3}{2} = \frac{T_0}{4} + \frac{3T_1}{4}$$

O valor de X_A do vapor é obtido da curva superior:

$$\frac{T_0}{4} + \frac{3T_1}{4} = T_0 - (T_0 - T_1)X_A^2$$

ou, reorganizando e substituindo os valores:

$$\boxed{X_A = \sqrt{3/4} = 0,866}$$

Vale ressaltar quer o vapor é rico em AX_A no liquido restante.

9.7.2 Show that if a small fraction $(-dN/N)$ of the material is boiled off ... [SUMÁRIO]

SOLUÇÃO:

Se o liquido estiver inicialmente em x_A e o vapor a x'_A temos que:

$$T_0 - (T_0 - T_1)x'_A = T_0 - (T_0 - T_1)x_A(2 - x_A)$$
$$\therefore \quad x'_A = \sqrt{x_A(2 - x_A)}$$

Portanto, se dN é fervido, a quantidade de A removida é dada por $-dN_A^4 = dN\sqrt{x_A(2 - x_A)}$ e a quantidade removida de B é $-dN_B^4 = dN[1 - \sqrt{x_A(2 - x_A)}]$.

O número de mol de A no líquido restante é:

$$Nx_A - dN\sqrt{x_A(2 - x_A)}$$

e o numero de mol de B restante é

$$N(1 - x_A) - dN\left[1 - \sqrt{x_A(2 - x_A)}\right]$$

e então:

$$x'_A = \frac{Nx_A - dN\sqrt{x_A(2 - x_A)}}{N - dN} = x_A + \frac{dN}{N}[x_A - \sqrt{x_A(2 - x_A)}] + ...$$

ou

$$\boxed{dx_A = \frac{dN}{N}\left[x_A - \sqrt{x_A(2 - x_A)}\right]} \quad Q.E.D.$$

9.7.3 The phase diagram of a solution of A in B, at a pressure of 1 atm ...

SOLUÇÃO:
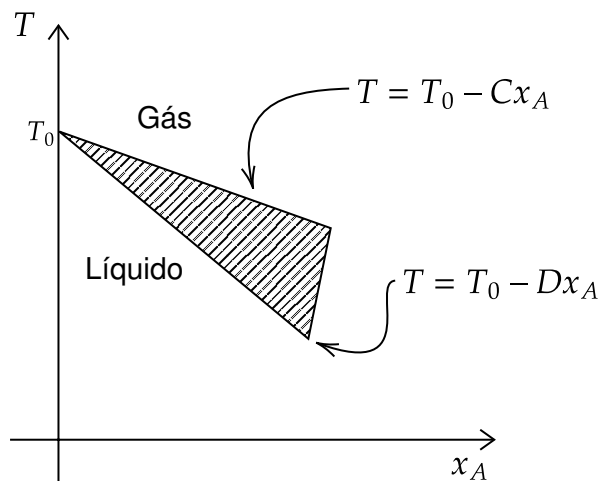
Seja x_i concentração inicial de líquido. Em ebulição, $T_i = T_0 - Dx_i^l$
Para encontrar x_i^g:

$$T_0 - Dx_i^l = T_0 - Cx_i^g \quad \text{ou} \quad \frac{D}{C}x_i^l.$$

Seja N o numero de mols existentes num liquido. Ao retirar δN mols de um gás a x^g, temos:

$$x^l + dx^l = \frac{x^l N - x^g dN}{N - dN} = x^l + (x^l - x^g)\frac{dN}{N}$$

ou

$$dx^l = (x^l - x^g)\frac{dN}{N} = x^l(1 - \frac{D}{C})\frac{dN}{N}$$

$$\therefore \quad \frac{dx^l}{x^l} = \left(1 - \frac{D}{C}\right)\frac{dN}{N}$$

que ao integrar dos dois lados, temos:

$$\boxed{\frac{x^l}{x_i^l} = \left(\frac{N}{N_i}\right)^{1-D/C}}$$

Se $\dfrac{D}{C} = 3$ e $\dfrac{N}{N_i} = \dfrac{1}{2}$ então $\dfrac{x^l}{x_i^l} = 4$.

10 CRITICAL PHENOMENA [SUMÁRIO]

10.6 SCALING AND UNIVERSALITY [SUMÁRIO]

10.6.1 Show that the following identities hold among ... [SUMÁRIO]

SOLUÇÃO:

Nos temos $\beta = \dfrac{2 - \alpha}{1 - \delta}$ e $\gamma = (\alpha - 2)\dfrac{1 - \delta}{1 + \delta}$.

Então

$$\alpha + 2\beta + \gamma = \alpha + 2\left(\frac{2 - \alpha}{1 + \delta}\right) + (\alpha - 2)\frac{1 - \delta}{1 + \delta} = 2$$

e de forma similar

$$\boxed{\frac{\gamma}{\beta} = \frac{(\alpha - 2)(1 - \delta)/(1 + \delta)}{(2 - \alpha)/(1 + \delta)} = \delta - 1}$$

10.6.2 Are classical values of the critical exponents consistent... [SUMÁRIO]

SOLUÇÃO:

Sim, pois o valor fornecido na tabela 10.2 satisfaz as duas relações de escala do problema 10.6-1 e são equivalentes a outras relações de escala.

11 THE NERNST POSTULATE

11.1 NERNST'S POSTULATE, AND THE PRINCIPLE OF THOMSEN AND BERTHELOT

11.1.1 Does the two-level system of problem 5.3-8 satisfy ...

SOLUÇÃO:

$$F = -\tilde{N}k_B T \ln(e^{-\beta\epsilon_u} + e^{-\beta\epsilon_d})$$

$$S = -\frac{\partial F}{\partial T} = \tilde{N}k_b T \ln(e^{-\beta\epsilon_u} + e^{-\beta\epsilon_d}) + \tilde{N}T + \frac{\epsilon_u e^{-\beta\epsilon_u} + \epsilon_d e^{-\beta\epsilon_d}}{e^{-\beta\epsilon_u} + e^{-\beta\epsilon_d}}$$

Tome $\epsilon_u = 0$ e $\epsilon_d > 0$:

Para $T \to 0$ e $\beta \to \infty$, $S \to \tilde{N}k_B \ln 1^{0} + \tilde{N}\epsilon_d e^{-\beta\epsilon_d/T}$. Porém, $e^{-\beta\epsilon_d/T} \to 0$ de forma exponencial se $T \to 0$ e então:

$$\therefore \quad \boxed{S \to 0}$$

O postulado de Nernst é satisfeito.

---

13 PROPERTIES OF MATERIALS

13.2 CHEMICAL REACTIONS IN IDEAL GASES

13.2.1 How is the equilibrium constant of the reaction in the Example ...

SOLUÇÃO:

Como se segue da eq. 13.11, a letra K então é o quadrado do primeiro.

13.2.2 What are the mole fractions of the reaction in the Example ...

SOLUÇÃO:

Para $P = 10^3$ temos que:

$$\frac{\left(\Delta\tilde{N}\right)^{\frac{3}{2}}}{(2 - \Delta\tilde{N})(2 + \frac{1}{2}\Delta\tilde{N})^{1/2}} = \sqrt{2}P^{-\frac{1}{2}}K(T) = \sqrt{2} \times 10^{-\frac{3}{2}} \times 0,0877 = 0,00392$$

$$\Delta\tilde{N} = 0,0491$$

$$\therefore \quad \boxed{X_{H_2O} = 0,9636; X_{H_2} = 0,0242; X_{O_2} = 0.0121}$$

13.2.3 In the Example, what would the final mole fractions ... [SUMÁRIO]

Solução:

$$N_{H_2O} = 2 - \Delta\tilde{N} \quad , \quad N_{H_2} = \Delta\tilde{N} \quad , \quad NO_2 = 1 + \frac{1}{2}\Delta\tilde{N} \quad ; \quad Soma : 3 + \frac{1}{2}\Delta\tilde{N}$$

$$X_{H_2O} = \frac{2 - \Delta\tilde{N}}{3 + \frac{1}{2}\Delta\tilde{N}} \quad , \quad X_{H_2} = \frac{\Delta\tilde{N}}{3 + \frac{1}{2}\Delta\tilde{N}} \quad , \quad X_{O_2} = \frac{1 + \frac{1}{2}\Delta\tilde{N}}{3 + \frac{1}{2}\Delta\tilde{N}}$$

$$\frac{\Delta\tilde{N}(1 + \frac{1}{2}\Delta\tilde{N})^{\frac{1}{2}}}{(2 - \Delta\tilde{N})(3 + \frac{1}{2}\Delta\tilde{N})^{\frac{1}{2}}} = P^{-\frac{1}{2}}K(T) = (0,00277)$$

$$\Delta\tilde{N} = 0,0095$$

$$\therefore \quad \boxed{X_{H_2O} = 0,6624 \quad , \quad X_{H_2} = 0,0032 \quad , \quad X_{O_2} = 0,3344}$$

13.2.4 In an ideal gas reaction an increase in presure at constant temperature ... [SUMÁRIO]

Solução:

$$\prod_i X_i^{\nu_i} = P^{-\sum \nu_i} K(T)$$

Se $\sum_i \nu_i > 0$ então os $X's$ dos reagentes diminuem com o aumento de P. Ou seja, se a soma dos números de moles estiver diminuindo pela reação, o aumento da pressão impulsionará a reação para frente. Como isso tende a diminuir a pressão, temos um caso do princípio Le Chatelier-Braun; a reação química prossegue na direção para compensar qualquer mudança de pressão imposta externamente.

13.2.5 In an ideal gas reaction an increase in presure at constant temperature ... [SUMÁRIO]

SOLUÇÃO:

$$S0_3 \rightleftarrows SO_2 + \frac{1}{2}O_2 \quad , \quad K(T) = 171,9 \ Pa^{\frac{1}{2}} \quad T = 10^3 K$$
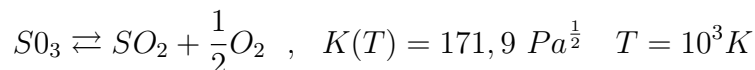
$$\frac{X_{SO_2}X_{0_2}^{\frac{1}{2}}}{X_{SO_3}} = P^{-\frac{1}{2}}K(T) = (0,4 \times 10^6)^{-\frac{1}{2}} \times 171,9$$

Porém,

$$N_{SO_3} = -\Delta \quad , \quad N_{SO_2} = 1 + \Delta \quad , \quad N_{O_2} = 2 + \frac{1}{2}\Delta \quad : \quad N = \sum N_j = 3 + \frac{1}{2}\Delta$$

$$\frac{\left(\frac{1+\Delta}{3+\frac{1}{2}\Delta}\right)\left(\frac{2+\frac{1}{2}\Delta}{3+\frac{1}{2}\Delta}\right)^{\frac{1}{2}}}{\left(-\frac{\Delta}{3+\frac{1}{2}\Delta}\right)} = (0,4 \times 10^6)^{-\frac{1}{2}} \times (171,9) = 0,272$$

$$\therefore \boxed{\Delta = -0,743}$$

$$\boxed{N_{SO_3} = 0,743 \text{ moles}} \quad , \quad \boxed{N_{SO_2} = 0,257 \text{ moles}} \quad , \quad \boxed{N_{O_2} = 1,628 \text{ moles}}$$

13.2.6 At temperatures above ∼ 500 K phosphorus pentachloride dissociates ... [SUMÁRIO]

SOLUÇÃO:

O "peso molar" do $PCl_3 = 30,97 + 5 \times 35,45 = 208,2 \ g$. Consequentemente, $1,9 \ g = 9,12 \times 10^{-3}$ moles.

Porém, pela lei dos gases ideais

$$PV = NRT \Rightarrow 0,314 \times 10^5 \times 2,4 \times 10^{-3} = N \times 8,314 \times 593 \Rightarrow N = 15,3 \times 10^{-3} \text{ moles}$$

e também,

$$N_{PCl_5} = 9,12 \times 10^{-3} - \Delta\tilde{N} \quad , \quad N_{PCl_3} = N_{Cl_2} = \Delta\tilde{N} \quad , \quad N_{total} = 9,12 \times 10^{-3} + \Delta\tilde{N}$$

e então

$$N_{total} = 9,12 \times 10^{-3} + \Delta\tilde{N} = 15,3 \times 10^{-3} \quad , \quad \Delta\tilde{N} = 6,18 \times 10^{-3} \text{ moles}$$

de modo que os graus de reações são:

$$\epsilon = \frac{\Delta\tilde{N}}{9,12 \times 10^{-3}} = \frac{6,18 \times 10^{-3}}{9,12 \times 10^{-3}} = 0,677$$

Então

$$N_{PCl_5} = 2,94 \times 10^{-3} \text{ moles} \quad , \quad N_{PCl_3} = N_{Cl_2} = 6,18 \times 10^{-3} \text{ moles}$$

$$X_{PCl_5} = \frac{2,94 \times 10^{-3}}{15,3 \times 10^{-3}} = 0,192 \quad , \quad X_{PCl_3} = X_{Cl_2} = \frac{6,18 \times 10^{-3}}{15,3 \times 10^{-3}} = 0,404$$

e portanto, para encontrar K(T):

$$\frac{X_{PCl_3} \times X_{Cl_2}}{X_{PCl_2}} = (0,314 \times 10^5)^{-1} K(T)$$

$$\boxed{K(T) = 2,71 \times 10^{-5} Pa}$$

13.2.7   A system containing 0,02 Kg of CO and 0.02 Kg of O$_2$... [SUMÁRIO]

$\boxed{\textsc{Solução:}}$

$$\frac{X_{CO}^2 X_{O_2}}{X_{CO_2}^2} = P^{-1} K$$

Inicialmente $\quad N_{CO_2}^0 = 0 \quad , N_{C_0}^0 = \frac{0,02}{0,028} = 0,714 \quad$ moles $\quad N_{0_2} = \frac{0,02}{0,032} = 0,625 \quad$ moles

$$N_{c0} = 0,714 + 2\Delta\tilde{N}, \quad N_{O_2} = 0,625 + \Delta\tilde{N}, \quad N_{CO_2} = -2\Delta\tilde{N} \quad \therefore N_{total} = 1,339 + \Delta\tilde{N}$$

$$X_{CO} = \frac{0,714 + 2\Delta\tilde{N}}{1,339 + \Delta\tilde{N}} \quad , \quad X_{O_2} = \frac{0,625 + \Delta\tilde{N}}{1,339 + \Delta\tilde{N}} \quad , \quad X_{CO_2} = \frac{-2\Delta\tilde{N}}{1,3391 + \Delta\tilde{N}}$$

$$\frac{(0,714 + 2\Delta\tilde{N})^2 (0,625 + \Delta\tilde{N})}{(-2\Delta\tilde{N})^2 (1,339 + \Delta\tilde{N})} = \left(0,2 \times 10^6\right)^{-1} \times 4,24 \times 10^4$$

Cuja solução numérica fornece $\Delta\tilde{N} = -0,203$

$$\therefore N_{CO_2} = -2\Delta\tilde{N} = 0,406 \quad \text{e} \quad M_{CO_2} = .406 \times 44 \text{ gramas } = 18 \text{ gramas}$$

13.2.8   Apply equation 13.8 to a single-component general ideal gas ...

$\boxed{\text{Solução:}}$

$$S_j = N s_j^0 + N_j \int_{T_0}^{T} \frac{c_{v_j}(T')}{T'} dT' + N_j R \ln\left(\frac{V}{V^0}\frac{N_j^0}{N_f}\right) \qquad \text{(equação 13.4)}$$

$$\frac{\mu_j}{T} = -\frac{\partial S_j}{\partial N_j} = \int_{T_0}^{T} \frac{cv_j(T')}{T'} dT' - R\ln\left(\frac{V}{V_0}\frac{N_j^0}{N_j}\right) - R$$

$$\therefore \boxed{\mu_j = T\int_{T_0}^{T} \frac{c_{v_j}(T')}{T'} dT' + RT\ln P + RT\ln x_j + RT\ln\frac{RT}{V_0}} \quad \text{e} \quad \boxed{\phi_j = \frac{1}{R}\int_{T_0}^{T} \frac{c_{v_j}(T')}{T'} dT' + \ln\frac{RT}{V_0}}$$

13.2.9   An experimenter finds that water vapor is 0.53% dissociated ...

$\boxed{\text{Solução:}}$

$$H_2O \rightleftharpoons H_2 + \frac{1}{2}O_2, \quad N_W = 1 - \Delta\tilde{N}, \quad N_{H_2} = \Delta\tilde{N}, \quad N_a = \frac{1}{2}\Delta\tilde{N}, \quad \therefore N = 1 + \frac{1}{2}\Delta\tilde{N}$$

$$\therefore \frac{1}{\sqrt{2}}\frac{(\Delta\tilde{N})^{3/2}}{(1-\Delta N)\left(1+\frac{1}{2}\Delta\tilde{N}\right)^{1/2}}P^{1/2} = K(T)$$

$$\text{A} \quad 2000 \text{ K}, \quad \Delta\tilde{N} = 0,0053 \quad \therefore K(2000) = 0,0866 \quad : \ln K(T) = -2,45$$

$$\text{A} \quad 2100 \text{ K}, \quad \Delta\tilde{N} = 0,0088 \quad \therefore K(2100) = 0,1858 \quad : \ln K(T) = -1,68$$

$$\Delta H = RT^2 \frac{d}{dT}\ln K(T) = 8,314 \times \left(4,2\times10^6\right) \times \frac{0,77}{100} = 27\times10^7 \text{Joules/mol}$$

13.3   SMALL DEVIATIONS FROM "IDEALITY "-THE VIRIAL EXPANSION

13.3.1   In a thermostatistical model in which each atom is treated as a small hard sphere ...

$\boxed{\text{Solução:}}$

$$\text{Da equação 13.2} \quad B \sim 10 \text{ cm}^3/\text{mole} = 4N_A\tau$$

$$\tau = \frac{10}{4\times6\times10^{23}}\frac{\text{cm}^3}{\text{molécula}} = \frac{4}{3}\pi r^3 \quad \text{ou} \quad r \simeq 5\times10^{-8} \text{ cm}$$

$$\text{Se} \quad C = 10N_A^2\tau \quad \text{e} \quad B = 4N_A\tau \quad \text{então} \quad C \simeq 10(B/4)^2 \simeq 62\frac{\text{cm}^6}{\text{mol}^2}$$

13.3.2 Expand the mechanical equation of state of Van de Waals gas (equation 3.41) ...

SOLUÇÃO:

$$P = \frac{RT}{v-b} - \frac{a}{v^2} = \frac{RT}{v}\left[\frac{1}{1-b/v} - \frac{a/RT}{v}\right] = \frac{RT}{v}\left[1 - \frac{b - \frac{a}{RT}}{v} + \frac{b^2}{v^2} + \frac{b^3}{v^3} + \cdots\right]$$

$$\therefore B(T) = b - \frac{a}{RT} \quad \text{e para} n \geq 2, \quad \text{coeficiente do virial} = b^n$$

13.3.3 Show that the second virial coefficient of gaseous nitrogen (Fig. 13.2) can...

SOLUÇÃO:

(a) A Hamiltoniana tem três termos translacionais e dois termos vibracionais (um cinético e um para energia potencial). Cinco termos $\Rightarrow \dfrac{5}{2}R$

(b) Da Fig. 13.2 $B \simeq 69\left[1 - \frac{320}{T}\right]$ cm^3/mol

$$\therefore B_0 \simeq 69 \text{ cm}^3/\text{mol}, \quad B_1 \simeq 69 \times 320 \approx 22 \times 10^3 \text{ cm}^3/\text{mol}$$

(c) $c_v = \frac{5}{2}R - \frac{69}{v}\frac{d}{dT}\left[T^2\left(1 - \frac{320}{T}\right)\right] = \frac{5}{2}R - \frac{69R}{v}[2T - 320]$

13.3.4 The simplest analytic form suggested by the qualitative shape of B(T) ...

SOLUÇÃO:

$$\text{Da equação 13.28} \quad f = f_{\text{ideal}} - RT\left[\frac{B_0 - B_1/T}{v} + \cdots\right]$$

$$\therefore c_p = T\left(\frac{\partial s}{\partial T}\right)_P = T\frac{\partial}{\partial T_p}s(T,v) = T\left(\frac{\partial s}{\partial T}\right)_v + T\left(\frac{\partial s}{\partial v}\right)_T\left(\frac{\partial v}{\partial T}\right)_P$$

$$c_p = -T\left(\frac{\partial^2 f}{\partial T^2}\right)_v + T\left(\frac{\partial^2 f}{\partial v^2}\right)_T\frac{\left(\frac{\partial P}{\partial T}\right)_v}{\left(\frac{\partial P}{\partial v}\right)_t} = -T\left(\frac{\partial^2 f}{\partial T^2}\right)_v - T\left(\frac{\partial P}{\partial T}\right)_V$$

$$c_p = -T\left[\left(\frac{\partial^2 f}{\partial T^2}\right)_v - \left(\frac{\partial^2 f}{\partial T \partial v}\right)\right]$$

Mas de $f = f_{ideal} - \frac{RT}{v}\left(B_0 - B_1/T\right)$ nós obtemos

$$c_p = c_{p_{\text{ideal}}} + B_0 RT/v^2 \quad \text{onde} \quad c_{p_{\text{ideal}}} = \begin{cases} \frac{5}{2}R & \text{para} \quad H_2 \\ \frac{3}{2}R & \text{para} \quad N_e \end{cases}$$

13.3.5 A "porous plug" experiment is carried out by installing a porous plug in ...

Solução:

Considere $\frac{1}{v}\left(\frac{\partial v}{\partial P}\right)_H = \kappa_T + \frac{\alpha v}{c_p}(1 - T\alpha)$.

Portanto, uma vez que a velocidade é proporcional ao volume molar,

$$\frac{\Delta \text{ velocity}}{\text{velocity}} = \left[\kappa_T + \frac{\alpha v}{c_p}(1 - T\alpha)\right]\Delta P$$

Para calcular κ_T : $P = \frac{RT}{v}\left[1 - \frac{B(T)}{v}\right]$

$$\left(\frac{\partial P}{\partial v}\right)_T = -\frac{RT}{v^2} + \frac{2RT}{v^3}B(T)$$

$$\therefore \kappa_T^{-1} = -v\left(\frac{\partial P}{\partial v}\right)_T = \frac{RT}{v} - \frac{2RT}{v^2}B(T) = \frac{RT}{v}\left[1 - \frac{2B}{v}\right] \quad \therefore \kappa_T = \frac{v}{RT} + \frac{2B}{RT}$$

Para calcula α:

$$v = \frac{RT}{P}\left[1 - \frac{B(T)}{V}\right] = \frac{RT}{P} - B\frac{RT}{PV} = \frac{RT}{P} - B$$

$$\therefore \alpha = \frac{1}{v}\left(\frac{\partial v}{\partial T}\right)_P = \frac{1}{v}\frac{R}{P} = \frac{R}{RT}\left[1 - \frac{B(T)}{v}\right]^{-1} = \frac{1}{T}\left[1 + \frac{B}{v}\right] \quad \text{and} \quad 1 - T\alpha = -\frac{B}{v}$$

Então, finalmente (substituindo na equação acima para $\frac{\Delta \text{ velocity}}{\text{velocity}}$)

$$\frac{\Delta \text{ velocity}}{\text{velocity}} = \left[\underbrace{\frac{v}{RT} + \frac{2B}{RT}}_{\kappa_T} + \frac{\alpha v}{c_p}\left(-\frac{B}{v}\right)\right]\Delta P = \left[\frac{v + 2B}{RT} - \frac{\alpha B}{c_p}\right]\Delta P$$

$$\therefore \boxed{\frac{\Delta \text{ velocity}}{\text{velocity}} = \left[\frac{v + 2B}{RT} - \frac{B}{Tc_p}\right]\Delta P} \quad \text{(desprezando termos de segunda ordem em } B\text{)}$$

13.5 DILUTE SOLUTIONS: OSMOTIC PRESSURE AND VAPOR PRESSURE [SUMÁRIO]

13.5.1 Assuming the latent heat of vaporization of a fluid to be constant ... [SUMÁRIO]

SOLUÇÃO:

$$\frac{dP}{dT} = \frac{l}{T\Delta v} \sim \frac{l}{Tv} \quad \text{e assuma } Pv = RT$$

$$\frac{dP}{dT} = \frac{lP}{RT^2} \quad \text{ou} \quad \frac{1}{P}dP = \frac{l}{R}\frac{dT}{T^2}$$

$$\therefore \quad P = P_0 e^{\frac{l}{R}\left(\frac{1}{T_0} - \frac{1}{T}\right)}$$

$$\text{para soluções} \quad \frac{\Delta P}{P} = -x$$
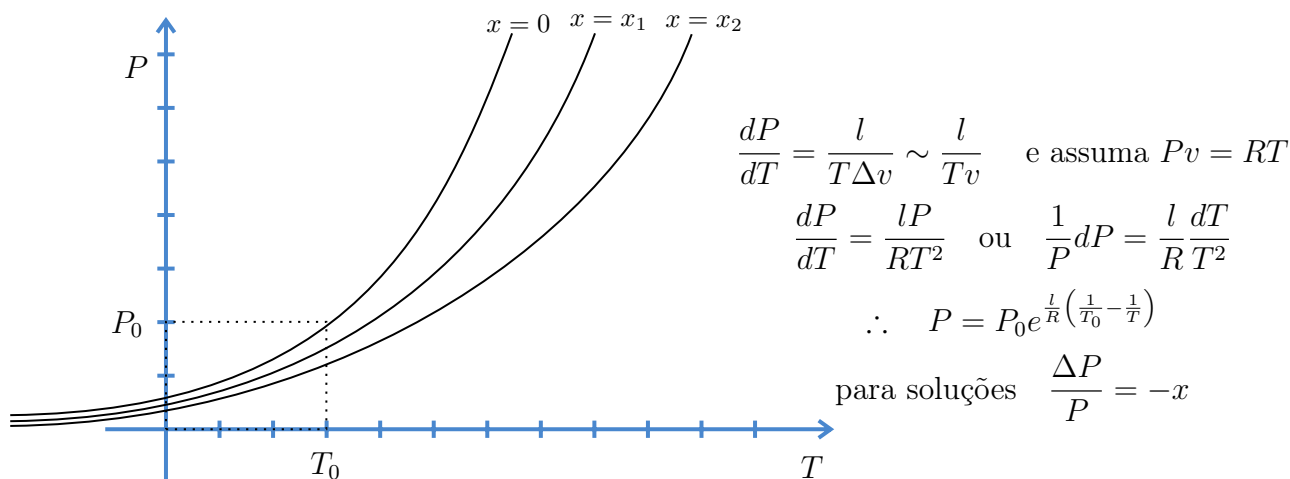
13.5.2 One hundred grams of a particular solute are dissolved in one liter of water ... [SUMÁRIO]

SOLUÇÃO:

$\Delta P/P = -x \simeq 0,03$. Também um litro de água é 10^3 cm^3 $\simeq 10^3$ gramas. O peso molecular da água é de 18 gramas. Logo, um litro de água contém $55,5$ mols. Pela lei de Raoult, existem portanto $0,03 \times 55,5 = 1,6$ mols de soluto. Então o peso molecular do soluto é 100 gramas/$1,67$ mols = 60 gramas por mol.

Mas $M_{\text{açúcar}} \simeq 342$ gramas,
$M_{Nacl} = 58$ gramas,
$M_{Na(O_3)_2} = 143$ gramas.
Portanto $Nacl$ é que é o soluto.

13.5.3 If 20 grams of sugar ($C_{12}H_{22}O_{11}$), are dissolved in 250 cm^3 of water ... [SUMÁRIO]

SOLUÇÃO:

$X = \frac{20}{250} = 0,08$ e portanto a pressão de vapor é diminuída em 8%, ou em $0,08$ atm (ou $\simeq 0,08 \times 0,1$ MPa $\simeq 0,008$ MPa). Mas da tabela 9.1, um aumento na temperatura de 5℃ aumenta a pressão de vapor em $\simeq 0,62$ MPa. Então é necessário $\simeq \frac{0,008}{0,02} \times 5$℃ $\simeq 2$℃ para compensar pela adição do soluto. A solução ferve em $\simeq 102$℃

15 STATISTICAL MECHANICS IN THE ENTROPY REPRESENTATION: THE MICROCANONICAL FORMALISM [SUMÁRIO]

15.1 PHYSICAL SIGNIFICANCE OF THE ENTROPY FOR CLOSED SYSTEMS [SUMÁRIO]

15.1.1 A system is composed of two harmonic oscillators each of natural frequency ω_0 ... [SUMÁRIO]

SOLUÇÃO:

A entropia do primeiro sistema é :

$$S_1 = k_B ln(n') = k_B ln\left(\frac{E'}{\hbar\omega_0}\right)$$

A entropia do segundo sistema é :

$$S_2 = k_B ln\left(\frac{E''}{2\hbar^2\omega_0^2}\right)$$

A entropia total (do sistema composto) é :

$$S = S_1 + S_2 = k_B ln\left(\frac{E'E''}{2\hbar^2\omega_0^2}\right)$$

15.1.2 A system is composed of two harmonic oscillators of natural frequencies ω_0 e $2\omega_0$ [SUMÁRIO]

SOLUÇÃO:

Os possíveis estados são :

$$\left.\begin{array}{cc} \#1 & \#2 \\ \hbar\omega_0 & \left(n-1+\frac{1}{2}\right)\hbar\omega_0 \\ 3\hbar\omega_0 & \left(n-3+\frac{1}{2}\right)\hbar\omega_1 \\ \vdots & \vdots \\ n\hbar\omega_0 & \left(n-n+\frac{1}{2}\right)\hbar\omega_0 \end{array}\right\} \quad \frac{n+1}{2} \text{ estados}$$

Assim temos um total de $\frac{n+1}{2}$ estados,

$$\therefore \boxed{S = k_B ln\left(\frac{n+1}{2}\right) = k_B ln\left(\frac{E}{2\hbar\omega_0} + \frac{1}{4}\right)}$$

Por fim, a entropia do sistema composto de dois subsistemas não interagentes é :

$$\therefore \boxed{S = k_B ln \left(\frac{E_1}{2\hbar\omega_0} + \frac{1}{4} \right) + k_B ln \left(\frac{E_2}{2\hbar\omega_0} + \frac{1}{4} \right)}$$

15.2 THE EINSTEIN MODEL OF A CRYSTALLINE SOLID [SUMÁRIO]

15.2.1 Calculate the molar heat capacity of the Einstein model by equation 15.7. [SUMÁRIO]

SOLUÇÃO:

A equação 15.7, encontrada na página 335, é :

$$\frac{U}{3NN_A} = \frac{\hbar\omega_0}{e^{\hbar\omega_0/k_B T} - 1}$$

portanto,

$$c = \frac{1}{N}\frac{dU}{dT} = \frac{3N_A (\hbar\omega_0)^2}{k_B T^2} \left(e^{\hbar\omega_0/2k_B T} - e^{-\hbar\omega_0/2k_B T} \right)^{-2}$$

na medida em que $T \to \infty$, temos que

$$e^{\hbar\omega_0/2k_B T} = 1 + \frac{\hbar\omega_0}{2k_B T} + \cdots$$

$$\therefore \boxed{c \to \frac{3N_A (\hbar\omega_0)^2}{k_B T} \left(\frac{\hbar\omega_0}{2k_B T} \right)^{-2} \frac{1}{T^2} = 3N_A k_B = 3R}$$

na medida em que $T \to 0$, temos que

$$\therefore \boxed{c \simeq \frac{3N_A (\hbar\omega_0)^2}{k_B} \frac{1}{T^2} e^{-\hbar\omega_0/k_B T} = 3R \left(\frac{\hbar\omega_0}{k_B T} \right)^2 e^{-\hbar\omega_0/k_B T}}$$

15.2.2 Obtain an equation for the mean quantum number n̄ of an Einstein oscillator as a ... [SUMÁRIO]

SOLUÇÃO:

A equação obtida deve ser

$$\bar{n} = \frac{1}{e^{\hbar\omega_0/k_B T} - 1}$$

Os valores obtidos foram :

$k_B T/\hbar\omega_0$	0	1	2	3	4	10	50	100
$\bar{n}$	0	0,58	1,54	2,56	3,52	$\sim 9,5$	49,5	99,5

15.2.3 Assume that the Einstein frequency ω_0 for a particular crystal depends upon the molar volume... [SUMÁRIO]

Solução:

a)

Faça $3N_A\hbar\omega_0 \equiv u_0 = u_0^0 - B\ ln\left(\dfrac{v}{v_0}\right)$ onde $B \equiv 3N_A\hbar A$. Assim,

$$u_0 = u_0^0 - B\ ln\left(\frac{v}{v_0}\right) \Longrightarrow \frac{\partial u_0}{\partial v} = -B\frac{v_0}{v}\frac{1}{v_0} = -\frac{B}{v}$$

A equação fundamental para o sólido de Einstein é :

$$s = 3R\ ln\left(1 + \frac{u}{u_0}\right) + 3R\frac{u}{u_0}ln\left(1 + \frac{u_0}{u}\right)$$

Então,

$$\frac{1}{T} = 3R\frac{u_0}{u_0 + u}\frac{1}{u_0} + \frac{3R}{u_0}\ ln\left(1 + \frac{u_0}{u}\right) + 3R\frac{u}{u_0}\frac{u}{u + u_0}\left(-\frac{u_0}{u^2}\right)$$

$$\Longrightarrow \frac{1}{T} = \frac{3R}{u_0}\ ln\left(1 + \frac{u_0}{u}\right)$$

A outra equação de estado é,

$$\frac{P}{T} = \frac{\partial s}{\partial v} = \frac{\partial s}{\partial u_0}\frac{\partial u_0}{\partial v} = -\frac{B}{v}\frac{\partial s}{\partial u_0}$$

Mas s é uma função de u/u_0, então

$$\frac{\partial s}{\partial u_0} = -\frac{u}{u_0}\frac{\partial s}{\partial u} = -\frac{u}{u_0}\frac{1}{T}$$

assim, temos que

$$\frac{P}{T} = \frac{B}{v}\frac{u}{u_0}\frac{1}{T} \quad e \quad Pv = B\frac{u}{u_0} \Longrightarrow \frac{u_0}{u} = \frac{B}{Pv}$$

$$\therefore \frac{1}{T} = \frac{3R}{u_0}ln\left(1 + \frac{B}{Pv}\right) \Longrightarrow 1 + \frac{B}{Pv} = e^{u_0/3RT} \Longrightarrow Pv = \frac{B}{e^{u_0/3RT} - 1}$$

Então se T é constante, $Pv = c$; c é constante.

A compressibilidade isotérmica é dada por :

$$\kappa_T = -\frac{1}{v}\left(\frac{\partial v}{\partial P}\right)_T$$

$$v = \frac{c}{P} \Longrightarrow \kappa_T = -\frac{1}{v}\left(-\frac{c}{P^2}\right) = \frac{c}{vP^2}$$

mas, sabemos que $c = Pv$, logo,

$$\kappa_T = \frac{Pv}{P^2v} \Longrightarrow \boxed{\kappa_T = \frac{1}{P}}$$

b)

Eliminando u da expressão para s e $\frac{1}{T}$:

$$s = -3R\, ln\left(1 - e^{-u_0/3RT}\right) + 3R\left(e^{u_0/3RT} - 1\right)^{-1} \frac{u_0}{3RT}$$

e

$$\boxed{T\Delta s = -3RT\, ln\left(\frac{1 - e^{-u_0^{(f)}/3RT}}{1 - e^{-u_0^{(i)}/3RT}}\right) + \left[\frac{u_0^{(f)}}{e^{u_0^{(f)}/3RT} - 1} - \frac{u_0^{(i)}}{e^{u_0^{(i)}/3RT} - 1}\right]}$$

15.3   THE TWO-STATE SYSTEM [SUMÁRIO]

15.3.1   In the two-state model system of this section suppose the excited state energy ε... [SUMÁRIO]

> **Solução:**

Faça $\beta = \dfrac{1}{k_B T}$

Da equação 15.12 (página 338) temos que $U = \dfrac{\tilde{N}\varepsilon}{1 + e^{\beta\varepsilon}} = \dfrac{\tilde{N}\left(\frac{a}{\tilde{v}^\gamma}\right)}{1 + e^{\beta a/\tilde{v}^\gamma}}$ e $\dfrac{U}{\varepsilon} = \dfrac{\tilde{N}}{1 + e^{\beta a/\tilde{v}^\gamma}}$

Da equação 15.10 (página 337) temos que $\tilde{s} = k_B\, ln(1 + e^{\beta a/\tilde{v}^2}) + \dfrac{a}{T\tilde{v}^\gamma}\dfrac{1}{1 + e^{\beta a/\tilde{v}^\gamma}}$

$$\therefore \tilde{f} = \tilde{u} - T\tilde{s} = -\frac{1}{\beta}\, ln(1 + e^{-\beta a/\tilde{v}^\gamma}) \quad \text{ou} \quad -\beta F = \tilde{N}\, ln(1 + e^{-\beta a/\tilde{v}^\gamma})$$

Calculando a pressão, dada por $P = -\dfrac{\partial F}{\partial V}$, temos :

$$P = -\frac{\partial F}{\partial V} = \frac{\gamma a}{\tilde{v}^{\gamma+1}}(e^{\beta a/\tilde{v}^\gamma} + 1)^{-1}$$

$$\therefore \boxed{P = \frac{\gamma a}{\tilde{v}^{\gamma+1}}(e^{a/k_B T\tilde{v}^\gamma} + 1)^{-1}}$$

15.4   A POLYMER MODEL-THE RUBBER BAND REVISITED [SUMÁRIO]

15.4.1   Is the sign correct in equation 15.19 ? Explain. [SUMÁRIO]

> NENHUMA SOLUÇÃO PARA ESSE PROBLEMA NO MOMENTO

15.4.2   Eliminate U/ε between equations 15.23 and 15.24 and show that the formal solution is equation 15.25... [SUMÁRIO]

> NENHUMA SOLUÇÃO PARA ESSE PROBLEMA NO MOMENTO

15.4.3 A rubber band consisting of n polumer chains is stretched from zero ... [SUMÁRIO]

SOLUÇÃO:

Da equação 15.23 (página 342) nós encontramos (tomando $L'_x = 0$), $U'_0 = \dfrac{\tilde{N}}{1 + e^{\varepsilon/k_B T}}$

e tomando $L'_x = N'$, temos $U_f = 0$

consequentemente $\Delta U = \varepsilon(U'_f - U'_0) = -\dfrac{\varepsilon \tilde{N}}{1 + e^{\varepsilon/k_B T}}$

e $S_f = 0$ (como pode ser confirmado pela equação 15.18)

enquanto que

$$S_0 = \tilde{N}k_B \, ln\tilde{N} + \tilde{N}k_B(1 + e^{-\varepsilon/k_B T})^{-1} \, ln\left(\frac{2 + 2e^{-\varepsilon/k_B T}}{\tilde{N}}\right) + \tilde{N}k_B(1 + e^{\varepsilon/k_B T})^{-1} \, ln\left(\frac{2 + 2e^{-\varepsilon/k_B T}}{\tilde{N}}\right)$$

Então,

$$\boxed{Q = T(S_f - S_0)n = -TS_0 n}$$

$$\boxed{W = (\Delta U - Q)n = -nU_0 + nTS_0}$$

A energia decresce, mas é realizado trabalho sobre o sistema.

15.4.4 Calculate the heat capacity at constant length for a "rubber band" consisting of n polymer... [SUMÁRIO]

SOLUÇÃO:

$$e^{\frac{2\varepsilon}{k_B T}} = \frac{(N' - U')^2 - L'_x}{U'}$$

$$\therefore \; U' = \frac{N' \pm \sqrt{L'^2_x - (N'^2 - L'^2_x)e^{2\varepsilon/k_B T}}}{1 - e^{2\varepsilon/k_B T}} \quad e \quad U = n\varepsilon U'$$

Se $L' = N'$, então $U' = 0$. Portanto use o sinal negativo $(-)$ antes da raiz.

$$\boxed{c_L = n\varepsilon \frac{dU'}{dT} = ...}$$

15.4.5 Calculate the heat capacity at constant length for a "rubber band" consisting of n polymer... [SUMÁRIO]

SOLUÇÃO:

$$L_x = (2\mathscr{T}_x \tilde{N}a^2)\beta/(2 + e^{-\beta\varepsilon})$$

$$\therefore \frac{1}{L_x}\left(\frac{\partial L_x}{\partial T}\right)_{\mathscr{T}_x} = -\frac{1}{T}\left[1 + \frac{\beta\varepsilon e^{-\beta\varepsilon}}{2 + e^{-\beta\varepsilon}}\right]$$

O aquecimento sempre *diminui* o tamanho.

Note que $\frac{1}{L_x}\left(\frac{dL_x}{dT}\right)_{\mathscr{T}_x}$ é independente de L ou $\mathscr{T}$, dependendo apenas de T.

Mais interessante é $-\frac{T}{L_x}\left(\frac{dL_x}{dT}\right)_{\mathscr{T}_x} = \left[1 + \frac{\beta\varepsilon e^{-\beta\varepsilon}}{2 + e^{-\beta\varepsilon}}\right]$, que é unitário em $T = 0$ e em $T = \infty$, com um fraco trabalho intermediário em $\beta\varepsilon = 1,463$

15.5 COUNTING TECHNIQUES AND THEIR CIRCUMVENTION; HIGH DIMENSIONALITY [SUMÁRIO]

15.5.1 To stablish equation 15.29 le Ω_n be the hyperplane in n dimensions. ... [SUMÁRIO]

NENHUMA SOLUÇÃO PARA ESSE PROBLEMA NO MOMENTO

15.5.2 Recalling that $\lim_{x \to 0} (1 + x)^{1/x} = e$... [SUMÁRIO]

NENHUMA SOLUÇÃO PARA ESSE PROBLEMA NO MOMENTO

15.5.3 Calculate the fraction of the hypervolume between the radii $0.9r$ and r ... [SUMÁRIO]

SOLUÇÃO:

seja $V_n = A_n r^n$, então $\Delta V_n / V_n = 1 - (0.9)^n$

n	1	2	3	4	5	10	20	30	40	50
$\Delta V_n / V_n$	0.1	0.19	0.27	0.34	0.41	0.65	0.88	0.96	0.98	0.995

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16 THE CANONICAL FORMALISM: STATISTICAL MECHANICS IN HELMHOLTZ REPRESENTATION

[SUMÁRIO]

16.1 THE PROBABILITY DISTRIBUTION [SUMÁRIO]

16.1.1 Show the equation 16.13 is equivalent to $U = F + TS$... [SUMÁRIO]

SOLUÇÃO:

$$U = -\frac{\partial}{\partial \beta} \ln Z = -\frac{\partial}{\partial \beta}(-\beta F) = F + \beta \frac{\partial F}{\partial \beta} = F - T \frac{\partial F}{\partial T} = F + TS$$

16.1.2 From the canonical algorithm expressed by equations 16.9 and 16.10... [SUMÁRIO]

SOLUÇÃO:

Da equação 16.9-16.10 $\qquad F = -k_B T \ln \sum e^{-\beta \epsilon_j}$

$$P = -\frac{\partial F}{\partial V} = \frac{1}{\beta Z}\left(\frac{\partial Z}{\partial V}\right)_\beta = \frac{\left[\sum_i \frac{\partial \epsilon_i}{\partial V} e^{-\beta \epsilon_i}\right]}{\sum_i e^{-\beta \epsilon_i}}$$

16.1.3   Show that $S/k_B = \beta^2 \partial F/\partial \beta$ and thereby express S...

SOLUÇÃO:

$$S = -\left(\frac{\partial F}{\partial T}\right)_V = -\left(\frac{\partial F}{\partial \beta}\right)_V \frac{\partial \beta}{\partial T} = k_B \beta^2 \frac{\partial F}{\partial \beta} = k_B \beta^2 \frac{\partial}{\partial \beta}\left[-\frac{1}{\beta}\ln Z\right]$$

16.1.4   Show that $c_v = -\beta(\partial s/\partial \beta)_v$ and thereby express c_v in...

SOLUÇÃO:

$$c_v = T\left(\frac{\partial s}{\partial T}\right)_v = T\left(\frac{\partial s}{\partial \beta}\right)_v \frac{d\beta}{dT} = \left(\frac{\partial s}{\partial \beta}\right)_v \left(-\frac{1}{k_B T}\right) = -\beta\left(\frac{\partial s}{\partial \beta}\right)_v$$

$$\text{Mas} \qquad Ns = k_B \ln Z - k_B \beta \frac{\partial}{\partial \beta}\ln Z$$

$$\therefore \quad \boxed{c_v = \frac{\beta^2 k_B}{N}\frac{\partial^2 \ln Z}{\partial \beta^2}}$$

16.2   ADDITIVE ENERGIES AND FACTORIZABILITY OF THE PARTITION SUM

16.2.1   Consider a system of three particles, each different. The first...

SOLUÇÃO:

$$Z = e^{-\beta(\epsilon_{11}+\epsilon_{21}+\epsilon_{31})} + e^{-\beta(\epsilon_{11}+\epsilon_{21}+\epsilon_{32})} + e^{-\beta(\epsilon_{11}+\epsilon_{22}+\epsilon_{31})} + e^{-\beta(\epsilon_{11}+\epsilon_{22}+\epsilon_{32})} +$$
$$+ e^{-\beta(\epsilon_{12}+\epsilon_{21}+\epsilon_{31})} + e^{-\beta(\epsilon_{12}+\epsilon_{21}+\epsilon_{32})} + e^{-\beta(\epsilon_{12}+\epsilon_{22}+\epsilon_{31})} + e^{-\beta(\epsilon_{12}+\epsilon_{22}+\epsilon_{32})}$$

$$\text{Ou} \qquad Z = \left(e^{-\beta\epsilon_{11}} + e^{-\beta\epsilon_{12}}\right)\left(e^{-\beta\epsilon_{21}} + e^{-\beta\epsilon_{22}}\right)\left(e^{-\beta\epsilon_{31}} + e^{-\beta\epsilon_{32}}\right)$$

16.2.2   Show that for the two level system the Helmholtz potential calculated in...

SOLUÇÃO:

$$\text{Da equação 16.21} \qquad -\beta F = \tilde{N}\ln\left(1 + e^{-\beta\epsilon}\right)$$

$$\therefore \quad U = \frac{\partial}{\partial \beta}(\beta F) = \tilde{N}\epsilon/\left(1 + e^{\beta\epsilon}\right) \qquad \text{que é a equação 15.12}$$

$$\therefore \quad e^{-\beta\epsilon} = \frac{U}{N\epsilon - U}$$

$$\frac{1}{k_B}S = \beta U - \beta F = \frac{U}{\epsilon}\ln\left[\frac{\tilde{N}\epsilon}{U} - 1\right] + \tilde{N}\ln\left[1 + \frac{U}{N\epsilon - U}\right] = \left(\frac{U}{\epsilon} - \tilde{N}\right)\ln\left(1 - \frac{U}{N\epsilon}\right) - \frac{U}{\epsilon}\ln\frac{U}{N}$$

Então $\quad \dfrac{1}{k_{\mathrm{B}}} S = \left(\dfrac{U}{\epsilon} - \tilde{N}\right) \ln\left(1 - \dfrac{U}{N\epsilon}\right) - \dfrac{U}{\epsilon}\ln\dfrac{U}{N}$ $\quad$ que é a equação 15.10

16.2.3 Is the energy additive over the particles of a gas if the particles are uncharged ... [SUMÁRIO]

SOLUÇÃO:

$$\text{Sim, não, não.}$$

16.2.4 Calculate the heat capacity per mode from the fundamental equation 16.24 ... [SUMÁRIO]

SOLUÇÃO:

$$\beta F = 3\tilde{N}\ln\left(1 - e^{-\beta\hbar\omega_0}\right) \qquad \text{e} \qquad \therefore U = \frac{\partial}{\partial\beta}(\beta F) = 3\tilde{N}\hbar\omega_0\left[e^{\beta\hbar\omega_0} - 1\right]^{-1}$$

$$\frac{c}{3\tilde{N}} = \frac{\partial}{\partial T}\frac{\hbar\omega_0}{e^{\beta\hbar\omega_0} - 1} = k_B\left(\beta\hbar\omega_0\right)^2 e^{\beta\hbar\omega_0}\left(e^{\beta\hbar\omega_0} - 1\right)^{-2}$$

$$\text{para valores baixos de} \quad T, \quad c \sim T^{-2}e^{-\beta\hbar\omega_0} \to 0$$
$$\text{para valores altos de} \quad T, \quad c \sim k_B$$

16.2.5 Calculate the energy per mode from equation 16.24. What is the leading... [SUMÁRIO]

SOLUÇÃO:

$$\text{do problema anterior} \qquad U = 3\tilde{N}\hbar\omega_0\left[e^{\beta\hbar\omega_0} - 1\right]^{-1}$$

$$\text{para valores baixos de} \quad T, \quad U \simeq 3\tilde{N}\hbar\omega e^{-\beta\hbar\omega_0}$$
$$\text{para valores altos de} \quad T, \quad U \simeq 3\tilde{N}\hbar k_B T$$

16.2.6 A binary alloy is composed of $\tilde{N}_{\mathbf{A}}$ atoms of type A and $\tilde{N}_{\mathbf{B}}$ ... [SUMÁRIO]

SOLUÇÃO:

$$Z = z_A^{\tilde{N}_A} z_B^{\tilde{N}_B}, \quad z_A = 1 + e^{-\beta\epsilon}, \quad z_B = 1 + e^{-2\beta\epsilon}$$

$$e^{-\beta F} = \left(1 + e^{-\beta\epsilon}\right)^{\tilde{N}_A}\left(1 + e^{-2\beta\epsilon}\right)^{\tilde{N}_B}$$

$$-\beta F = \tilde{N}_A\ln\left(1 + \mathrm{e}^{-\beta\epsilon}\right) + \tilde{N}_B\ln\left(1 + \mathrm{e}^{-2\beta\epsilon}\right)$$

$$U = \frac{\partial}{\partial\beta}(\beta F) = \tilde{N}_A\frac{\epsilon}{e^{\beta\epsilon}+1} + \tilde{N}_B\frac{2\epsilon}{e^{2\beta\epsilon}+1}$$

$$c = \frac{dU}{dT} = k_B\beta^2\epsilon^2\left[\frac{\tilde{N}_A}{\left(e^{\beta\epsilon/2}+e^{-\beta\epsilon/2}\right)^2} + \frac{4\tilde{N}_B}{\left(e^{\beta\epsilon}+e^{-\beta\epsilon}\right)^2}\right]$$

16.2.7 A paramagnetic salt is composed of 1 mole of noninteracting ions, each with ... [SUMÁRIO]

SOLUÇÃO:

$$f_\uparrow = e^{-\beta \mu_B B_e}/z, \quad f_\downarrow = e^{\beta \mu_B B_e}/z, \quad z = e^{-\beta \mu_B B_e} + e^{\beta \mu_B B_e}$$

$$-\beta F = N_A \left(e^{-\beta \mu_B B_e} + e^{\beta \mu_B B_e} \right)$$

$$S = -\frac{\partial F}{\partial T} = R \left(e^{-\beta \mu_B B_e} + e^{\beta \mu_B B_e} \right) - \frac{N_A \mu_B B_e}{T} \left(e^{\beta \mu_B B_e} - e^{-\beta \mu_B B_e} \right)$$

$$\text{Faça } \mu_B B_e / k_B T = x, \quad \text{Então} \quad S/R = \left(e^x + e^{-x} \right) - x \left(e^x - e^{-x} \right)$$

Também, se $B_e = 1$ Tesla e $T = 1$ K, então $x(1,1) = \frac{\mu_B B}{k_B T} = 0,669$

(a):

$$\Delta S/R = \left[\left(e^{10/4} + e^{-10/4} \right) - \frac{10}{4} \left(e^{\frac{10}{4}} - e^{-10/4} \right) \right] - \left[\left(e^{1/4} + e^{-1/4} \right) - \frac{1}{4} \left(e^{1/4} - e^{-1/4} \right) \right] = 18,57$$

$$\text{Então} \qquad Q = T\Delta S = 4 \times 18,57 \times R = 6,17 \times 10^6 \text{ Joules}$$

(b):

$$S\left(T = 4k, B_e = 10 \text{ Tesla }\right) = S\left(T, B_e = 1 \text{ Tesla }\right)$$

Ou, uma vez que S é uma função só de x,

$$x_{final} = x_{inicial}$$

Mas $x_{inicial} = 0,0669$ e $x_{final} = \dfrac{0,669}{T_f}$

$$\therefore \boxed{T = 10 \text{ K}}$$

16.3 INTERNAL MODES IS A GAS [SUMÁRIO]

16.3.1 Calculate the average rotational energy per molecule and the rotational heat... [SUMÁRIO]

SOLUÇÃO:

$\epsilon_l = l(l+1)\epsilon, \quad l = 0, 1, 2 \ldots$ cada nível de energia é $(2l+1)$ degenerado

$$z_{rot} = \sum_{l=0}^{\infty} (2l+1)e^{-\beta l(l+1)\epsilon} \simeq \int_0^\infty (2l+1)e^{-\beta l(l+1)\epsilon}dl = \int_0^\infty e^{-\beta x \epsilon}dx = \frac{k_B T}{\epsilon}$$

$$-\beta F = \ln z_{rot}^{\tilde{N}} = \tilde{N} \ln\left(\frac{k_B T}{\epsilon}\right) = -\tilde{N}\ln(\beta\epsilon)$$

$$U = \frac{\partial}{\partial \beta}(\beta F) = \tilde{N}k_B T \quad \text{ou} \quad U/\tilde{N} = k_B T \quad \text{e} \quad c \equiv \frac{d}{dT}\frac{U}{N} = k_B$$

16.3.2 Calculate the rotational contribution of the Helmholtz potential per molecule ... [SUMÁRIO]

SOLUÇÃO:

$$z_{rot} = \sum_{l=0}^{\infty}(2l+1)e^{-\beta l(l+1)\epsilon} = 1 + 3e^{-2\beta\epsilon} + \sum_{l=2}^{\infty}(2l+1)e^{-\beta l(l+1)\epsilon}$$

$$\text{But} \quad \sum_{l=2}^{\infty}(2\ell+1)e^{-\beta\ell(l+1)\epsilon} = \sum_{j=0}^{\infty}(2j+5)e^{-\beta(j+2)(j+3)\epsilon}$$

$$\text{Na eq.Euler-McLaurin} \quad f(\theta) = (2\theta+5)e^{-\beta\epsilon\left(\theta^2+5\theta+6\right)}, \quad f(0) = 5e^{-6\beta\epsilon}, \quad f'(0) = (2-25\beta\epsilon)e^{-6\beta\epsilon}$$

$$\therefore z_{rot} = 1 + 3e^{-2\beta\epsilon} + (2-25\beta\epsilon)e^{-6\beta\epsilon}$$

$$\text{E} \quad F/\tilde{N} = -k_B T \ln\left[1 + 3e^{-2\beta\epsilon} + (2-25\beta\epsilon)e^{-6\beta\epsilon}\right]$$

16.3.3 A particular heteronuclear diatomic gas has one vibrational mode, of frequency ... [SUMÁRIO]

SOLUÇÃO:

$$F = F_{\text{transl}} + F_{\text{rot}} + F_{\text{vib}}$$

$$F_{\text{transl}} = F_{\text{ideal}} = \frac{3}{2}NRT - -NT\left[s_0 + R\ln\frac{T^{3/2}v}{T_0^{3/2}v_0}\right]$$

$$F_{rot} = -NRT\ln\left(k_B T/\epsilon\right) \qquad (\text{da equação } 16.30)$$

$$F_{\text{vib}} = NRT\ln\left(1 - e^{-\beta\hbar\omega_0}\right) \qquad (\text{da equação } 16.24)$$

$$\therefore \frac{F}{NRT} = \left(\frac{3}{2} - \frac{s_0}{R}\right) + \ln\left[\frac{1 - e^{-\beta h\omega_0}}{vT^{5/2}}\frac{\epsilon v_0 T_0^{3/2}}{k_B}\right]$$

16.4 PROBABILITIES IN FACTORIZABLE SYSTEMS [SUMÁRIO]

16.4.1 The probability that the ith element is in its jth orbital... [SUMÁRIO]

SOLUÇÃO:

NENHUMA SOLUÇÃO PARA ESSE PROBLEMA NO MOMENTO

16.4.2 Demonstrate the equivalence of the fundamental equations found in... [SUMÁRIO]

SOLUÇÃO:

NENHUMA SOLUÇÃO PARA ESSE PROBLEMA NO MOMENTO

16.5 STATISTICAL MECHANICS OF SMALL SYSTEMS: ENSEMBLES [SUMÁRIO]

16.5.1 The energies of the orbital states of a given molecule ar such that ... [SUMÁRIO]

SOLUÇÃO:

$$z = 1 + e^{-2/3} + e^{-1} + e^{-4/3} = 1 + 0,5134 + 0,3679 + 0,2636 = 2,145$$

$$f_0 = \frac{1}{2,145} = 0,466, \quad f_1 = 0,239, \quad f_2 = 0,171^5, \quad f_3 = 0,123$$

$$\langle \epsilon \rangle / k_B = \sum f_j \epsilon_j / k_B = 148$$

$$\langle \epsilon^2 \rangle / k_B^2 = \sum f_j \left(\epsilon_j / k_B \right)^2 = 4,47 \times 10^4$$

$$\sigma / K_B = \left[\langle \epsilon^2 \rangle / k_B^2 - \langle \epsilon / k_B \rangle \right]^{1/2} = 150,4$$

16.5.2 A hydrogen atim in equilibrium with a radiation field at temperature A hydrogen atim in equilibrium with a radiation field at temperature ... [SUMÁRIO]

SOLUÇÃO:

$$z = \underbrace{2}_{1s} + \underbrace{2e^{-\beta\epsilon}}_{2s} + \underbrace{6e^{-\beta\epsilon}}_{2p} \implies \therefore \mathscr{P}(orbital = p) = \frac{6e^{-\beta\epsilon}}{2 + 8e^{-\beta\epsilon}} = \frac{3}{e^{\beta\epsilon} + 4}$$

16.5.3 A small system has two normal modes of vibration, with natural... [SUMÁRIO]

SOLUÇÃO:

Relativo a $T = 0$, as energias são $n\hbar\omega_1$ e $2l\hbar\omega_1$, n e l inteiros positivos.

$$z_1 = \sum_0^\infty e^{-\beta n \hbar \omega_1} = \frac{1}{1 - e^{-\beta \hbar \omega_1}} \quad z_2 = \sum_0^\infty e^{-2\beta l \hbar \omega_1} = \frac{1}{1 - e^{-2\beta \hbar \omega_1}}$$

Os únicos estados com $E < \frac{5}{2}\omega_1$ são $(0,0)$, $(0,1)$, $(1,0)$, $(2,0)$ com energias 0, $2\hbar\omega_1$, $\hbar\omega_1$, $2\hbar\omega_1$

$$\therefore \mathscr{P}\left(E < \frac{5}{2}\omega_1 \right) = \frac{1 + e^{-\beta\hbar\omega_1} + 2e^{-2\beta}\hbar\omega_1}{z_1 z_2} = \left(1 - e^{-\beta\hbar\omega_1} \right)\left(1 - e^{-2\beta\hbar\omega_1} \right)\left(1 + e^{-\beta\hbar\omega_1} + 2e^{-\beta\hbar\omega_1} \right)$$

$$\therefore \mathscr{P}\left(E < \frac{5}{2}\omega_1 \right) = (1 - x)\left(1 - x^2 \right)\left(1 + x + 2x^2 \right) \quad \text{onde} \quad x \equiv e^{-\beta\hbar\omega_1}$$
$$= 1 - x^3 \left(2 + x - 4x^2 \right)$$

16.5.4 DNA, the genetic molecule deoxyribonucleic acid, exists as a...

Solução:

(a) Se as moléculas se soltarem de apenas uma extremidade,

$$Z_1 = \sum_0^n e^{-n\beta\epsilon} = \frac{\left(1 + e^{-(N+1)\beta\epsilon}\right)}{\left(1 - e^{-\beta\epsilon}\right)}$$

$$\mathscr{P}_1(n) = e^{-n\beta\epsilon}/Z_1$$

(b) Se as moléculas se soltarem de ambas as extremidades,

$$Z_2 = \sum_0^N n e^{-n\beta\epsilon} = -\frac{\partial Z_1}{\partial(\beta\epsilon)} = -\frac{(N+1)e^{-(N+1)\beta\epsilon}}{1 - e^{-\beta\epsilon}} + \frac{\left(1 - e^{-(N+1)\beta\epsilon}\right)e^{-\beta\epsilon}}{\left(1 - e^{-\beta\epsilon}\right)^2}$$

$$\therefore \quad Z_2 == \left(1 - e^{-\beta\epsilon}\right)^{-2} e^{-\beta\epsilon} \left[-(N+1)e^{-N\beta\epsilon} + N e^{-(N+1)\beta\epsilon} + 1\right]$$

$$\text{e} \qquad \mathscr{P}_2(n) = \frac{n e^{-n\beta\epsilon}}{Z_2}$$

16.5.5 Calculate the probability that a harmonic oscillator of natural ...

Solução:

$\mathscr{P}_o = 1 - \mathscr{P}_e$ onde $\mathscr{P}_e$ é a probabilidade do oscilador possuir um número quântico par.

$$\mathscr{P}_e = \sum_{n\ par} e^{-\beta\left(n+\frac{1}{2}\right)\hbar\omega_0} \bigg/ \sum_n e^{-\beta(n+\frac{1}{2})\hbar\omega_0} = e^{-\beta\hbar\omega_0/2} \sum_{n=par} \left(e^{-\beta\hbar\omega_0}\right)^n / z = \frac{e^{-\beta\hbar\omega_1/2}}{z} \sum_n e^{-2\beta\omega_0 n}$$

$$\mathscr{P}_e = \frac{e^{-\beta\hbar\omega_0/2}}{z} \frac{1}{1 - e^{-2\beta\hbar\omega_0}}$$

$$\text{como} \qquad z = \frac{e^{-\beta\hbar\omega_0/2}}{1 - e^{-\beta\hbar\omega_0}}$$

$$\therefore \mathscr{P}_e = \frac{1}{1 + e^{-\beta\hbar\omega_0}} \qquad \text{e} \qquad \mathscr{P}_{\text{odd}} = 1 - \mathscr{P}_{\text{even}} = \frac{1}{e^{-\beta\hbar\omega_0} + 1}$$

Casos limite:

$$\text{na medida em que} \quad T \to 0, \quad \mathscr{P}_{\text{odd}} \to 0$$

$$\text{na medida em que} \quad T \to \infty, \quad \mathscr{P}_{\text{odd}} \to \frac{1}{2}$$

$$\text{para baixos valores de} \quad T, \quad \mathscr{P}_{\text{odd}} \sim e^{-\beta\hbar\omega}$$

$$\text{para altos valores de} \quad T, \quad \mathscr{P}_{\text{odd}} \sim \frac{1}{1 + e^{-\beta\hbar\omega} + \cdots} \sim \frac{1}{2} - \frac{1}{4}\beta\hbar\omega + \cdots$$

16.5.6   A small system has two energy levels, of energies 0 and ε...

Solução:

$$-\beta F = \ln\left(g_0 + g_1 e^{-\beta\epsilon}\right)$$

$$U = \frac{\partial}{\partial\beta}(\beta F) = -\frac{\partial}{\partial\beta}\ln\left(g_0 + g_1 e^{-\beta\epsilon}\right) = \frac{g_1\epsilon e^{-\beta\epsilon}}{g_0 + g_1 e^{-\beta\epsilon}}$$

$$c = \frac{dU}{dT} = k_B\beta^2\frac{g_0 g_1\epsilon^2 e^{-\beta\epsilon}}{(g_0 + g_1 e^{-\beta\epsilon})^2}$$

$$S = \frac{U-F}{T} = \frac{U}{T} + k_B\ln z = \frac{1}{T}\frac{g_1\epsilon e^{-\beta\epsilon}}{g_0 + g_1 e^{-\beta\epsilon}} + k_B\ln\left(g_0 + g_1 e^{-\beta\epsilon}\right)$$

Note que $S \to 0$ na medida em que $T \to 0$ e $S \to k_B\ln\left(g_0 + g_1\right)$ na medida em que $T \to \infty$.
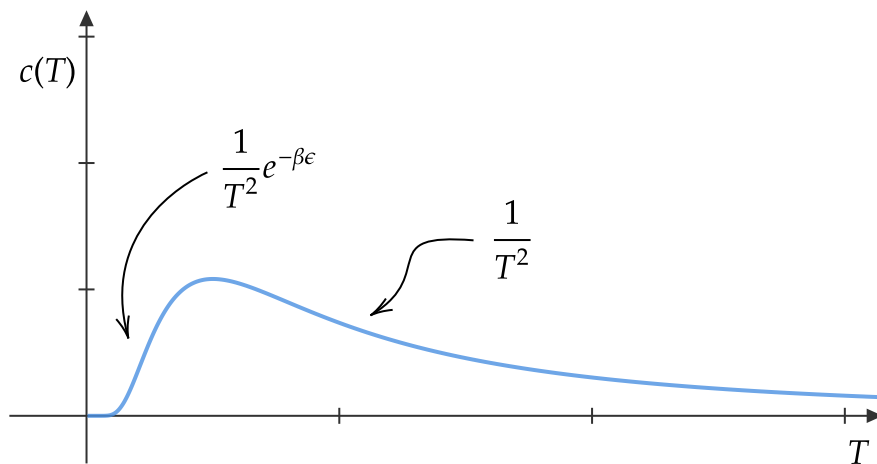
16.5.7   Two simple harmonic oscillators, each of natural frequency ω...

Solução:

$$z = \sum_{n,m} e^{-\beta\left[\left(n+\frac{1}{2}\right)\hbar\omega + \left(m+\frac{1}{2}\right)\hbar\omega\right]} + \sum_n\left[e^{-\beta 2\left(n+\frac{1}{2}\right)\hbar\omega + \Delta} - e^{-\beta(2n+1)\hbar\omega}\right]$$

onde o segundo termo é uma correção para a interação

$$z = \frac{e^{-\frac{1}{2}\beta\hbar\omega}}{1-e^{-\beta\hbar\omega}}\frac{e^{-\frac{1}{2}\beta\hbar\omega}}{1-e^{-\beta\hbar\omega}} + \left(e^{-\beta\Delta} - 1\right)\frac{e^{-\beta\hbar\omega}}{1-e^{-\frac{1}{2}\beta\hbar\omega}} = \frac{x}{(1-x)^2} + \left(e^{-\beta\Delta} - 1\right)\frac{x}{1-x^2}, \quad x \equiv e^{-\beta\hbar_0\omega}$$

$$\therefore \mathscr{P}_{\text{equal}} = e^{-\beta\Delta}\frac{x}{1-x^2}\Bigg/ Z = e^{-\beta\Delta}\left[\frac{1+x}{1-x} + e^{-\beta\Delta} - 1\right]^{-1}$$

Na medida em que $T \to 0$, $e^{-\beta\Delta} \to 0$ e $x \to 0$

$$\therefore \mathscr{P}_{\text{equal}} \simeq \frac{1}{2e^{\beta(\Delta-\hbar\omega)}} \to 0 \qquad \text{se}\Delta > \hbar\omega$$

E também

$$\therefore \mathscr{P}_{\text{equal}} \simeq \frac{1}{2e^{\beta(\Delta-\hbar\omega)}} \to 1 \qquad \text{se}\Delta < \hbar\omega$$

Note que se $\Delta < \hbar\omega$ o estado fundamental é $(0,0)$, enquanto que se $\Delta > \hbar\omega$ o estado fundamental é ou $(0,1)$ ou $(1,0)$.

16.6 DENSITY OF STATES AND DENSITY OF ORBITAL STATES [SUMÁRIO]

16.6.1 Show that the number of orbital states in the energy interval... [SUMÁRIO]

SOLUÇÃO:

$$\text{Modos em } d\varepsilon = D(\varepsilon)d\varepsilon = D(\varepsilon)d(\hbar\omega) = D(\varepsilon)\hbar d\omega \equiv D'(\omega)d\omega$$

16.6.2 For the particles of a gas $\varepsilon = \mathbf{p}^2/2\mathbf{m} = (\hbar^2/2\mathbf{m})\mathbf{k}^2$... [SUMÁRIO]

SOLUÇÃO:

NENHUMA SOLUÇÃO PARA ESSE PROBLEMA NO MOMENTO

16.6.3 For excitations obeying the spectral relation $\omega = \mathbf{Ak^n}$, $\mathbf{n} > \mathbf{0}$... [SUMÁRIO]

SOLUÇÃO:

$$D'(\omega) = \frac{V}{2\pi^2}k^2(\omega)\frac{dk}{d\omega} = \frac{V}{2\pi^2}k^2 \bigg/ \frac{d\omega}{dK} = \frac{V}{2\pi^2}k^2 \bigg/ nAK^{n-1} = \frac{V}{2\pi^2 nA}k^{3-n}$$

$$\text{Mas} \quad K^{3-n} = (\omega/A)^{\frac{3-n}{n}}$$

$$\therefore D'(\omega) = \frac{V}{2\pi^2 An}\left(\frac{\omega}{A}\right)^{\frac{3}{n}-1}$$

16.7 THE DEBYE MODEL OF NONMETALLIC CRYSTALS [SUMÁRIO]

16.7.1 Calculate the energy of a cristal in the Debye approximation. Show ... [SUMÁRIO]

SOLUÇÃO:

$$U = \frac{\partial}{\partial\beta}(\beta F) = \frac{\partial}{\partial\beta}\sum_{\text{modos}} \ln\left(1 - e^{-\beta\hbar\omega}\right) = \sum_{\text{modos}} \frac{\hbar\omega e^{-\beta\hbar\omega}}{1 - e^{-\beta\hbar\omega}} = \sum_{\text{modos}} \frac{\hbar\omega}{e^{\beta\hbar\omega-1}}$$

$$\text{Portanto} \quad U = \frac{\partial}{\partial\beta}(\beta F) = \int_0^{\omega_{max}} \frac{\hbar\omega}{e^{\beta\hbar\omega} - 1}D'(\omega)d\omega \quad \text{com} \quad D'(\omega) = \frac{9N_A}{\omega_{\max}^3}\omega^2 \quad \text{(das equações 16.54-16.56)}$$

$$U = \frac{9N_A\hbar}{\omega_{\max}^3} \int_0^{\omega_{\max}^3} \frac{\omega^3}{e^{\beta\hbar\omega-1}}d\omega \quad \text{e} \quad c_v = \frac{\partial U}{\partial T}$$

16.7.2 Calculate the entropy of a cristal in the Debye approximation, and ... [SUMÁRIO]

> **SOLUÇÃO:**

$$F = k_B T \sum_{\text{modes}} \ln\left(1 - e^{-\beta\hbar\omega(\lambda)}\right) \qquad \text{equação 16.50}$$

$$S = -\frac{\partial F}{\partial T} = -\frac{F}{T} + \frac{1}{T}\sum_{\text{modes}} \frac{\hbar\omega(\lambda)}{e^{\beta k\omega(\lambda)} - 1} \qquad \text{o que é equivalente a} \ S = -\frac{F}{T} + \frac{U}{T}$$

$$S = \frac{9R}{\omega_{max}^3} \int_0^{\omega_{max}} \left[-\ln\left(1 - e^{-\beta\hbar\omega}\right) + \frac{\beta\hbar\omega}{e^{\beta\hbar\omega} - 1} \right] \omega^2 d\omega$$

$$c_v = T\frac{dS}{dT} = -\beta\frac{ds}{d\beta} = \frac{9\beta R}{\omega_{max}^3} \int_0^{\omega_{max}} \left[\frac{\hbar\omega e^{-\beta\hbar\omega}}{1 - e^{-\beta\hbar\omega}} - \frac{\hbar\omega}{e^{\beta\hbar\omega} - 1} + \frac{\beta\hbar^2\omega^2}{\left(e^{\beta\hbar\omega} - 1\right)^2} \right] \omega^2 d\omega$$

Os dois primeiros termos da integral se anulam (verifique!), assim

$$= \frac{9\beta^2 R\hbar^2}{\omega_{max}^3} \int_0^{\omega_{max}} \frac{\omega^4 d\omega}{\left(e^{\beta\hbar\omega} - 1\right)^2} = \frac{9R}{u_m^3} \int_0^{u_m} \frac{u^4 du}{\left(e^u - 1\right)^2} \quad u \equiv \beta\hbar\omega$$

16.7.3 The frequency $\omega(\lambda)$ of the vibrational mode of wave... [SUMÁRIO]

> **SOLUÇÃO:**

$$F = k_B T \sum_{\text{modes}} \ln\left(1 - e^{-\beta\hbar\omega(\lambda)}\right)$$

$$P = -\frac{\partial F}{\partial V} = +\frac{\gamma}{V}\sum_{\text{modes}} \frac{\hbar\omega(\lambda)}{e^{\beta\hbar\omega(\lambda)} - 1} = \frac{\gamma}{V}U \implies PV = \gamma U$$

Considere c_v:

$$c_v = \left(\frac{\partial u}{\partial T}\right)_V = \frac{v}{\gamma}\left(\frac{dP}{dT}\right)_V = \frac{v}{\gamma}\frac{\alpha}{\kappa_T} \qquad (\text{ou} \quad v\alpha = \gamma\kappa_T c_v)$$

16.8 ELECTROMAGNETIC RADIATION [SUMÁRIO]

16.8.1 Show that including the "zero-point energies"of the electromagnetic... [SUMÁRIO]

> **SOLUÇÃO:**

A adição de energias de ponto-zero na equção 16.48 leva a

$$z(\lambda) = \frac{e^{-\beta\hbar\omega_0/2}}{1 - e^{-\beta\hbar\omega_0}}$$

E daí na equação 16.58 para uma contribuição adicional

$$\Delta F = \sum_{\text{modos}} \frac{\hbar\omega_0}{2} \qquad \text{o que diverge}$$

16.8.2 Show that the energy per unit volume of electromagnetic radiation ...
[SUMÁRIO]

> **SOLUÇÃO:**

Isso segue diretamente da equação 16.63 _____

16.8.3 Evaluating the number of photons per unit volume in the frequency ...
[SUMÁRIO]

> **SOLUÇÃO:**

$$\frac{1}{V}N_\omega d\omega = \frac{1}{V}\left(U_\omega/\hbar\omega\right)d\omega = \frac{2}{\pi^2 c^3}\frac{\omega^2}{e^{\beta\hbar\omega}-1}d\omega$$

$$N/V = \frac{2}{\pi^2 c^3}\int_0^\infty \frac{\omega^2 d\omega}{e^{\beta\hbar\omega}-1} = \frac{2\left(k_B T\right)^3}{\pi^2\hbar^3 c^3}\int_0^\infty \frac{x^2}{e^x-1}dx$$

$$\text{Mas}\quad \xi(3) = \frac{1}{3!}\int_0^\infty \frac{x^2}{e^x-1}dx \quad \text{e}\quad \xi(3) = 1,202 \qquad \xi\ (\text{é a função zeta})$$

$$\therefore \int_0^\infty \frac{x^2}{e^x-1} = 6\times 1,202 = 7,212$$

$$N/V = \frac{2\left(k_B T\right)^3}{\pi^2\hbar^3 c^3}\times 7,212 \qquad \text{e}\quad \frac{U}{V} = \frac{\pi^2\left(k_B T\right)^4}{15\hbar^3 c^3}$$

$$\therefore \frac{U}{N} = \frac{15}{\pi^2}\frac{2\times 7,212}{\pi^2}k_B T \simeq 2,2\ k_B T$$

16.8.4 Since radiation within a cavity propagates isotropically with velocity c...
[SUMÁRIO]

> **SOLUÇÃO:**

> **NENHUMA SOLUÇÃO PARA ESSE PROBLEMA NO MOMENTO**

16.10   THE CLASSICAL IDEAL GAS [SUMÁRIO]

16.10.1 Show that the calculation of $Z = z^{\tilde{N}}$, with z given by equation ... [SUMÁRIO]

> **SOLUÇÃO:**

> **NENHUMA SOLUÇÃO PARA ESSE PROBLEMA NO MOMENTO**

16.10.2 Show that the fundamental equations of a "multicomponent simple gas"...
[SUMÁRIO]

> **SOLUÇÃO:**

16.10.3   The factors $(1/\tilde{N}_1!)(1/\tilde{N}_2!)$ in equation 16.74 give and additive... [SUMÁRIO]

SOLUÇÃO:

$$e^{-\beta F} = \frac{1}{N_1!}\frac{1}{N_2!}z_1^{N_1}z_2^{N_2} = \frac{(N_1+N_2)!}{N_1!N_2!}\frac{1}{(N_1+N_2)!}z_1^{N_1}z_2^{N_2}$$

$$\therefore -\beta F = -\beta F_{\text{classical}} + \ln\frac{(N_1+N_2)!}{N_1!N_2!}$$

$$\therefore S = -\frac{\partial F}{\partial T} = S_{\text{classical}} + k_B\ln\frac{(N_1+N_2)!}{N_1!N_2!}$$

$$\therefore \Delta S = k_B\left\{(N_1+N_2)\ln(N_1+N_2) - N_1\ln N_1 - N_2\ln N_2\right\}$$

$$= -k_B N_1\ln\frac{N_1}{N_1+N_2} - k_B N_2\ln\frac{N_2}{N_1+N_2}$$

$$\therefore \boxed{\Delta S = -Nk_B\left\{x_1\ln x_1 + x_2\ln x_2\right\}}$$

16.10.4   Consider a particle of mass m in a cubic container of volume V ... [SUMÁRIO]

SOLUÇÃO:

$$E = \frac{\hbar^2 k^2}{2m} \;\; \text{e} \;\; k \sim \frac{n\pi}{V^{1/3}} \quad \text{então} \quad \frac{\Delta E}{h_B T} \sim \frac{\hbar^2\pi^2}{2mV^{2/3}k_B T} \sim \frac{(10^{-34})^2 \times 10}{2\times\left(\frac{4\times 10^{-3}}{6\times 10^{23}}\right)\times 1\times 10^{-23}\times 10^{-8}} \sim 10^{-10}$$

16.10.5   A single particle is contained in a vessel of volume 2V which... [SUMÁRIO]

SOLUÇÃO:

$$\mathcal{Z} = z_{\text{int}}z_{\text{momentum}}\left[z_{\text{left}} + z_{\text{right}}\right] \quad \text{onde} \quad z_{\text{left}} = \iiint e^{-\beta V_l(\vec{r})}dxdydz$$

e ainda

$$z_{\text{right}} = z_{\text{left}}e^{-\beta\epsilon_e}$$

A probabilidade de estar no lado direito é

$$\frac{z_{\text{right}}}{z_{\text{right}} + z_{\text{left}}} = \frac{e^{-\beta\epsilon_e}}{1 + e^{-\beta\epsilon_e}} = \frac{1}{e^{\beta\epsilon_e}+1}$$

Se tem 1 mol no recipiente então tem $\dfrac{1}{e^{\beta\epsilon_e}+1}$ mols na direita e $\dfrac{e^{\beta\epsilon_e}}{1+e^{\beta\epsilon_e}}$ mols na esquerda.

Mas $PV = NRT$, então

$$\mathscr{P}_{\text{right}} = \frac{1}{e^{\beta\epsilon_e}+1}\frac{RT}{V} \qquad \text{e} \qquad \mathscr{P}_{\text{left}} = \frac{e^{\beta\epsilon_e}}{e^{\beta\epsilon_e}+1}\frac{RT}{V}$$

17 ENTROPY AND DISORDER: GENERALIZED CA-NONICAL FORMULATIONS [SUMÁRIO]

17.1 ENTROPY AS A MEASURE OF DISORDER [SUMÁRIO]

17.1.1 Consider the quantity $x \ln x$ in the limit $x \to 0$. Show ... [SUMÁRIO]

> **SOLUÇÃO:**

Pela regra de L'Hospital,

$$\lim_{x \to 0} x \ln x = \lim_{x \to 0} \frac{\left(\frac{d \ln x}{dx} \right)}{\left(\frac{d}{dx} \frac{1}{x} \right)} = \lim_{x \to 0} \frac{(1/x)}{(-1/x)} = \lim_{x \to 0} (-x) = 0$$

Se $f_j = 1$ e $f_i = 0$ para $i \neq j$, então $\sum f_j \ln f_j = 0$ termo a termo.

17.1.2 Prove that the disorder, defined in equation 17.6, is nonnegative... [SUMÁRIO]

> **SOLUÇÃO:**

$$Disordem = - \sum_j f_j \ln f_j \quad \text{e} \quad 0 \leq f_j \leq 1$$

Mas cada termo $-f_j \ln f_j \geq 0$, então devemos ter $Disordem \geq 0$

17.1.3 Prove that the quantity $-k \sum_j f_j$ is maximum if all the... [SUMÁRIO]

> **SOLUÇÃO:**
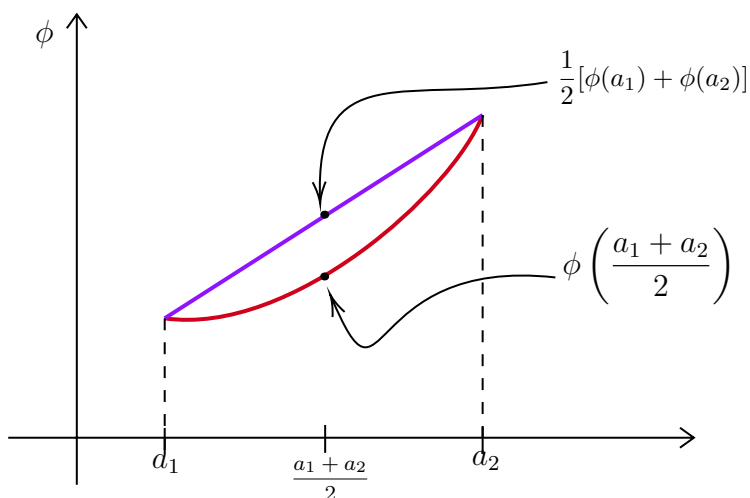
Faça $\quad \phi = x \ln x$

$$\frac{d^2 \phi}{dx^2} = + \frac{1}{x^2} > 0 \quad \therefore \phi \text{ é convexa}$$

Tomando $\quad a_j = f_j, \quad$ tal que $\sum a_j = 1$

$$\phi \left(\frac{1}{\Omega} \right) = \frac{1}{\Omega} \ln \frac{1}{\Omega} \leqslant \frac{1}{\Omega} \sum f_j \ln f_j$$

17.2 DISTRIBUTIONS OF MAXIMAL DISORDER

17.2.1 Show that the maximum value of disorder, as calculate in this section...

SOLUÇÃO:

NENHUMA SOLUÇÃO PARA ESSE PROBLEMA NO MOMENTO

17.2.2 Given the identification of the disorder as the entropy, and of ...

SOLUÇÃO:

NENHUMA SOLUÇÃO PARA ESSE PROBLEMA NO MOMENTO

17.3 THE GRAND CANONICAL FORMALISM

17.3.1 Calculate $(\partial \log \mathbf{Z}/\partial \beta)_{\beta\mu}$ directly from equation 17.27...

SOLUÇÃO:

NENHUMA SOLUÇÃO PARA ESSE PROBLEMA NO MOMENTO

17.3.2 A system is contained in a cylinder with diathermal impermeable walls...

SOLUÇÃO:

Substitua μ por $-P$ e N_j por V em todas as equações da seção 17.3, então

$$f_j = e^{\beta\Psi'}e^{-\beta\left(E_f + PV\right)}$$

Note que o somatório sobre N_j se transforma em uma integral sobre V, e $E_j = E_j(V)$

17.3.3 For the surface adsorption model of the preceding example, investigate...

SOLUÇÃO:

Faça $\epsilon_1 + \mu_0 = -x$ e $\epsilon_2 + 2\mu_0 = -y$

$$\therefore \bar{n} = \frac{\left(e^{\beta x} + z e^{\beta y}\right)}{\left(1 + e^{\beta x} + e^{\beta y}\right)}$$

Na medida em que $\beta \to \infty$:
(a) Se ambos x e y são negativos, $\bar{n} = 0$

(b) Se $y < 0$ então $\bar{n} \to \frac{e^{\beta x}}{1+e^{\beta x}} \to \begin{cases} 1 & se \quad x > 0 \\ 0 & se \quad x < 0 \end{cases}$

(c) Se $x < 0$ e $y > 0$, $\bar{n} \to \frac{2e^{\beta y}}{1+e^{\beta y}} \to 2$

(d) Se $x > 0$ e $y > 0$ então podemos desprezar a unidade no denominador, e aí $\bar{n} = \frac{1+2e^{\beta(y-x)}}{1+e^{\beta(y-x)}}$ e podemos distinguir dois casos:

$$y - x > 0, \quad \bar{n} \to 2$$
$$y - x < 0; \quad \bar{n} \to 1$$
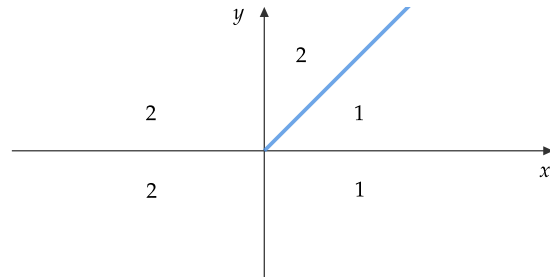
Para reescrever isso em termos de $\epsilon_1 + \mu$ e $\epsilon_2 + \mu$, que tem sinais opostos a x e y, basta "refletir" o diagrama através da origem (para o terceiro quadrante):
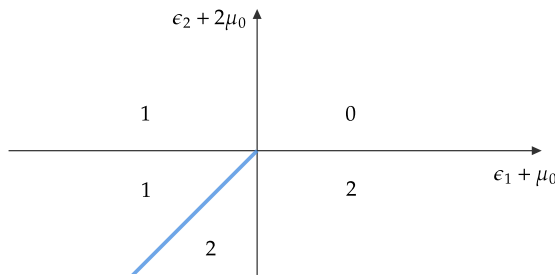
Ou, em um plano com $\epsilon_1 + \mu$ sendo abiscissa e $\epsilon_2 + \mu$ sendo a ordenada,

$\bar{n} \to 0$ No primeiro quadrante

$\bar{n} \to 1$ No segundo quadrante

$\bar{n} \to 2$ No quarto quadrante

e o terceiro quadrante é dividido ao meio pela diagonal com $\bar{n} \to 1$ acima da diagonal e com $\bar{n} \to 2$ abaixo da diagonal

17.3.4 Suppose the adsorption model to be augmented by assuming that two... [SUMÁRIO]

SOLUÇÃO:

$$z = 1 + e^{-\beta\epsilon_1'} + e^{-\beta\epsilon_2'}\left(1 + e^{-\beta\hbar\omega} + e^{-2\beta\hbar\omega} + \cdots\right) \quad \text{onde} \quad \epsilon' \equiv \epsilon - \mu$$

$$\therefore z = 1 + e^{-\beta\epsilon_1'} + e^{-\beta\epsilon_2'}\frac{1}{1 - e^{-\beta\hbar\omega}}$$

$$\therefore \not{Z} = \left(1 + e^{-\beta\epsilon_1'} + \frac{e^{-\beta\epsilon_2'}}{1 - e^{-\beta\hbar\omega}}\right)^{\tilde{N}}$$

As respostas dos itens (b), (c), ..., (e) são dadas no texto.

17.3.5 Calculate the fundamental equation of the polymer model of section 15.4 ... [SUMÁRIO]

SOLUÇÃO:

$$e^{-\beta\Psi} = z^{\tilde{N}}$$

$$z = \sum_{\ell_x=\pm a} \sum_{\ell_y=\pm a} e^{-\beta(-\ell_x\mathcal{T}-\epsilon|\ell_y|)} = \left(e^{-\beta a\mathcal{T}} + e^{+\beta a\mathcal{T}} + e^{-\beta\epsilon} + e^{+\beta\epsilon}\right)$$

$$\langle L_x \rangle = \tilde{N}\langle \ell_x \rangle = \frac{\tilde{N}}{\beta}\frac{\partial \ln z}{\partial \mathcal{T}} = \frac{\tilde{N}a}{z}\left(-e^{-\beta a\mathcal{T}} + e^{\beta a\mathcal{T}}\right)$$

$$U = \tilde{N}\left(\frac{\partial \ln z}{\partial \beta}\right)_{\beta a} = \frac{\tilde{N}}{z}\left[a\mathcal{T}\left(e^{-\beta a\mathcal{T}} - e^{\beta a\mathcal{T}}\right) + \epsilon\left(e^{-\beta\epsilon} + e^{\beta\epsilon}\right)\right]$$

17.3.6 A system contains Ñ sites and Ñ electrons. At a given site... [SUMÁRIO]

SOLUÇÃO:

(a):

$$\langle n \rangle = \frac{0 + e^{-\beta(g\mu_B H - \mu)} + e^{-\beta(-g\mu_B H - \mu)} + 2e^{-\beta(\epsilon - 2\mu)}}{1 + e^{-\beta(g\mu_B H - \mu)} + e^{-\beta(-g\mu_B H - \mu)} + e^{-\beta(\epsilon - 2\mu)}}$$

Mas $\langle n \rangle = 1$. Tal que $1 = e^{-\beta(\epsilon - 2\mu)}$ ou $\mu = \dfrac{\epsilon}{2}$

(b):

$$\langle E \rangle = \frac{\epsilon e^{-\beta(\epsilon - 2\mu)}}{1 + e^{-\beta(g\mu_B H - \mu)} + e^{-\beta(-g\mu_B H - \mu)} + e^{-\beta(\epsilon - 3\mu)}} = \frac{\epsilon}{2 + 2\cosh\left(\beta g\mu_B H\right)e^{\beta\epsilon/2}}$$

$$C = \frac{d\langle E \rangle}{dT}$$

(c):

$$\chi = -\frac{d\langle E \rangle}{dH} = -\epsilon\frac{2\sinh\left(\beta g\mu_B H\right)\beta g\mu_B e^{\beta\epsilon/2}}{\left[2 + 2\cosh\left(\beta g\mu_B H\right)e^{\beta\epsilon/2}\right]^2}$$

e para $H \to 0$, temos que $\sinh\left(\beta g\mu_B H\right) \to \beta g\mu_B H$ e $\sinh\left(\beta g\mu_B H\right) \to 1$

$$\chi_0 = \frac{-\epsilon}{4\left(1 + e^{\beta\epsilon/2}\right)^2}\left[2\beta^2 g^2 \mu_B^2 e^{\beta\epsilon/2}\right]$$

17.3.7 Carbon monoxide molecules (CO) can be adsorbed at specific sites on a solid... [SUMÁRIO]

SOLUÇÃO:

Para encontrar μ do gas:

$$F = -Nk_B T \ln\left[\frac{eV}{N}\left(\frac{mk_B T}{2\pi\hbar^2}\right)^{3/2} z_{\text{vib}}\, z_{\text{rot}}\right]$$

$$\therefore \mu = \frac{\partial F}{\partial N} = -k_B + \ln\left[\frac{V}{N}\left(\frac{mk_BT}{2\pi\hbar^2}\right)^{3/2} z_{\text{vib}} z_{\text{rot}}\right]$$

Cinsidere um único sítio, com probabilidade de ocupação $\mathscr{P}_{oc}$.

$$\mathscr{P}_{oc} = \frac{\tilde{z}_v e^{-\beta\mu}}{1 + \tilde{z}_v e^{-\beta\mu}}$$

onde $\tilde{z}_v$, a soma de partição vibracional do sítio ocupado é dada por

$$\tilde{z}_v = \frac{1}{1 - e^{-\beta\hbar\tilde{\omega}}}, \quad \text{com} \quad \tilde{\omega} = \omega\left(\frac{m_0}{m_0 + m_c}\right)^{1/2} \quad \text{sendo a frequência vibracional da molécula ligada}$$

Novamente, retornando ao gás:

$$z_v = \frac{1}{1 - e^{-\beta\hbar\omega}} \quad \omega \text{ é a frequência vibracional da molécula livre}$$

$$z_{rot} = \sum_{\ell=1}^{\infty} e^{-\beta\ell(\ell+1)\hbar^2/2I}(2l+1) \simeq 2\sum_{\ell=0}^{\infty} \ell e^{-\beta\ell(\ell+1)\hbar^2/2I} \simeq \int_0^\infty e^{-\beta\hbar^2 x^2/2I}dx = \frac{2I}{\beta\hbar^2}$$

Então, para a fase gasosa,

$$e^{-\beta\mu} = \frac{V}{N}\left(\frac{mk_BT}{2\pi\hbar^2}\right)^{3/2} \frac{1}{1 - e^{-\beta\hbar\omega}} \frac{2I}{\beta\hbar^2}$$

e usando a expressão $\tilde{z}_v^{-1} = \left(1 - e^{-\beta\hbar\tilde{\omega}}\right)$, podemos finalmente avaliar a probabilidade $\mathscr{P}_{oc}$

$$\therefore \boxed{\mathscr{P}_{oc} = \frac{e^{-\beta\mu}}{\tilde{z}_v^{-1} + e^{-\beta\mu}}}$$

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18 QUANTUM FLUIDS [SUMÁRIO]

18.1 QUANTUM PARTICLES: A"FERMION PRE-GAS MODEL" [SUMÁRIO]

18.1.1 Obtain the mean number of particles in the fermion pre-gras model... [SUMÁRIO]

Solução:

NENHUMA SOLUÇÃO PARA ESSE PROBLEMA NO MOMENTO

18.1.2 The entropy of a system is given by $S = -k_B \sum_j f_j$, where f_j... [SUMÁRIO]

Solução:

(a) Os $2^6 = 64$ microestados possíveis correspondem ao número de formas de independentemente atribuir os rótulos e ($empty$) ou f ($filled$) para cada um dos seis estados orbitais.

(b) $S = -k_b \sum_{n,m} f_{n,m} \ln f_{n,m}$ tem seis termos, correspondendo aos seis estados orbitais mencionados no item (a). A "propriedade especial do modelo"é a visão de que o sistema está em

contato com um reservatório de partículas, tornando assim a ocupação de cada estado orbital independente da ocupação dos outros estados orbitais

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18.1.3 Apply equation 17.27 for U to the fundamental equation of the...

18.1.4 Show that $df/d\varepsilon = -\beta/4$ at $\varepsilon = \mu$. With this result...

18.1.5 Show that Fig. 17.2 (of $f(\varepsilon, T)$ as a function of ε) is...

18.1.6 .Suppose $f(\varepsilon, T)$ is to be approximated as a function of..
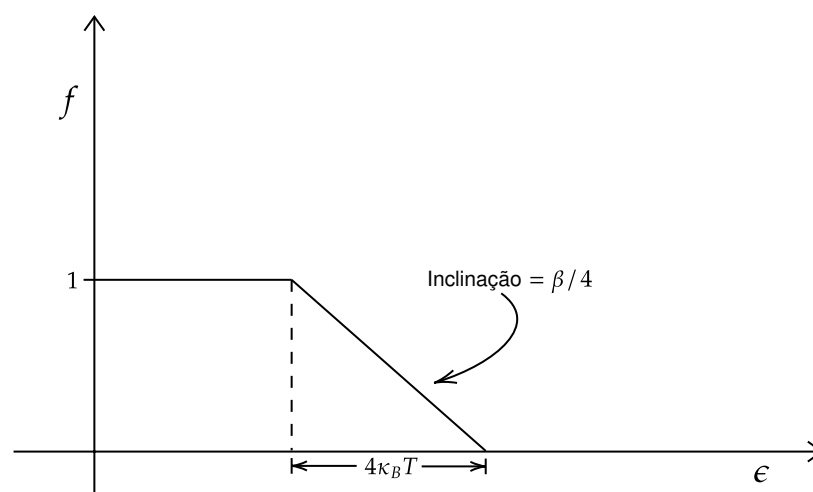
18.2 THE IDEAL FERMI FLUID

18.2.1 Prove equations c, g, h, i and j of table 18.1 (for fermions only)...

Solução:

NENHUMA SOLUÇÃO PARA ESSE PROBLEMA NO MOMENTO

18.3 THE CLASSICAL LIMIT AND THE QUANTUM CRITERION

18.3.1 Calculate the definite integrals appearing in equations 18.25 and...

Solução:

NENHUMA SOLUÇÃO PARA ESSE PROBLEMA NO MOMENTO

18.3.2 Validate the interpretation of λ_T as the "thermall wavelength" by ...

Solução:

NENHUMA SOLUÇÃO PARA ESSE PROBLEMA NO MOMENTO

18.4 THE STRONG QUANTUM REGIME: ELECTRONS IN A METAL

18.4.1 Show that equation 18.32 can be interpreted as $\mu_0 = \hbar^2 k_f^2$ where...

Solução:

NENHUMA SOLUÇÃO PARA ESSE PROBLEMA NO MOMENTO

18.4.2 Derive equation 18.35 by the following sequence of operations:...

Solução:

NENHUMA SOLUÇÃO PARA ESSE PROBLEMA NO MOMENTO

18.6 NONCONSERVED IDEAL BOSON FLUIDS: ELECTROMAGNETIC RADIATION REVISITED [SUMÁRIO]

18.6.1 Calculate the number of photons in the lowest orbital state... [SUMÁRIO]

SOLUÇÃO:

(a): O estado em questão tem $\lambda_x = \lambda_y = \lambda_z = 0,5$ metros $\therefore \lambda = 0,5\sqrt{3}$ metros.

$$\therefore \beta\epsilon_k = \hbar ck/k_B T = \frac{hc}{\lambda k_B T} = 0,57 \times 10^{-4}$$

$$\bar{n} = \frac{1}{e^{\beta\epsilon_k} - 1} \sim \frac{1}{\beta\epsilon_k} = 1,7 \times 10^4$$

(b): Se $\lambda = 5000$Å, $\epsilon_k = \frac{hc}{\lambda} = 4 \times 10^{-19}$ Joules

$$\beta\epsilon_k = 10^2$$
$$\bar{n} = \frac{1}{e^{\beta\epsilon_k} - 1} \simeq 2,7 \times 10^{43}$$

18.6.2 (a) In applying the grand canonical formalismo...(b) Denoting the... [SUMÁRIO]

SOLUÇÃO:

(a) Não. Nós retornamos para a queção 16.47:

$$D'(\omega) = \frac{V}{2\pi^2}k^2\frac{dk}{d\omega} \quad \text{e para fótons}\omega = ck$$

$$\therefore D'(\omega) = \frac{V}{2\pi^2 c}k^2 = \frac{V}{2\pi^2 c^3}\omega^2$$

18.7 BOSE CONDENSATION [SUMÁRIO]

18.7.1 Show that equations 18.56 and 18.58, for $\tilde{N}_e$ and U, respectively... [SUMÁRIO]

SOLUÇÃO:

NENHUMA SOLUÇÃO PARA ESSE PROBLEMA NO MOMENTO

18.7.2 Show that $F_{3/2}(1)$, $F_{5/2}(1)$ and $F'_{5/2}(1)$ are all finite... [SUMÁRIO]

SOLUÇÃO:

NENHUMA SOLUÇÃO PARA ESSE PROBLEMA NO MOMENTO

18.7.3 Show that the explicit inclusion of the orbital ground state... [SUMÁRIO]

SOLUÇÃO:

NENHUMA SOLUÇÃO PARA ESSE PROBLEMA NO MOMENTO

19 FLUCTUATIONS [SUMÁRIO]

19.2 MOMENTS OF THE ENERGY FLUCTUATIONS [SUMÁRIO]

19.2.1 A molecule has a vibrational mode of natural frequency ω. The... [SUMÁRIO]

SOLUÇÃO:

$$\langle \hat{E}^2 \rangle - \langle \hat{E} \rangle^2 = \left\langle (\hat{E} - U)^2 \right\rangle = -\frac{\partial U}{\partial \beta} \qquad (U \equiv \langle E \rangle) \quad (19.6)$$

$$U = \frac{\hbar\omega}{e^{\beta\hbar\omega} - 1}; \quad \therefore \left\langle (\hat{E} - U)^2 \right\rangle = -\frac{\partial U}{\partial \beta} = \frac{(\hbar\omega)^2 \, e^{\beta\hbar\omega}}{(e^{\beta\hbar\omega} - 1)^2}$$

19.2.2 Calculate the third central moment for the molecule in the preceding problem. [SUMÁRIO]

SOLUÇÃO:

$$\left\langle (E - U)^3 \right\rangle = -\frac{\partial}{\partial \beta} \left\langle (\hat{E} - U)^2 \right\rangle + 2\langle \hat{E} - U \rangle \frac{\partial U}{\partial \beta}$$

$$= -\frac{\partial^2 U}{\partial \beta^2}$$

$$\therefore \quad \boxed{\left\langle (E - U)^3 \right\rangle = \frac{\partial}{\partial \beta} \frac{(\hbar\omega)^2 e^{\beta h\omega}}{(e^{\beta\hbar\omega} - 1)^2} = -\frac{(\hbar\omega)^3 \left(e^{\beta\hbar\omega} + 1\right) e^{\beta\hbar\omega}}{(e^{\beta\hbar\omega} - 1)^3}}$$

19.2.3 Calculate the mean square deviation of the energy contained within a... [SUMÁRIO]

SOLUÇÃO:

$$\left\langle (\hat{E} - U)^2 \right\rangle = -\frac{\partial U}{\partial \beta} = k_B T^2 N c_v \quad \text{(equação 19.6)}$$

$$\text{Mas} \quad U = b\mathrm{v}'T^4 = b\mathrm{v}'k_B^4/\beta^4 \quad \text{(equação 3.52)}$$

$$\therefore \quad \boxed{\left\langle (\hat{E} - U)^2 \right\rangle = 4b\mathrm{v}'k_B^{-4}/\beta^5 = 4b\mathrm{v}'k_B T^5}$$

19.3 GENERAL MOMENTS AND CORRELATION MOMENTS [SUMÁRIO]

19.3.1 An ideal gas is in contact with a thermal and a pressure reservoir... [SUMÁRIO]

SOLUÇÃO:

$$\langle \Delta \hat{E} \Delta \hat{V} \rangle = -k_B \left(\frac{\partial V}{\partial (1/T)} \right)_{P/T,\ N_1 \cdots} \quad \text{(equação 19.16)}$$

$$\text{Mas } V = \frac{NR}{(P/T)} \quad \text{o que e constante a } P/T \text{ fixo}$$

$$\therefore \quad \boxed{\langle \Delta \hat{E} \Delta \hat{V} \rangle = 0}$$

19.3.2 .Repeat Problem 19.3-1 for a van der Waals gas (recall Problem 3.8-3) [SUMÁRIO]

SOLUÇÃO:

$$\text{Novamente} \quad \langle \Delta \hat{E} \Delta \hat{V} \rangle = -k_B \left(\frac{\partial V}{\partial (1/T)} \right)_{P/T}$$

$$\text{Mas} \quad \frac{P}{T} = \frac{R}{v-b} - \frac{a}{v^2}\frac{1}{T}$$

$$\text{ou} \quad \frac{1}{T} = \frac{v^2}{a} \left[\frac{R}{v-b} - \frac{P}{T} \right]$$

$$\left(\frac{\partial (1/T)}{\partial V} \right)_{P/T} = \frac{1}{N} \left(\frac{\partial (1/T)}{\partial v} \right)_{P/T} = \frac{1}{N} \left\{ \frac{1}{Tv} - \frac{v^2}{(v-b)^2}\frac{R}{a} \right\}$$

$$\therefore \quad \boxed{\langle \Delta \hat{E} \Delta \hat{V} \rangle = -Nk_B \left\{ \frac{1}{Tv} - \frac{v^2}{(v-b)^2}\frac{R}{a} \right\}^{-1}}$$

19.3.3 A conceptual subsystem of N moles in a single-component simple... [SUMÁRIO]

SOLUÇÃO:

$$\left\langle (\Delta \hat{E})^2 \right\rangle = k_B T^2 N c_v \quad \text{(equação 19.6)}$$

$$\text{Mas} \quad U \equiv \langle E \rangle = cNRT \quad \text{e} \quad c_v = cR$$

$$\left\langle (\Delta \hat{E})^2 \right\rangle = k_B T^2 NcR = c(RT)^2 \frac{N}{N_A} = \frac{U^2}{cNN_A}$$

$$\therefore \quad \frac{\left\langle (\Delta \hat{E})^2 \right\rangle^{1/2}}{U} = (cNN_A)^{-1/2} = 0,01$$

$$\therefore \quad cNN_A = 10^4$$

$$\text{Ou} \quad N \sim 10^{-19}/c$$

19.3.4 What is the order of magnitude of the mean square deviation of the... [SUMÁRIO]

SOLUÇÃO:

$$\left\langle (\Delta \hat{V})^2 \right\rangle^{1/2} = (k_B T V \kappa_T)^{1/2}$$

$$= \left(1,4 \times 10^{-23} \times 300 \times 10^{-6} \times 10^{-12}\right)^{1/2}$$

$$\therefore \quad \boxed{\left\langle (\Delta \hat{V})^2 \right\rangle^{1/2} \simeq 10^{-21} \text{ m}^3 \simeq 10^{-15} \text{ cm}^3}$$

19.3.5 Consider a small volume V within a two-component simple system... [SUMÁRIO]

SOLUÇÃO:

$$x_1 = \frac{\hat{N}_1}{\hat{N}_1 + \hat{N}_2} \quad \therefore \delta x_1 = \frac{\delta \hat{N}_1}{\hat{N}} - \frac{\hat{N}_1}{\left(\hat{N}_1 + \hat{N}_2\right)^2} \left(\delta \hat{N}_1 + \delta \hat{N}_2\right)$$

$$= \frac{1}{\hat{N}} \left(1 - x_1\right) \delta \hat{N}_1 - \frac{x_1}{\hat{N}} \delta \hat{N}_2$$

$$= \frac{x_2}{\hat{N}} \delta \hat{N}_1 - \frac{x_1}{\hat{N}} \delta \hat{N}_2$$

$$\therefore \quad (\delta x_1)^2 = x_2^2 \left(\frac{\delta \hat{N}_1}{\hat{N}}\right)^2 - 2 x_1 x_2 \frac{\delta \hat{N}_1}{\hat{N}} \frac{\delta \hat{N}_2}{\tilde{N}} - x^2 \left(\frac{\delta \hat{N}_2}{\hat{N}}\right)^2$$

$$\text{Mas} \quad \left\langle \delta \hat{N}_j \delta \hat{N}_k \right\rangle = -k_B \left(\frac{\partial N_j}{\partial (\mu_k/T)}\right)_{\frac{1}{T}\cdots} = -k_B T \left(\frac{\partial N_j}{\partial \mu_k}\right)_{\frac{1}{T}\cdots} \quad \text{(equação 19.14)}$$

$$\text{Ou} \quad \boxed{\left\langle \delta \hat{N}_j \delta \hat{N}_k \right\rangle = -k_B T / \left(\frac{\partial \mu_k}{\partial N_j}\right)_{1/T\cdots}}$$

19.3.6 Consider a small quantity of matter consisting of a fixed number N... [SUMÁRIO]

SOLUÇÃO:

$$\Delta \rho = \Delta \frac{M}{V} = -M \frac{\Delta V}{V^2} = -\rho \frac{\Delta V}{V}$$

$$\text{Ou} \quad \frac{\Delta \rho}{\rho} = -\frac{\Delta V}{V}$$

$$\text{Mas} \quad \frac{\langle (\Delta V)^2 \rangle}{V^2} = \frac{h_B T \kappa_T}{V} \quad \text{(equação 19.17)}$$

$$\therefore \boxed{\frac{\langle (\Delta\rho)^2 \rangle}{\rho^2} = \frac{k_B T \kappa_T}{V}}$$

19.3.7 Show that the density fluctuations of an ideal gas are given by... [SUMÁRIO]

SOLUÇÃO:

Do problema 19.3-6 $\dfrac{\langle (\Delta\rho)^2 \rangle}{\rho^2} = \dfrac{k_B T \kappa_T}{V}$

Mas para um gás ideal, $\kappa_T = \frac{1}{P}$

$$\therefore \frac{\langle (\Delta\rho)^2 \rangle}{\rho^2} = \frac{k_B T}{PV} = \frac{(R/N_A)\,T}{NRT} = \frac{1}{N N_A} \implies \boxed{\frac{\langle (\Delta\rho)^2 \rangle}{\rho^2} = \frac{1}{\tilde{N}}}$$

19.3.8 Show that the relative root mean square deviation in density of... [SUMÁRIO]

SOLUÇÃO:

10^{-6} gramas $= 10^{-6}$ gramas$/(31$ gramas/mol $= 3,2 \times^{-8}$ mols.
Mas o volume de um mol à T e P ambiente é $V = RT/P = 8,3 \times 300/10^5 = 2,5 \times^4$ cm^3/mol.
Então $3,2 \times^{-8}$ mols ocupam um volume de $3.2 \times 10^{-8} \times 2.5 \times 10^4$ cm$^3 = 10^{-3}$ cm$^3 = 1(\text{ mm})^3$
e 10^{-18} gramas ocupam um volume de $10^{-12} \times 1(\text{ mm})^3 = (10^{-4}\text{ mm})^3 = (10^3\text{Å})^3$ enquanto λ
da luz visível é ~ 5000 Å.

19.3.9 The dielectric constant ε of a fluid varies with... [SUMÁRIO]

SOLUÇÃO:

$$\frac{\epsilon - 1}{\epsilon + 2} = A\rho \quad \text{e diferenciando} \quad \frac{3}{(\epsilon+2)^2}d\epsilon = A d\rho$$

$$\text{Ou} \quad (d\epsilon)^2 = \frac{A^2}{9}(\epsilon+2)^4 (d\rho)^2$$

$$\langle (d\epsilon)^2 \rangle = \frac{A^2}{9}(\epsilon+2)^4 \rho^2 \frac{k_B T \kappa_T}{V} \qquad \text{(do probema 19.3-6)}$$

$$\therefore \boxed{\langle (d\epsilon)^2 \rangle = \frac{1}{9}(\epsilon-1)^2 \frac{k_B T \kappa_T}{V}}$$

19.3.10 If light of intensity $\mathbf{I_0}$ is incident on a region of volume V, which... [SUMÁRIO]

SOLUÇÃO:

NENHUMA SOLUÇÃO PARA ESSE PROBLEMA NO MOMENTO

19.3.11 **The classical theory of fluctuations, due to Einstein, proceeds from...**

> **SOLUÇÃO:**

> NENHUMA SOLUÇÃO PARA ESSE PROBLEMA NO MOMENTO

20 VARIATIONAL PROPERTIES, PERTURBATION EXPANSIONS, AND MEAN FIELD THEORY

20.1 THE BOGOLIUBOV VARIATIONAL THEOREM

20.1.1 **Derive equation (h) of Example 1, fisrt showing that for a harmonic...**

> **SOLUÇÃO:**

$$z' = \sum_0^\infty e^{-\beta\hbar\omega_0 n} = \frac{1}{1 - e^{-\beta\hbar\omega_0}} \quad \text{e } z' = e^{\frac{1}{2}\beta\hbar\omega_0} z$$

$$\langle n \rangle = -\frac{\partial}{\partial\beta\hbar\omega_0} \ln z' = \frac{\partial}{\partial\beta\hbar\omega_0} \ln\left(1 - e^{-\beta\hbar\omega_0}\right) = \frac{1}{e^{\beta\hbar\omega_0} - 1}$$

$$\langle n^2 \rangle = \left(\frac{\partial^2}{\partial(\beta\hbar\omega_0)^2} \sum_n e^{-\beta\hbar\omega_0 n}\right) \bigg/ \sum_n e^{-\beta\hbar\omega_0 n} = \frac{1}{z'} \frac{\partial^2}{\partial(\beta\hbar\omega^2)} z' = \left(1 - e^{-\beta\hbar\omega_0}\right) \frac{\partial^2}{\partial(\beta\hbar\omega_0)^2} \frac{1}{1 - e^{-\beta\hbar\omega_0}}$$

$$\therefore \quad \boxed{\langle n^2 \rangle = \left(1 - e^{-\beta\hbar\omega_0}\right) \frac{\partial}{\partial\beta\hbar\omega_0} \frac{-e^{-\beta\hbar\omega_0}}{(1 - e^{-\beta\hbar\omega})^2} = \cdots = \frac{e^{\beta\hbar\omega_0} + 1}{(e^{\beta\hbar\omega} - 1)^2}} \quad \text{o que é o resultado correto}$$

20.1.2 **Solve the quartic potential problem of Example 2 assuming the...**

> **SOLUÇÃO:**

$$e^{-\beta F} = \iint \frac{dx\,dp_x}{h} e^{-\beta\left(p_x^2/2m + Dx^4\right)} = \frac{1}{h} \int_{-\infty}^\infty dx\, e^{-\beta Dx'} \int_{-\infty}^\infty dp_x\, e^{-\beta p_x^2/2m}$$

$$e^{-\beta F} = \frac{1}{h} \beta D^{-1/4} C \times \sqrt{2\pi m k_B T} \quad \text{onde} C \equiv \int_{-\infty}^\infty e^{-y^4} dy$$

Note que a dependência em T de F é $F \simeq T \ln T + \text{constante} \times T$, o que é o mesmo no exemplo 2.

20.1.3 Complete Example 2 by writing the Helmholtz potential $\mathbf{F}(\mathbf{T}, \alpha)$...

SOLUÇÃO:

$$F = -k_B T \ln \left[\frac{1}{h} \left(2\pi m k_B T \right)^{1/2} L \right] + \frac{1}{80} D \left(\frac{L}{a} \right)^4$$

$$\text{Mas} \quad L/a = 20 \left(k_B T / D \right)^{1/F}$$

$$\therefore \quad F = -k_B T \ln \left[\frac{a}{h} (2\pi m)^{1/2} \left(\frac{20}{D} \right)^{1/4} (k_B T)^{3/4} \right] + \frac{1}{4} k_B T$$

$$= -k_B T \ln \left[\text{constante} \times T^{3/4} \right] - k_B T \ln a + \frac{1}{4} k_B t$$

$$\text{E ainda} \quad \mathscr{T} \equiv \left(\frac{\partial F}{\partial a} \right)_T = -\frac{k_B T}{a}$$

Alternativamente, pode-se definir $\mathscr{T} \equiv - \left(\frac{\partial F}{\partial a} \right)_T$

Então

$$\kappa_T \equiv \frac{1}{a} \left(\frac{\partial a}{\partial \mathscr{T}} \right)_T = \frac{a}{k_B T}$$

20.1.4 Consider a particle in a quadratic potential $\mathbf{V(x) = ax^2/2a^2}$. Despite...

SOLUÇÃO:

$$\langle \mathscr{H}_1 \rangle_0 = \frac{\text{tr} \left\{ \left[Aa^{-2} x^2 - V_0(x) \right] e^{-\beta \mathscr{H}_0} \right\}}{\text{tr} \{ e^{-\beta \mathscr{H}_0} \}}$$

$$\text{E ainda} \quad F \leq -k_B T \ln \left[\frac{1}{h} \left(2\pi m k_B T \right)^{1/2} L \right] + \frac{\Delta L^2}{12 a^2}$$

Minimizando com respeito a L:

$$-\frac{k_B T}{L} + \frac{AL}{6a^2} = 0 \quad \text{ou} \quad L/a = \left(\frac{6 k_B T}{A} \right)^{1/2}$$

$$F \simeq -k_B T \ln \left[\frac{(2\pi m k_B T)^{1/2}}{h} a \left(\frac{6 k_B T}{A} \right)^{1/2} \right] + \frac{1}{2} k_B T$$

$$\mathscr{T} = \left(\frac{\partial F}{\partial a} \right)_T = -\frac{k_B T}{a} \qquad \text{Mesma coisa do problema anterior!}$$

$$\kappa_T = \frac{1}{a} \left(\frac{\partial a}{\partial \mathscr{T}} \right)_T = \frac{a}{k_B T}$$

20.2 MEAN FIELD THEORY [SUMÁRIO]

20.2.1 Formulate the exact solution of the two-particle Ising model... [SUMÁRIO]

SOLUÇÃO:

(a)

$$U = \frac{(-J-2B)e^{-\beta(-J-2B)} + 2Je^{-\beta J} + (-J+2B)e^{-\beta(-J+2B)}}{e^{-\beta(-J-2B)} + 2e^{-\beta J} + e^{-\beta(-J+2B)}}$$

$$\langle\sigma\rangle = \frac{e^{-\beta(-J-2B)} - e^{-\beta(-J+2B)}}{e^{-\beta(-J-2B)} + 2e^{-\beta J} + e^{-\beta(-J+2B)}} = \frac{e^{2\beta B} - e^{-2\beta B}}{e^{2\beta B} + e^{-2\beta B} + 2e^{-2\beta J}}$$

Note que $\sigma \to \tanh 2\beta B$ na medida em que $J \to 0$ (verificando o modelo paramgnético).

(b) Na teoria de campo médio $\mathscr{H}_1 = -J\langle\sigma\rangle\sigma - B\sigma = -[J\langle\sigma\rangle + B]\sigma$

$$\langle\sigma\rangle = \frac{\rho^{\beta J\langle\sigma\rangle + \beta B} - e^{-\beta J\langle\sigma\rangle - \beta B}}{e^{\beta J\langle\sigma\rangle + \beta B} + e^{-\beta J\langle\sigma\rangle - \beta B}} = \tanh[\beta J\langle\sigma\rangle + \beta B]$$

E também $\quad U = -J\langle\sigma\rangle^2 + 2\langle\sigma\rangle B$

(c) Na solução exata $\langle\sigma\rangle \to 0$ na medida em que $B \to 0$ em qualquer T. Não existe transição na teoria de campo médio, para $B = 0$

Mas $\tanh x = x - \frac{1}{2}x^3 + \cdots$

$$\therefore \quad \langle\sigma\rangle = \beta J\langle\sigma\rangle - \frac{1}{2}\beta^3 J^3\langle\sigma\rangle^3$$

Essa equação possui 3 raízes: $\langle\sigma\rangle = 0, \quad \pm\sqrt{2\beta J - 1}$

fazendo $\sqrt{2\beta J - 1} = 0$ obtemos $T_c = 2$ J/k_B. Também, próximo de T_c,

$$\langle\sigma\rangle = \pm\left(\frac{2J - k_B T}{k_B T}\right)^{1/2} \qquad \text{ou} \quad \alpha = \frac{1}{2}$$

20.2.2 Formulate mean field theory for the three state Ising model... [SUMÁRIO]

SOLUÇÃO:

As equações (20.13)-(20.20) permanecem formamlmente válidas.

A equação (20.21) se torna $\langle\sigma\rangle_0 = \left(e^{\beta B^*} - e^{-\beta B^*}\right)/\left(e^{\beta B^*} + 1 + e^{-\beta B^*}\right)$

e a equação (20.22) permanece: $B^* - B = \hat{B} = 2z_{nn}J\langle\sigma\rangle_0$

ou a equação (20.23): $x = \beta B^* = \beta\left[2z_{nn}J\langle\sigma\rangle_0 + B\right]$

$$\therefore \quad \langle\sigma\rangle_0 = \frac{k_B T}{2z_{nn}J}x - \frac{B}{2x_{nn}J} = \frac{e^{\beta B^*} - e^{-\beta B^*}}{e^{\beta B^*} + 1 + e^{-\beta B^*}} \qquad \text{substitui a equação 20.24}$$

$$\text{Mas para } \beta B^* \text{ pequeno}, \quad \frac{e^{\beta B^*} - e^{-\beta B^*}}{e^{\beta B^*} + 1 + e^{-\beta B^*}} \simeq \frac{2\beta B^*}{3 + \cdots}$$

Daí através da linha em analogia da Fig 20.1 tem uma inclinação inicial de $\frac{k_B T}{2z_{nn}J}$, enquanto que a vurva tem uma inclinação inicial de $\frac{2}{3}$. Portanto T_c é determinado por

$$\frac{k_B T_c}{2z_{nn}J} = \frac{2}{3} \quad \text{ou} \quad T_c = \frac{2}{3} \times \frac{2z_{nn}J}{k_B}$$

e T_c é $\frac{2}{3}$ daquela para o modelo de Ising de dois estados. Minimizando com respeito a $\hat{B}$,

$$\frac{dF}{d\hat{B}} = \frac{\tilde{N}\beta e^{\beta\hat{B}}}{\left(1 + e^{\beta\hat{B}}\right)^3}\left[\hat{B}\left(1 + e^{\beta\hat{B}}\right) - 2\epsilon\right] = 0$$

$$\text{e} \quad \frac{1 + e^{\beta\hat{B}}}{2} = \frac{\epsilon}{\hat{B}}$$

Essa equação determina $\hat{B}$, e então

$$\langle\sigma\rangle_0 = \frac{1}{1 + e^{\beta\hat{B}}}$$

20.2.3 For the Heisenberg ferromagntic model the Hamiltonian is... [SUMÁRIO]

> **Solução:**

NENHUMA SOLUÇÃO PARA ESSE PROBLEMA NO MOMENTO

20.2.4 A metallic surface is covered by a monomolecular layer of $\tilde{N}$... [SUMÁRIO]

> **Solução:**

$$\mathscr{H} = \frac{1}{2}\sum_{i,j}\epsilon_{ij}\sigma_i\sigma_j \qquad \text{onde} \quad \sigma_j = 1 \text{ se } oblate \text{ e} = 0 \text{ se } prolate$$

Também $\epsilon_{ij} = \epsilon$ se i,j são vizinhos ($\epsilon_{ij} = 0$) caso contrário.

$$\mathscr{H}_0 = \hat{B}\sum_j\sigma_j \quad \text{e} \quad F_0 = -\tilde{N}k_B T\ln\left[1 + e^{-\beta\hat{B}}\right]$$

$$\therefore F \leqslant F_0 + \left\langle\frac{1}{2}\sum_{i,j}\epsilon_{ij}\sigma_i\sigma_j - \hat{B}\sum_j\sigma_j\right\rangle_0$$

$$F \leqslant F_0 + \tilde{N}\epsilon\langle\sigma\rangle_0^2 - \hat{B}\tilde{N}\langle\sigma\rangle_0$$

$$\text{E ainda} \quad \langle\sigma\rangle_0 = \frac{e^{-\beta\hat{B}}}{e^{-\beta\hat{B}} + 1} = \frac{1}{1 + e^{\beta\hat{B}}}$$

$$\therefore F \leqslant -\tilde{N}k_B T\ln\left[1 + e^{-\beta\hat{B}}\right] + \frac{\tilde{N}\epsilon}{\left(1 + e^{\beta\hat{N}}\right)^2} - \frac{\hat{B}\tilde{N}}{1 + e^{\beta\hat{B}}}$$
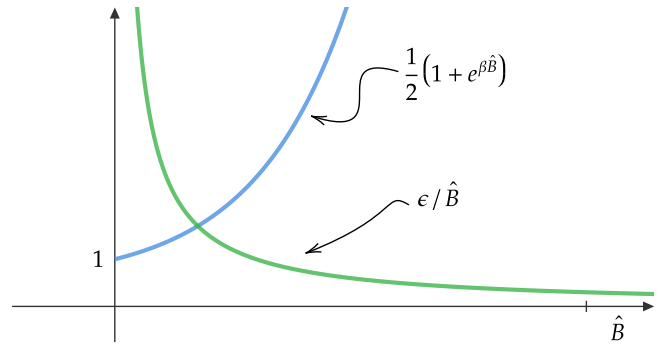

Minimizando com respeito a $\tilde{B}$

$$\frac{dF}{d\hat{B}} = \frac{\tilde{N}\beta e^{\beta\hat{B}}}{\left(1 + e^{\beta\hat{B}}\right)^3}\left[\hat{B}\left(1 + e^{\beta\hat{B}}\right) - 2\epsilon\right] = 0$$

$$\text{ou} \quad \frac{1 + e^{\beta\hat{B}}}{2} = \frac{\epsilon}{\hat{B}}$$

Essa equação determina $\tilde{B}$, e então

$$\langle\sigma\rangle_0 = \frac{1}{1 + e^{\beta\hat{B}}}$$

20.2.5 Solve the preceding problem if the molecules can exist in three steric...

SOLUÇÃO:

Seja $\sigma = 0$ para o *oblate* $\qquad\qquad \sigma = 1, -1 \sim$ *esférico* e *prolate*

$$\mathscr{H} = \epsilon\sum_{(i,j)}\left(1 - \sigma_i^2\right)\left(1 - \sigma_j^2\right)$$

$$H_0 = B\sum_i\left(1 - \sigma_1^2\right); \quad -\beta F_0 = \ln\left(2 + e^{-\beta B}\right)^N$$

$$\text{e} \quad \langle\sigma_i^2\rangle_0 = \frac{2}{2 + e^{-\beta B}} \quad \text{e} \quad \langle\mathscr{H}_0\rangle_0 = \frac{\tilde{N}B}{1 + 2e^{\beta B}}$$

$$\therefore \langle\mathscr{H}\rangle_0 = 2\epsilon\tilde{N}\left(\frac{1}{1 + 2e^{\beta B}}\right)^2$$

$$F \leq -\tilde{N}k_B T\ln\left(2 + e^{-\beta B}\right) + 2\tilde{N}\epsilon\left(1 + 2e^{\beta B}\right)^{-2} - \tilde{N}B\left(1 + 2e^{\beta B}\right)^{-1}$$

Para minimizar com respeito a B, primeiro faça $e^{\beta B} = x$, assim,

$$\frac{\beta F}{\tilde{N}} \leq -\ln(1 + 2x) + \ln x + \frac{2\beta\epsilon}{(1 + 2x)^2} - \frac{\ln x}{1 + 2x}$$

$$\text{Minimizando:} \quad -\frac{2}{1 + 2x} + \frac{1}{x} - \frac{8\beta\epsilon}{(1 + 2x)^3} - \frac{1}{x(1 + 2x)} + \frac{2}{(1 + 2x)^2}\ln x = 0$$
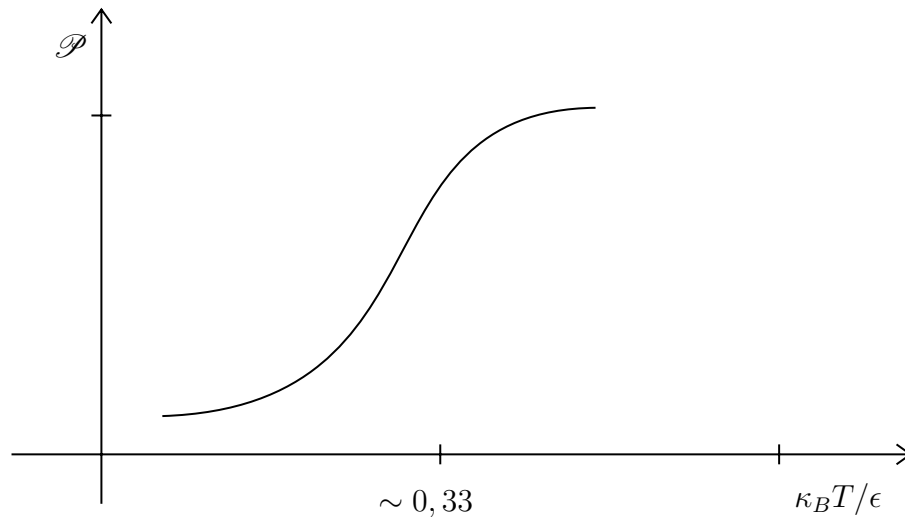
ou multiplicando por $x(1 + 2x)^3$:

$$-8\beta\epsilon x + 2x(1 + 2x)\ln x = 0$$

$$(1 + 2x)\ln x = 4\beta\epsilon, \quad \text{onde} \quad x = e^{\beta B}$$

podemos transformar para variáveis mais convenientes: seja $\mathscr{P} = 1 - \langle\sigma^2\rangle_0 = \frac{1}{1+2x}$ de modo que $\mathscr{P}$ é a probabilidade da molécula ser *oblate*. Então $\mathscr{P}$ satisfaz

$$\frac{1}{\mathscr{P}}\ln\left(\frac{1 - \mathscr{P}}{2\mathscr{P}}\right) = 4\beta\epsilon$$

Alguns valores numéricos podem ser encontrados,

$\mathscr{P}$	0,05	0,09	0,15	0,20	0,24	0,27	0,30	0,325	0,33
$\frac{k_B T}{\epsilon}$	0,043	0,222	0,576	1,15	2,09	3,58	7,78	34,4	87,6

Note a mudança muito rápida de $\mathscr{P}$ na região de $\mathscr{P} \sim \frac{1}{3}$

20.2.6 In the classic Heisenberg model each spin can take any orientation... [SUMÁRIO]

SOLUÇÃO:

O análogo da equação 20.15 é

$$\mathscr{H}_0 = -\sum_j \hat{B}_j S_j^z - B \sum_j S_j^2 = -\sum_j \left(\hat{B}_j + B \right) S_j^z$$

Então, (equação 20.22) $\hat{B}_i = 2 \sum_j J_{ij} \langle S_i^z \rangle_0 = 2 Z_{nn} J \langle S_z \rangle_0$

$$\mathscr{H}_0 = -(\hat{B} + B) S \cos\theta$$

$$\langle S_z \rangle = \frac{S \int \cos\theta e^{\beta(\hat{B}+\beta)s\cos\theta}}{\int e^{\beta(\hat{B}+B)S\cos\theta} d\Omega} = S \frac{\int \cos\theta e^{c\cos\theta} d\theta d\phi}{\int e^{c\cos\theta} \operatorname{sen}\theta d\theta d\phi} \quad \text{onde} \quad c = \beta(\hat{B}+B)S$$

$$\text{Então} \quad \langle s_z \rangle = \frac{d}{dc} \ln \int_0^\pi e^{c\cos\theta} \operatorname{sen}\theta dt = S \frac{d}{dc} \ln\left(\frac{e^c - e^{-c}}{c}\right)$$

$$\langle s_z \rangle = S \frac{e^c + e^{-c}}{e^c - e^{-c}} - S \frac{1}{c}$$

$$\therefore \quad \boxed{\langle s_z \rangle = S \coth[\beta(\hat{B}+B)S] - \frac{k_B T}{\hat{B}+B}}$$

20.2.7 2Ñ two-valued Ising spins are arranged sequentially on a circle... [SUMÁRIO]

SOLUÇÃO:

NENHUMA SOLUÇÃO PARA ESSE PROBLEMA NO MOMENTO

20.2.8 Consider a sequence of 2Ñ alternating A sites and B sites...

$\boxed{\text{Solução:}}$

$\boxed{\textcolor{red}{\text{NENHUMA SOLUÇÃO PARA ESSE PROBLEMA NO MOMENTO}}}$

21 POSTLUDE: SYMMETRY AND THE CONCEPTUAL FOUNDATIONS OF THERMOSTATISTICS

21.1 STATISTICS

21.1.1 The probability of throwing a "seven "on two dice can be viewed as ...

$\boxed{\text{Solução:}}$

$\boxed{\textcolor{red}{\text{NENHUMA SOLUÇÃO PARA ESSE PROBLEMA NO MOMENTO}}}$

21.1.2 Associate the value +1 with one side of a coin (head) and...

$\boxed{\text{Solução:}}$

$\boxed{\textcolor{red}{\text{NENHUMA SOLUÇÃO PARA ESSE PROBLEMA NO MOMENTO}}}$

21.5 BROKEN SYMMETRY AND GOLDSTONE'S THEOREM

21.5.1 Draw a longitudinal vibrational mode in a one-dimensional system...

$\boxed{\text{Solução:}}$

$\boxed{\textcolor{red}{\text{NENHUMA SOLUÇÃO PARA ESSE PROBLEMA NO MOMENTO}}}$

The End

AAEEIIOOOOOOUUFGMPRRRLLLNSTTVD