Termodinâmica II - Prova 2

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Início: 13:30 - duração: 2:30 horas

Só serão consideradas as respostas que forem devidamente justificadas.
É proibido o uso de calculadoras, smartphones ou computadores.

Questão 01: (2,5) Fluido ideal de Van der Waals

Demonstre que a variação do volume molar v e da temperatura T de um fluido ideal de Van der Waals em uma expansão adiabática quase-estática segue a relação

$$(v-b)T^c = \text{constante}.$$

Dado – Equações de estado do fluido ideal de Van der Waals:

$$P = \frac{RT}{v-b} - \frac{a}{v^2} \qquad \frac{1}{T} = \frac{cR}{u + a/v}$$

Questão 02: Teorema do Trabalho Máximo

Dois corpos idênticos têm cada um capacidades caloríficas constantes e iguais (C). Considere que uma fonte de trabalho reversível está disponível. As temperaturas iniciais dos dois corpos são T_0 e $3T_0$.

(a) (1,5) Mostre que o trabalho máximo que pode ser entregue para a fonte de trabalho reversível, deixando os dois corpos no equilíbrio térmico, é dado por

$$W_{\text{máx}} = 2CT_0(2-\sqrt{3})$$

(b) (1,0) Qual é a temperatura de equilíbrio nesse caso?

Questão 03: Energia livre de Helmholtz

A partir equação fundamental da radiação eletromagnética em uma cavidade na representação da entropia,

$$S = \frac{4}{3} b^{1/4} U^{3/4} V^{1/4}$$

faça o que se pede:

(a) (1,5) Escreva a equação fundamental da representação de Helmholtz e

(b) (1,5) Demonstre as seguintes equações de estado:

$$S = \frac{4}{3} bVT^3 \qquad P = \frac{1}{3} bT^4,$$

Questão 04: (2,0) Relações de Maxwell

Deduza uma das relações de Maxwell (à sua escolha) apresentadas na segunda página desta prova. Indique qual delas você escolheu, por exemplo, Eqs. (7.13).

U	S, V	$\left(\frac{\partial T}{\partial V}\right)_{S,N} = -\left(\frac{\partial P}{\partial S}\right)_{V,N}$	(7.3)
$dU = T\,dS - P\,dV + \mu\,dN$	S, N	$\left(\frac{\partial T}{\partial N}\right)_{S,V} = \left(\frac{\partial \mu}{\partial S}\right)_{V,N}$	(7.4)
	V, N	$-\left(\frac{\partial P}{\partial N}\right)_{S,V} = \left(\frac{\partial \mu}{\partial V}\right)_{S,N}$	(7.5)
$U[T] \equiv F$	T, V	$\left(\frac{\partial S}{\partial V}\right)_{T,N} = \left(\frac{\partial P}{\partial T}\right)_{V,N}$	(7.6)
$dF = -S\,dT - P\,dV + \mu\,dN$	T, N	$-\left(\frac{\partial S}{\partial N}\right)_{T,V} = \left(\frac{\partial \mu}{\partial T}\right)_{V,N}$	(7.7)
	V, N	$-\left(\frac{\partial P}{\partial N}\right)_{T,V} = \left(\frac{\partial \mu}{\partial V}\right)_{T,N}$	(7.8)
$U[P] \equiv H$	S, P	$\left(\frac{\partial T}{\partial P}\right)_{S,N} = \left(\frac{\partial V}{\partial S}\right)_{P,N}$	(7.9)
$dH = T\,dS + V\,dP + \mu\,dN$	S, N	$\left(\frac{\partial T}{\partial N}\right)_{S,P} = \left(\frac{\partial \mu}{\partial S}\right)_{P,N}$	(7.10)
	P, N	$\left(\frac{\partial V}{\partial N}\right)_{S,P} = \left(\frac{\partial \mu}{\partial P}\right)_{S,N}$	(7.11)
$U[\mu]$	S, V	$\left(\frac{\partial T}{\partial V}\right)_{S,\mu} = -\left(\frac{\partial P}{\partial S}\right)_{V,\mu}$	(7.12)
$dU[\mu] = T\,dS - P\,dV - N\,d\mu$	S, μ	$\left(\frac{\partial T}{\partial \mu}\right)_{S,V} = -\left(\frac{\partial N}{\partial S}\right)_{V,\mu}$	(7.13)
	V, μ	$\left(\frac{\partial P}{\partial \mu}\right)_{S,V} = \left(\frac{\partial N}{\partial V}\right)_{S,\mu}$	(7.14)
$U[T, P] \equiv G$	T, P	$-\left(\frac{\partial S}{\partial P}\right)_{T,N} = \left(\frac{\partial V}{\partial T}\right)_{P,N}$	(7.15)
$dG = -S\,dT + V\,dP + \mu\,dN$	T, N	$-\left(\frac{\partial S}{\partial N}\right)_{T,P} = \left(\frac{\partial \mu}{\partial T}\right)_{P,N}$	(7.16)
	P, N	$\left(\frac{\partial V}{\partial N}\right)_{T,P} = \left(\frac{\partial \mu}{\partial P}\right)_{T,N}$	(7.17)
$U[T, \mu]$	T, V	$\left(\frac{\partial S}{\partial V}\right)_{T,\mu} = \left(\frac{\partial P}{\partial T}\right)_{V,\mu}$	(7.18)
$dU[T, \mu] = -S\,dT - P\,dV$ $- N\,d\mu$	T, μ	$\left(\frac{\partial S}{\partial \mu}\right)_{T,V} = \left(\frac{\partial N}{\partial T}\right)_{V,\mu}$	(7.19)
	V, μ	$\left(\frac{\partial P}{\partial \mu}\right)_{T,V} = \left(\frac{\partial N}{\partial V}\right)_{T,\mu}$	(7.20)
$U[P, \mu]$	S, P	$\left(\frac{\partial T}{\partial P}\right)_{S,\mu} = \left(\frac{\partial V}{\partial S}\right)_{P,\mu}$	(7.21)
$dU[P, \mu] = T\,dS + V\,dP + N\,d\mu$	S, μ	$\left(\frac{\partial T}{\partial \mu}\right)_{S,P} = -\left(\frac{\partial N}{\partial S}\right)_{P,\mu}$	(7.22)
	P, μ	$\left(\frac{\partial V}{\partial \mu}\right)_{S,P} = -\left(\frac{\partial N}{\partial P}\right)_{S,\mu}$	(7.23)

GABARITO

1-

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

$$\frac{1}{T} = \frac{cR}{u + a/v}$$

$$u + \frac{a}{v} = cRT$$

$$u = cRT - \frac{a}{v}$$

$$dU = T\cancel{dS} - P\,dV$$

$$du = -P\,dv$$

$$du = cR\,dT + \frac{a}{v^2}\,dv \Rightarrow$$

$$cR\,dT + \cancel{\frac{a}{v^2}\,dv} = -\frac{RT}{v-b}\,dv + \cancel{\frac{a}{v^2}\,dv}$$

$$c\cancel{R}\,dT = -\frac{\cancel{R}T}{v-b}\,dv$$

$$\int c\frac{dT}{T} = \int -\frac{dv}{v-b}$$

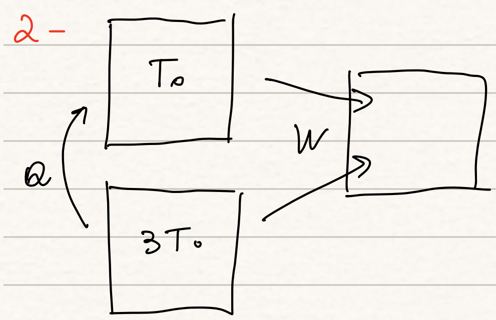
$$c\ln T = -\ln(v-b) + C$$

$$\ln T^c + \ln(v-b) = C$$

$$\ln\left[T^c(v-b)\right] = C$$

$$\Rightarrow \boxed{(v-b)T^c = C}$$

2-



$$\Delta U = \Delta U_1 + \Delta U_2$$

$$\Delta U = \int_{T_0}^{T_f} c\,dT_1 + \int_{3T_0}^{T_f} c\,dT_2$$

$$\Delta U = c(T_f - T_0) + c(T_f - 3T_0)$$

$$\Delta U = 2cT_f - 4cT_0$$

$$W = -\Delta U$$

$$\Rightarrow W = 4cT_0 - 2cT_f$$

$$\Delta S_1 + \Delta S_2 = 0$$

$$\int_{T_0}^{T_f} \frac{đQ_1}{T_1} + \int_{3T_0}^{T_f} \frac{đQ_2}{T_2} = 0$$

$$c\int \frac{dT_1}{T_1} + c\int \frac{dT_2}{T_2} = 0$$

$$\ln\left(\frac{T_f}{T_0}\right) + \ln\left(\frac{T_f}{3T_0}\right) = 0$$

$$\ln\left(\frac{T_f^2}{3T_0^2}\right) = 0$$

$$\Rightarrow \boxed{T_f = T_0\sqrt{3}} \quad B)$$

$$\Rightarrow W_{máx} = 4cT_0 - 2cT_0\sqrt{3}$$

$$\boxed{W_{máx} = 2cT_0(2-\sqrt{3})} \quad A)$$

3- $S = \frac{4}{3} b^{1/4} U^{3/4} V^{1/4}$

A) $F(T,V,N) = U - TS$

$$\frac{1}{T} = \frac{\partial S}{\partial U}$$

$$\frac{1}{T} = \frac{3}{4} \cdot \frac{4}{3} b^{1/4} U^{-1/4} V^{1/4}$$

$$\frac{1}{T} = b^{1/4} U^{-1/4} V^{1/4}$$

$$U^{1/4} = b^{1/4} V^{1/4} T$$

$$U = bVT^4 \Rightarrow$$

$$F = U - TS$$

$$F = bVT^4 - T . \frac{4}{3} b^{1/4} U^{3/4} V^{1/4}$$

$$F = bVT^4 - \frac{4}{3} b^{1/4} V^{1/4} T . b^{3/4} V^{3/4} T^3$$

$$F = bVT^4 - \frac{4}{3} bVT^4$$

$$\boxed{F(T,V) = -\frac{1}{3} bVT^4}$$

B) $F = U - TS$

$$dF = dU - TdS - SdT$$

$$dF = \cancel{TdS} - PdV - \cancel{TdS} - SdT$$

$$dF = -SdT - PdV$$

$$dF = \left(\frac{\partial F}{\partial T}\right)_V dT + \left(\frac{\partial F}{\partial V}\right)_T dV$$

$$\Rightarrow S = -\left(\frac{\partial F}{\partial T}\right)_V \qquad P = -\left(\frac{\partial F}{\partial V}\right)_T$$

$$S = \frac{bV}{3} . 4T^3 \qquad \boxed{P = \frac{bT^4}{3}}$$

$$\boxed{S = \frac{4}{3} bVT^3}$$

4- Eq. (7.9):

$$dH = TdS + VdP + \mu dN$$

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

$$dH = \left(\frac{\partial H}{\partial S}\right)_{P,N} dS + \left(\frac{\partial H}{\partial P}\right)_{S,N} dP + \left(\frac{\partial H}{\partial N}\right)_{S,P} dN$$

$$\Rightarrow T = \left(\frac{\partial H}{\partial S}\right)_{P,N}$$

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

$$\mu = \left(\frac{\partial H}{\partial N}\right)_{S,P}$$

$$\frac{\partial}{\partial S}\left(\frac{\partial H}{\partial P}\right) = \frac{\partial}{\partial P}\left(\frac{\partial H}{\partial S}\right)$$

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