Potenciais Termodinâmicos

1) Coeficientes Termodinâmicos

i) Derivadas parciais.

Nos sistemas termodinâmicos em geral, pressão, temperatura e volume variam em um processo. No cálculo do trabalho é mais conveniente algumas vezes expressá-lo em termos das variações de pressão e temperatura.

Devido a uma relação funcional entre pressão, volume e temperatura, expressa pela equação de estado, podemos fazer pequenas variações em duas delas, mas não as três ao mesmo tempo.

Por exemplo:

Considere um gás ou fluido em um cilindro onde há um pistão móvel. Podemos fazer pequenas variações dV e simultaneamente variar a temperatura dT. Quando isto é feito verifica-se que ocorre uma pequena variação de pressão dp. Os novos valores de p, T e V satisfazem a equação de estado. Portanto variando duas grandezas a terceira variará expressada pelas respectivas variações.

Vejamos as possibilidades

A equação de estado em geral é dada por

$$F(p, v, T) = 0$$

$$\therefore \quad p = F_1(v, T)$$

$$v = F_2(T, p)$$

$$T = F_3(p, v)$$

Derivadas parciais

Vamos generalizar supondo que $F(x, y, z) = 0$, considerar duas delas independentes, por exemplo

$$z = f(x, y)$$

Assim

$$dz = \frac{\partial f}{\partial x}dx + \frac{\partial f}{\partial y}dy$$

$$= \frac{\partial z}{\partial x}dx + \frac{\partial z}{\partial y}dy \quad \text{ou}$$

$$= \left.\frac{\partial z}{\partial x}\right)_y dx + \left.\frac{\partial z}{\partial y}\right)_x dy.$$

$\therefore$ Notação

$$\frac{\partial f}{\partial x} \equiv \frac{\partial z}{\partial x} \equiv \left.\frac{\partial z}{\partial x}\right)_y.$$

Considere agora.

$$x = F_1(y, z) \qquad y = F_2(x, z)$$

Então

$$dx = \frac{\partial x}{\partial y} dy + \frac{\partial x}{\partial z} dz$$

$$dy = \frac{\partial y}{\partial x} dx + \frac{\partial y}{\partial z} dz$$

Vamos eliminar dy e obter os coeficientes de dx e dz.

$$\therefore \quad dx = \frac{\partial x}{\partial y}\left[\frac{\partial y}{\partial x} dx + \frac{\partial y}{\partial z} dz\right] + \frac{\partial x}{\partial z} dz$$

$$\left[1 - \frac{\partial x}{\partial y}\frac{\partial y}{\partial x}\right] dx = \left[\frac{\partial x}{\partial y}\frac{\partial y}{\partial z} + \frac{\partial x}{\partial z}\right] dz$$

Como dx e dz variam independentemente.

Seja $\underline{dz = 0}$ e $\underline{dx \neq 0}$

$$\therefore \left[1 - \frac{\partial x}{\partial y}\frac{\partial y}{\partial x}\right] = 0 \quad \text{ou} \quad \frac{\partial x}{\partial y} = \frac{1}{(\partial y / \partial x)} \qquad (1)$$

Similarmente $dx = 0$ e $dz \neq 0$.

$$\left[\frac{\partial x}{\partial y}\frac{\partial y}{\partial z} + \frac{\partial x}{\partial z}\right] = 0 \Rightarrow \frac{\partial x}{\partial y} \cdot \frac{\partial y}{\partial z} \cdot \frac{\partial z}{\partial x} = -1 \qquad (2)$$

com (1) para $\frac{\partial x}{\partial z}$

Observação

Para o trabalho W $\left.\frac{\partial W}{\partial T}\right)_p$ ou $\left.\frac{\partial W}{\partial p}\right)_T$ não têm significado físico pois $W \neq W(p,T)$. No entanto $\frac{d' W_T}{dp_T}$ sim, pois corresponde a uma pequena variação de W em relação a dp num processo isotérmico!

Vamos verificar os resultados obtidos para um gás ideal. $x = p$, $y = v$ e $z = T$

$$\boxed{pv = RT}$$

Assim

$$\left.\frac{\partial z}{\partial x}\right)_y = \left.\frac{\partial T}{\partial p}\right)_v = \left[\frac{\partial}{\partial p}\left(\frac{pv}{R}\right)\right]_v = v/R$$

= eq (1)

$$\left(\frac{\partial x}{\partial z}\right)_y = \left.\frac{\partial p}{\partial T}\right)_v = \left[\frac{\partial}{\partial p}\left(\frac{RT}{v}\right)\right]_v = R/v$$

$$\left.\frac{\partial x}{\partial y}\right)_z = \left(\frac{\partial p}{\partial v}\right)_T = \left[\frac{\partial}{\partial v}\left(\frac{RT}{v}\right)\right]_T = -RT/v^2$$

$$\left.\frac{\partial y}{\partial z}\right)_z = \left(\frac{\partial v}{\partial T}\right)_p = \left[\frac{\partial}{\partial T}\left(\frac{RT}{p}\right)\right]_p = \frac{R}{p}$$

e $$\left(\frac{\partial p}{\partial v}\right)_T \left(\frac{\partial v}{\partial T}\right)_p \left(\frac{\partial T}{\partial T}\right)_v = \left(-\frac{RT}{v^2}\right)\left(\frac{R}{p}\right)\left(\frac{v}{R}\right) = -\frac{RT}{v} = -1$$

de acordo com (2) e 4.

Coeficiente de expansão e compressibilidade

Embora uma equação de estado de um sistema ou substância não possa ser expressa em uma forma analítica simples, as derivadas parciais $\partial v/\partial T)_p$ e $\partial v/\partial p)_T$ podem ser encontradas de medidas do coeficiente de expansão cúbica β e compressibilidade k

Definição.

$$\bar{\beta} = \frac{V_2 - V_1}{V_1 (T_2 - T_1)} \quad \equiv \text{valor médio} \quad (K^{-1})$$

A forma correta é dada por.

$$\beta = \frac{dV}{V\,dT} = \frac{1}{V} \cdot \frac{dV}{dT} = \frac{1}{V} \frac{(dV)_p}{(dT)_p}$$

como $\dfrac{(dV)_p}{(dT)_p} = \left.\dfrac{\partial V}{\partial T}\right)_p \equiv$ relação funcional p, T e v.

$$\beta = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p$$

ou em função do volume específico

$$\beta = \frac{1}{v}\left(\frac{\partial v}{\partial T}\right)_p \rightarrow \beta v = \left(\frac{\partial v}{\partial T}\right)_p$$

Ex 1: gás ideal

$$\beta v = \left(\frac{\partial v}{\partial T}\right)_p \rightarrow \beta v = \frac{R}{p}$$

$$\therefore \boxed{\beta = \frac{1}{T}}$$

Ex 2: gás de van de Waals $\quad p = \frac{RT}{v-b} - \frac{a}{v^2}$

Aparece uma dependência cúbica em v. Logo de

eq (1) e (2)

$$\left.\frac{\partial v}{\partial T}\right)_p = - \frac{\left(\frac{\partial p}{\partial T}\right)_v}{\left(\frac{\partial p}{\partial v}\right)_T}$$

$$\therefore \left.\frac{\partial p}{\partial T}\right)_v = \frac{R}{v-b} \quad e \quad \left.\frac{\partial p}{\partial v}\right)_T = -\frac{RT}{(v-b)^2} + \frac{2a}{v^3}$$

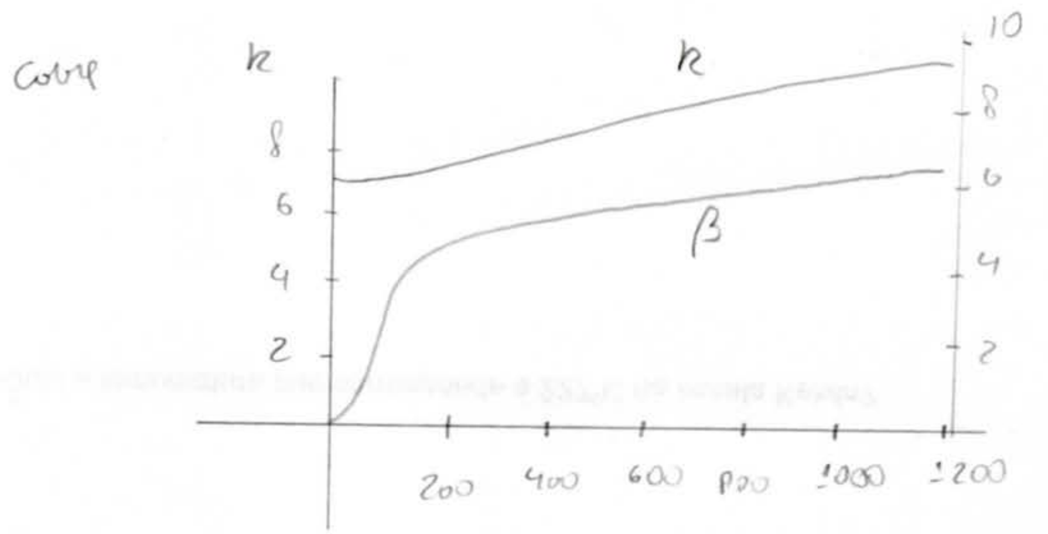
$$\therefore \beta = \frac{1}{v}\left(\frac{\partial v}{\partial T}\right)_p = - \frac{\frac{R}{(v-b)}}{\left(-\frac{RT}{(v-b)^2} + \frac{2a}{v^3}\right)}$$

$$= -\frac{R}{(v-b)} \div \left(\frac{-RTv^3 + 2a(v-b)^2}{(v-b)^2\, v^3\, v^2}\right)\frac{1}{v}$$

$$(v-b)$$

$$\boxed{\beta = \frac{R v^2 (v-b)}{RTv^3 - 2a(v-b)^2}}$$

7



β não pode ser obtido de uma equação de estado!

Coeficiente de compressibilidade k

$$\bar{k} = -\frac{(V_2 - V_1)}{V_1(p_2 - p_1)}$$

k real é dado por

$$k = -\frac{dV}{V dp} = -\frac{1}{V}\frac{dV}{dp} \qquad (N/m^2)^{-1}$$

∴ analogamente a obtenção de β.

$$k = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_T \quad \text{ou}$$

$$k = -\frac{1}{v}\left(\frac{\partial v}{\partial p}\right)_T \qquad \boxed{\left(\frac{\partial v}{\partial p}\right)_T = -kv}$$

Para o gás ideal

$$\boxed{k = -\frac{1}{v}\left(-\frac{RT}{p^2}\right) = \frac{1}{p}}$$

Para o gás de van der Waals.

$$\boxed{k = \frac{v^2(v-b)^2}{RTv^3 - 2a(v-b)^2}}$$

Obs:

Temos das eq. (1) e (2)

$$\left.\frac{\partial p}{\partial T}\right)_v = -\frac{(\partial v/\partial T)_p}{(\partial v/\partial p)_T}$$

$$\therefore \left.\frac{\partial p}{\partial T}\right|_v = -\frac{\beta v}{-kv} = \frac{\beta}{k}$$

Do ponto de vista experimental

$$\frac{\Delta p}{\Delta T} \simeq \frac{\beta}{k} \rightarrow \boxed{(p_2 - p_1)_v = \frac{\beta}{k}(T_2 - T_1)}$$

Exercício:

Usando o fato de que

$$\frac{\partial^2 v}{\partial T \partial p} = \frac{\partial^2 v}{\partial p \partial T} \quad \text{mostre que}$$

$$\left.\frac{\partial \beta}{\partial p}\right)_v = -\left.\frac{\partial k}{\partial T}\right)_p$$

Vamos considerar agora os casos em que $u(T,v)$, $u(T,p)$ e $u(p,v)$ e para cada caso obter as relações para β e k

Assim

$$u(T,v) \Rightarrow du = \frac{\partial u}{\partial T} dT + \frac{\partial u}{\partial v} dv \qquad (10)$$

$$u(T,p) \Rightarrow du = \frac{\partial u}{\partial T} dT + \frac{\partial u}{\partial p} dp \qquad (11)$$

$$u(p,v) \Rightarrow du = \frac{\partial u}{\partial p} dp + \frac{\partial u}{\partial v} dv. \qquad (12)$$

$T - v$ independentes

$$du = \frac{\partial u}{\partial T} dT + \frac{\partial u}{\partial v} dv$$

considerando $w = p dv$

$$dq = du + p dv \equiv \left[\frac{\partial u}{\partial T} dT + \frac{\partial u}{\partial v} dv \right] + dv\, p$$

$$\therefore dq = \frac{\partial u}{\partial T} dT + \left[p + \frac{\partial u}{\partial v} \right] dv.$$

$v = cte$ $\quad dv = 0 \quad dq = c_v dT$

$$\therefore c_v dT = \frac{\partial u}{\partial T} dT \rightarrow c_v = \left.\frac{\partial u}{\partial T}\right)_v \quad (a)$$

para $v \neq cte$

$$dq = c_v dT + \left[p + \frac{\partial u}{\partial v} \right] dv \quad (*) (c)$$

$p = cte$ $\quad dq = c_p dT$

$$\therefore c_p dT = c_v dT + \left[p + \frac{\partial u}{\partial v} \right] dv.$$

ou $$c_p = c_v + \left[p + \frac{\partial u}{\partial v} \right] \frac{\partial v}{\partial T} \quad (b)$$

para $T = cte$. de (c)

$$dq = \left[p + \frac{\partial u}{\partial v} \right] dv$$

$T - v$ independentes

Para um processo adiabático. (reversível). 10 - ③

$$dq = 0 \rightarrow ds = 0. \quad \text{(isentálpico)!}$$

de $(*)$(c) $0 = c_v dT + \left[p + \frac{\partial u}{\partial v} \right] dv.$

$$\therefore \quad c_v \left.\frac{\partial T}{\partial v}\right)_s = -\left[p + \frac{\partial u}{\partial v_T} \right] \qquad (c)$$

Como $\beta = \frac{1}{v}\left(\frac{\partial v}{\partial T}\right)_p$ e $k = -\frac{1}{v}\left(\frac{\partial v}{\partial p}\right)_T$

Temos

$\frac{\partial u}{\partial T} = c_v$ ✓ de (a)

$\left.\frac{\partial u}{\partial v}\right)_T$ de (b) $\quad c_p = c_v + \left[p + \frac{\partial u}{\partial v} \right] \frac{\partial v}{\partial T}$

$$\therefore \quad c_p - c_v = \left[p + \frac{\partial u}{\partial v} \right] \beta v$$

$$\left\{ \frac{c_p - c_v}{\beta v} - p = \frac{\partial u}{\partial v} \right. \quad \checkmark$$

T - v independentes

$$dq = c_v dT + \left[p + \frac{\partial u}{\partial v}\right] dv \quad (*)(c)$$

a T = cte

$$dq = \left[p + \frac{\partial u}{\partial v}\right] dv_T$$

$$= \left[\cancel{p} + \left(\frac{c_p - c_v}{\beta v}\right) - \cancel{p}\right] dv_T$$

$$dq = \left(\frac{c_p - c_v}{\beta v}\right) dv_T$$

Do processo adiabático e $(*)(c)$ e que $\frac{dT}{dv} = \frac{\partial T}{\partial v}$

$$c_v \left.\frac{\partial T}{\partial v}\right)_s = -\left[p + \frac{\partial u}{\partial v}\right]$$

$$\left.\frac{\partial T}{\partial v}\right)_s = \frac{-\left[\cancel{p} + \frac{(c_p - c_v)}{\beta v} - \cancel{p}\right]}{c_v}$$

$$\therefore \left.\frac{\partial T}{\partial v}\right)_s = \frac{(c_p - c_v)}{\beta v c_v}$$

Para $u(T, v)$

Usando as definições de β e k 10 - 4

$$\left.\frac{\partial u}{\partial T}\right) = c_v$$

$$\left.\frac{\partial u}{\partial v}\right)_T = \frac{c_p - c_v}{\beta v} - p$$

$$dq_T = \left(\frac{c_p - c_v}{\beta v}\right) dv_T$$

$$\left.\frac{\partial T}{\partial v}\right)_S = \frac{c_v - c_p}{\beta v c_v}$$

e.

$$dq = c_v\, dT + \left[p + \frac{\partial u}{\partial v}\right] dv$$

T e p independentes - (v)

$$du = \frac{\partial u}{\partial T} dT + \frac{\partial u}{\partial p} dp$$

$$dv = \frac{\partial v}{\partial T} dT + \frac{\partial v}{\partial p} dp$$

1ª Lei $\quad du = dq - dw \quad \rightarrow \quad dq = du + dw$

$$dw = p\,dv$$

$$dq = \frac{\partial u}{\partial T} dT + \frac{\partial u}{\partial p} dp + p\left(\frac{\partial v}{\partial T} dT + \frac{\partial v}{\partial p} dp\right)$$

$$dq = dT\left(\frac{\partial u}{\partial T} + p\frac{\partial v}{\partial T}\right)^{*} + dp\left(\frac{\partial u}{\partial p} + p\frac{\partial v}{\partial p}\right)$$

$dp = 0 \qquad dq = c_p\,dT$

$$c_p\,dT = \left(\frac{\partial u}{\partial T} + p\frac{\partial v}{\partial T}\right)^{*} dT \qquad (a)$$

Em geral $\quad p = c^{te}$

$$dq = c_p\,dT + dp\left[\frac{\partial u}{\partial p} + p\frac{\partial v}{\partial p}\right] \qquad (**)$$

Para $\quad v = c^{te} \quad dv = 0 \quad \rightarrow \quad dq = c_v\,dT$

$$\therefore \; c_v\,dT = c_p\,dT + dp\left[\frac{\partial u}{\partial p} + p\frac{\partial v}{\partial p}\right]$$

ou $$c_v = c_p + \frac{\partial p}{\partial T}\left[\frac{\partial u}{\partial p} + p\frac{\partial v}{\partial p}\right] \qquad (b)$$

Se $T = cte$ de (**) $(T - p) \equiv$ independentes

$$dq = dp\left[\frac{\partial u}{\partial p} + p\frac{\partial v}{\partial p}\right]$$

No processo adiabático $dq = 0$ de (**)

$$0 = c_p\, dT_s + dp\left[\frac{\partial u}{\partial p} + p\frac{\partial v}{\partial p}\right]$$

$$c_p\, dT_s = -dp\left[\frac{\partial u}{\partial p} + p\frac{\partial v}{\partial p}\right]$$

$$\therefore\ c_p\frac{\partial T}{\partial p} = -\left[\frac{\partial u}{\partial p} + p\frac{\partial v}{\partial p}\right] \quad (c)$$

$k = -\frac{1}{v}\left(\frac{\partial v}{\partial p}\right)_T$ e $\beta = \frac{1}{v}\left(\frac{\partial v}{\partial T}\right)_p$

de (a) $\frac{\partial u}{\partial T} = c_p - p\frac{\partial v}{\partial T} = c_p - p\beta v$ ∴ (d)

$$\boxed{\frac{\partial u}{\partial T} = c_p - p\beta v}$$

de (c) $-\frac{\partial u}{\partial p} = +p\frac{\partial v}{\partial p} + c_p\frac{\partial T}{\partial p}$

$$= p(-kv) + c_p\frac{\partial T}{\partial p}$$

$T-p$ = independentes

$$\frac{\partial u}{\partial p} = p k v - (c_p - c_v)\frac{k}{\beta}$$

$$\frac{\partial u}{\partial T} = c_p - p\beta v$$

dq.

$$dq_T = \left[\frac{\partial u}{\partial p} + p\left(\frac{\partial v}{\partial p}\right)\right]dp$$

$$= \left[p \cancel{k v} - (c_p - c_v)\frac{k}{\beta} + p\left(\cancel{-k v}\right)\right]dp$$

$$dq_T = \frac{k}{\beta}\left[(c_v - c_p)\right]dp_T$$

$(\partial T/\partial p)_s$

$$\left.\frac{\partial T}{\partial p}\right)_s = -\frac{1}{c_p}\left[\left(\frac{\partial u}{\partial p}\right)_T + p\left(\frac{\partial v}{\partial p}\right)_T\right]$$

$$= -\frac{1}{c_p}\left[p \cancel{k v} - (c_p - c_v)\frac{k}{\beta} + p \cancel{k v}\right]$$

$$\left.\frac{\partial T}{\partial p}\right)_s = \frac{k}{\beta}\frac{(c_p - c_v)}{c_p}$$

$$-\frac{\partial u}{\partial p} = -phv + c_p \frac{\partial T}{\partial p}$$

$$\frac{\partial T}{\partial p} = \frac{1}{\partial p/\partial T}$$ de

b) $$\frac{\partial p}{\partial T} = \frac{c_v - c_p}{\left[\frac{\partial u}{\partial p} + p\frac{\partial v}{\partial p}\right]}$$

$$\frac{\partial p}{\partial T} = \frac{c_v - c_p}{\left[\frac{\partial u}{\partial p} - phv\right]}$$

obs: $$\frac{\partial T}{\partial p} = \frac{\frac{\partial v}{\partial p}}{\frac{\partial v}{\partial T}} = \frac{-hv}{\beta v}$$

$$\left[\frac{\partial u}{\partial p} - phv\right] = (c_v - c_p)\frac{\partial T}{\partial p}$$

$$\frac{\partial T}{\partial p}\cdot\frac{\partial v}{\partial T}\cdot\frac{\partial p}{\partial v} = -1$$

$$\frac{\partial u}{\partial p} = phv + (c_v - c_p)\frac{\partial T}{\partial p}$$

$$\frac{\partial T}{\partial p}\cdot\beta v\left(-\frac{1}{hv}\right) = -1$$

$$\therefore \left(\frac{\partial u}{\partial p}\right) = phv + (c_v - c_p)\left(\frac{h}{\beta}\right) \qquad \therefore \frac{\partial T}{\partial p} = \frac{h}{\beta}$$

$$\boxed{\left(\frac{\partial u}{\partial p}\right) = phv - (c_p - c_v)\frac{h}{\beta}}$$

Para $u(T,p)$

Em função de β e k.

$$\left.\frac{\partial u}{\partial T}\right)_p = c_p - p\beta v$$

$$\left.\frac{\partial u}{\partial p}\right)_T = pvk - \frac{k}{\beta}(c_p - c_v)$$

$$\left.\frac{\partial T}{\partial p}\right)_s = \frac{k(c_p - c_v)}{\beta c_p}.$$

e $dq = c_p\,dT + \left[\frac{\partial u}{\partial p} + p\frac{\partial v}{\partial p}\right]dp$

p - V independientes $\qquad v = u(p, v)$

$$du = \left(\frac{\partial u}{\partial v}\right) dv + \left(\frac{\partial u}{\partial p}\right) dp$$

$$dq = du + dw = \left(\frac{\partial u}{\partial v}\, dv\right) + \left(\frac{\partial u}{\partial p}\right) dp$$
$$+$$
$$+ \; p\, dv$$

$$dq = \frac{\partial u}{\partial p} dp + \left[p + \frac{\partial u}{\partial v} \right] dv$$

i) $dv = 0 \qquad dq = c_v\, dT$

$$c_v\, dT = \frac{\partial u}{\partial p} dp + \left[p + \frac{\partial u}{\partial v} \right] dv \; *$$

$$\therefore \quad c_v = \frac{\partial u}{\partial p} \frac{\partial p}{\partial T} + \left[p + \frac{\partial u}{\partial v} \right] \frac{\partial v}{\partial T}$$

$$c_v - \left[p + \frac{\partial u}{\partial v} \right] \frac{\partial v}{\partial T} = \frac{\partial u}{\partial p} \frac{\partial p}{\partial T}$$

$$\frac{c_v - \left[p + \frac{\partial u}{\partial v} \right] \cdot \frac{\partial v}{\partial T}}{\partial p / \partial T} = \frac{\partial u}{\partial p}$$

p-V independientes

$$\frac{c_v - \left[p + \frac{\partial u}{\partial v}\right]\beta v}{\partial p/\partial T} = \frac{\partial u}{\partial p}$$

$$\frac{c_v - \left[\cancel{p} + \frac{Ep}{\beta v} - \cancel{p}\right]\beta v}{-k/\beta.} = \frac{\partial u}{\partial p}$$

---

de $*$ $$c_v \frac{dT}{dp} - \left[p + \frac{\partial u}{\partial v}\right]\frac{dv}{dp} = \frac{\partial u}{\partial p}$$

Para $\underline{v = cte}$ $$\frac{\partial u}{\partial p} = c_v \frac{\partial T}{\partial p} = c_v \frac{k}{\beta}$$ ✓

a $p = cte.$ $$dq = c_p\, dT$$

$$c_p\, dT = \frac{\partial u}{\partial p} dp + \left[p + \frac{\partial u}{\partial v}\right] dv.$$

$$\therefore\ c_p\, dT = \left[p + \frac{\partial u}{\partial v}\right] dv.$$

$$c_p \frac{dT}{dv} - p = \frac{\partial u}{\partial v}$$

$$c_p \frac{\partial T}{\partial v} - p = \frac{\partial u}{\partial v} = \frac{c_p}{\beta v} - p = \frac{\partial u}{\partial v}$$ ✓

p-V independentes

$$dq = \frac{\partial u}{\partial p} dp + \left[p + \frac{\partial u}{\partial v} \right] dv$$

$$= \frac{n c_v}{\beta} . dp + \left[\cancel{p} + \frac{c_p}{\beta v} - \cancel{p} \right] dv$$

$$dq = \frac{n c_v}{\beta} dp + \frac{c_p}{\beta v} dv$$

Adiabático $\quad dq = 0$

$$0 = \frac{n c_v}{\cancel{\beta}} dp + \frac{c_p}{\cancel{\beta} v} dv$$

$$\frac{dp}{dv} = - \frac{c_p}{n c_v} \frac{1}{v} \rightarrow \left. \frac{\partial p}{\partial v} \right)_s = - \frac{c_p}{n c_v}$$

$u = u(p, v)$

Em função de β e k

$$\left.\frac{\partial u}{\partial p}\right)_v = \frac{k}{\beta} c_v$$

$$\left.\frac{\partial u}{\partial v}\right)_p = \frac{c_p}{\beta v} - p$$

$$\left.\frac{\partial p}{\partial v}\right)_s = -\frac{c_p}{c_v k v}$$

e $$dq = \frac{c_v k}{\beta} dp_T + \left[p + \frac{\partial u}{\partial v} \right] dv$$