الباب السادس
تغـيرات الحـــالة

$p - v - T$: :

( )

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$p - v - T$ $p - v - T$.

.

.

$p - v - T$ ( ) ( )

( ) (1)

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( ) ( )

:

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( )

)

(.

$$p - v - T \qquad (\quad)$$

$$p - v - T \qquad (\quad)$$

$$(\quad) \quad (\quad)$$

ruled surfaces

.

88

p – T   ( ) ( )

.

p – T   ( ) ( )

.

.

Substance	T (°C)	p (mm of mercury)
O_2	–218	2.0
N_2	– 210	96.4
A	– 190	512
CO_2	– 56.6	3880
H_2O	+ 0.0098	4.579

v – T

.

p – v – T

a T_2 ( )

. f

.

T_2

(   )   a   .

.

.   b

bc   .

.   .

89

p – v – T

.

( )

.   (   )
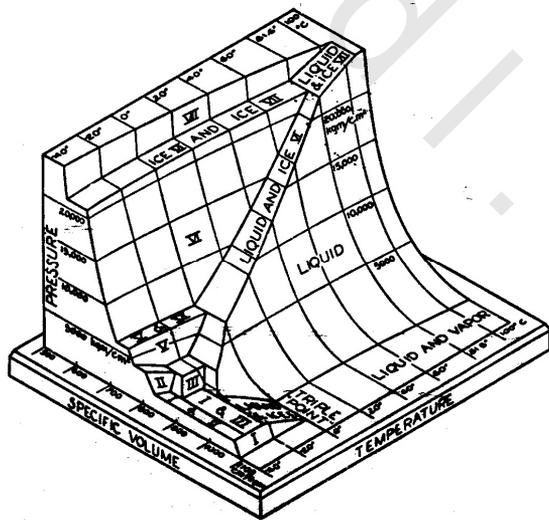
T_c .

.

T_c
) .

.(

:

$\cdot p_c$

$p - v - T$ T_c, v_c, p_c

:

Substance	p_e n/m^3	v_e M^3/kgm-mole	T_e deg K
He	2.3×10^5	0.062	5.25
H_2	13	0.065	33.2
N_2	34	0.090	126
O_2	51	0.075	154
CO_2	74	0.005	304
H_2O	221	0.057	647
Hg	3600	0.040	1900

91

a

b

.

PRESSURE

VOLUME   TEMPERATURE

T_c

a

b,   a

.

(   )
. (   )

b   a

. $p - v - T$

92

( )

.

.

.

p_1

            a

p_1

b

. c   b

T_b

.

93
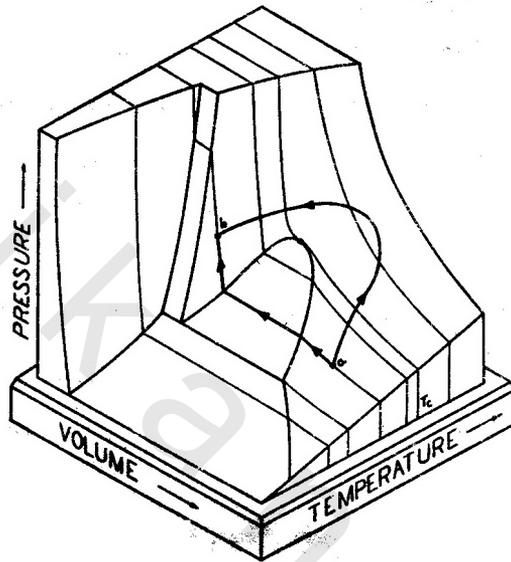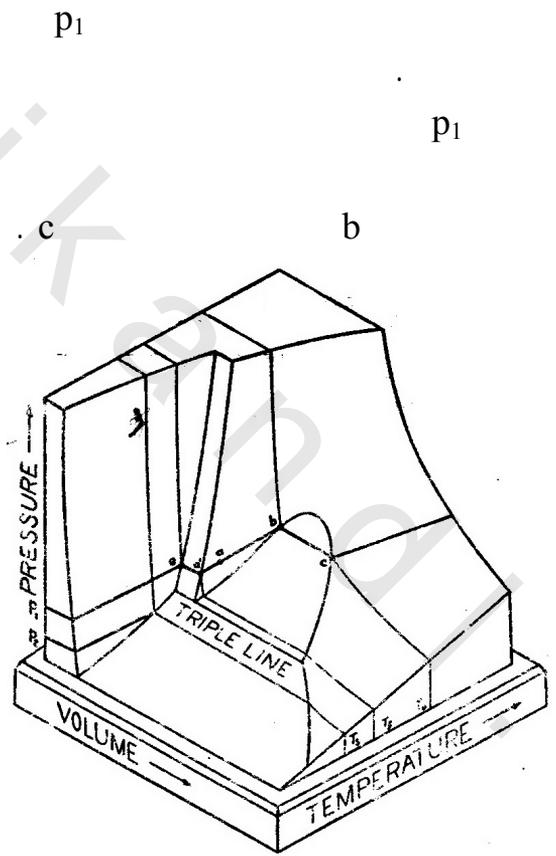
T_b

p_1

$. 373°K \quad 100°C$

.

a

. d

:

e   d

.

p – T

p_1 (a)

. T_f

.

.

p_2

(   )   .

. T_5

)

. $(T_S$

$56.6°C – CO_2$

.   5.1

CO_2

( )

. ( )

. $p - v - T$

. $4°K$

2.26 $5.25°K$

$5.25°K$

. I $2.18°K$

$2.18°K$

II   I   . II

II   I

95

II   .   2.18°K

.

I

II

.

b $p - v - T$

.c   a

a

. c
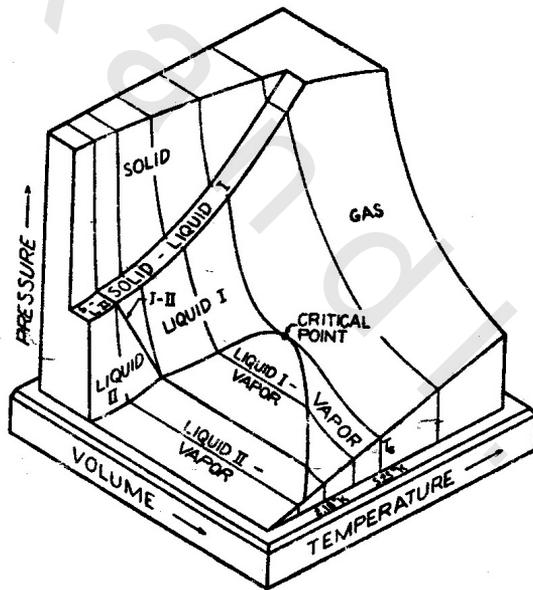
states   a   c

.   (   )

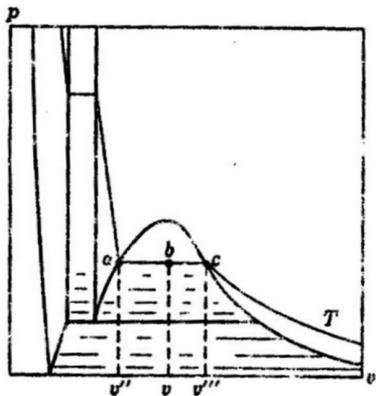c   v''', v'', v'

v'''

T

v"   a

.

b

v", v'''

96

v

. m   v

m₂,   v", v'''

: m₃

$$V = V''' + V'' \, , \, m = m_2 + m_3,$$

$$v''' = \frac{V'''}{m_3} \, , \, v'' = \frac{V''}{m_2}, \, v = \frac{V}{m}.$$

:

$$\frac{m_3}{m} = \frac{v - v''}{v''' - v''}, \, \frac{m_2}{m} = \frac{v''' - v}{v''' - v''},$$

ab   ac bc $v''' - v'', \, v' - v, \, v - v''$

m^2/m m^3/m

.

( )   ( ) $p - v - T$

20°C   .

$10^{-3} m^3/kgm$

. $58 m^3/kgm$

:   :

:

$$\left(\frac{\partial p}{\partial v}\right)_T = \left(\frac{\partial^2 p}{\partial v^2}\right)_T = 0$$

p

:   p

97

$$p = \frac{RT}{v - T} - \frac{a}{v^2}$$

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

$$\left(\frac{\partial^2 p}{\partial v^2}\right)_T = \frac{2RT}{(v - b)^3} - \frac{6a}{v^4}$$

$v_c = v$ $\qquad\qquad T_C = T$

$T_C,\ v_c$

:

$$p_c = \frac{a}{27b^2},$$
$$v_c = 3b,$$
$$T_c = \frac{8a}{27Rb} \qquad\qquad (2)$$

b, a

: $\qquad\qquad\qquad$ K $\qquad\qquad\qquad\qquad$ b a :

$$b = \frac{v_c}{3},$$

$. \ b = \frac{RT_c}{Sp_c}$:

$\qquad\qquad\qquad\qquad\qquad\qquad p_c,\ v_c,\ T_c$

$p - v - T \qquad\qquad\qquad\qquad\qquad\qquad\qquad b$

.

.

. b a

98

$$\frac{RT}{pv}$$

.

:

$$\frac{RT_c}{b_c - v_c} = \frac{8}{3} = 2.07,$$

$$\frac{8}{3}$$

$$(= \hspace{4cm}) .$$

.

$RT_c/p_c v_c$	
Substance	$RT_c/p_c v_c$
He	3.66
H_2	3.27
O_2	3.42
CO_2	3.61
H_2O	4.30
Hg	1.10

:

$$p_v = \frac{p}{p_c}, \ v_r = \frac{v}{v_c}, \ T_r = \frac{T}{T_c}$$

$$( )$$

:

$$p_v = \left(p_r + \frac{3}{v_c} \right)(3v_r - 1) = 8T. \qquad (3)$$

99

( )   b   a

. p_r, v_r, T_r (1, 1, 1)   .

( )

)

.(

:   :

m

.   Q

m   Q

)

. (n

$$l = \frac{Q}{m} = q, \qquad /$$

$$l = \frac{Q}{n} = q, \qquad /$$

$l_{13},\ l_{23},\ l_{12}$

.

.

:

.

.

:

$$w = p(v_2 - v_1), \qquad\qquad (5)$$

. $v_1, \ v_2$

:

$$u_2 - u_1 = q - w$$
$$= l - p(v_2 - v_1), \qquad\qquad (\ )$$

                                                                100°C

. (100°C   ) $m^2/$ $1.01 \times$

    , ×   /

$10^{-3} \ m^3/Kgm$ v'' 1.8 m/ v'''

.

$$u''' - u'' = l_{23} - p(v''' - v'')$$
$$= 22.6 \times 10^6 - 1.01 \times 10^3 (1.8 - 10^{-3})$$
$$= 20.8 \times 10^5 \quad /$$

:   ( )

$$l = (u_2 + pv_2) - (u_2 + pv_1),$$

:

$$l = h_2 - h_1 \qquad\qquad (7)$$

.

.

.

l_{13}

l_{12} :

: $+ l_{23}$

$$l_1 = l_{12} + l_{23} \qquad\qquad (8)$$

.

: :

. p – v $\qquad$ p – v – T

a $\qquad\qquad$ abcd

T + dT $\qquad$ T

T + dT $\qquad\qquad$ bc

T

da

.

cd   ab
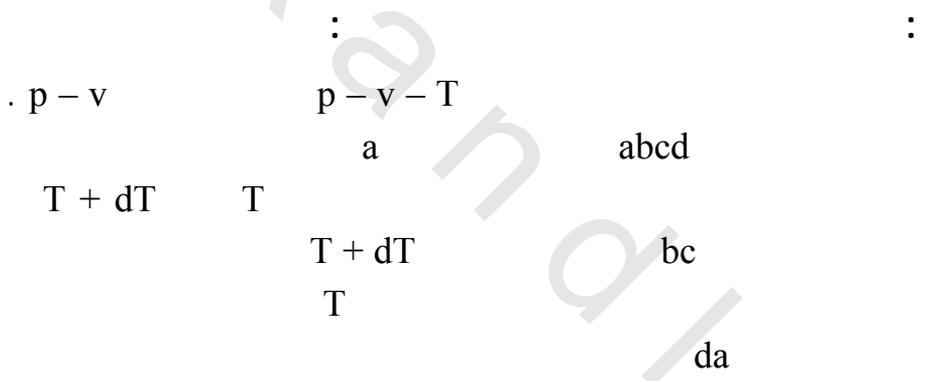
c_S

.

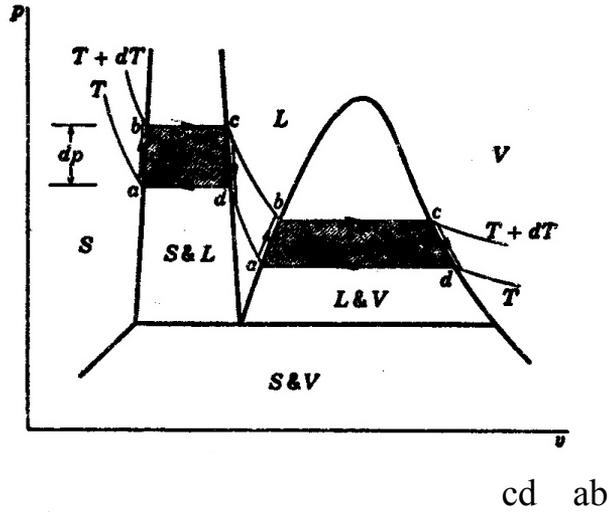c_p c_S

:   .

T + dT , T $l(T + dT), l(T)$

:

$$q = c_s^{"} dT + l(T + dT) - c_s^{"} dT\, dT - l(T)$$

$$w = dp(v''' - v'') :$$

$$l(T + dT) = l(T) + \frac{dl}{dT}\, dT \qquad :$$

:   dT   w, q

$$c_s^{"'} - c_s^{"} = \frac{dl}{dT} - \frac{dp}{dT}\, (v''' - v'').$$

:

$$\frac{dp}{dT}\, (v''' - v'') = \frac{l}{T}$$

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:

$$c_s''' - c_s'' = \frac{\mathrm{d}l}{\mathrm{d}T} - \frac{l}{T},$$

:

$$c_s''' - c_s'' = T \frac{\mathrm{d}}{\mathrm{d}T}\left(\frac{l}{T}\right),$$

.

.

l

: $w = 0$

$$c_2 - c_1 = \frac{\mathrm{d}p}{\mathrm{d}T}$$

q c_2 c_1

.   q .

.

❅ ❅ ❅

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1 –

$300°K$ $8m^3$ 8

. $300°K$.

$v''' = 0.5 \ m^3/$, $h''' = 1800$ /

$v'' = 0.1 \ m^3/$, $h'' = 600$ /

$1.6m^3$.   :

(a) .

(b) $p - v$.

(c)

(d)

– $250 \ cm^3$

$1mm$ $10 \ cm$.

$1 \ cm$

.

$20°C$

$10^{-3} \ mm$:

(a) .

(b)

(b):

$20°C$ $17.5mm$.

–

.

Bul.
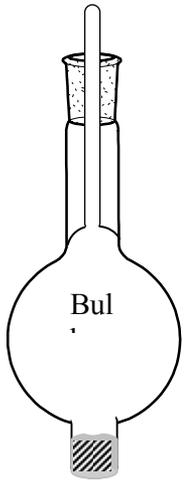
b –

.

. p_c , T_c (b)   . v_c (a)

: CO_2 –

$p_c = 74 \times 10^5 \ n/m^2$, $v_c = 0.095 \ m^3/mole$, $T_c = 304 \ °K$

$66 \times 10^5 \ n/m^2$ $299°K$

$T = 216°K$. $0.063 \ m^3/mole$

: $p = 5.1 \times 10^5 \ n/m^2$

. $0.037 \ m^3/mole$,

. $p - v$ (a)

(b)

$10^7 \ V \times p = 7$:

. n/m^2 p   V

. $310°K$

:   (a)–

$$p \, (v - b) \exp \left(\frac{a}{v} \, RT \right) = RT$$

$$p_c = \frac{a}{4e^2 b^2} , \ v_c = 2b , \ T_c = \frac{a}{4Rb}$$

. $RT_c / p_c v_c$ (b)

p_r .   –

:

$1.2 \ T_c$, $1.0 \ T_c$, $0.9 \ T_c$, $0.7 \ T_c$,

p_r ,   , v_r

v_r $1.5 , \ 0$

. p_r T_r