§ 8.9 Approximate entropy for liquids and solids

$$dS = \frac{\delta Q}{T} \doteq \frac{m\, C_{(p)}\, dT}{T}$$

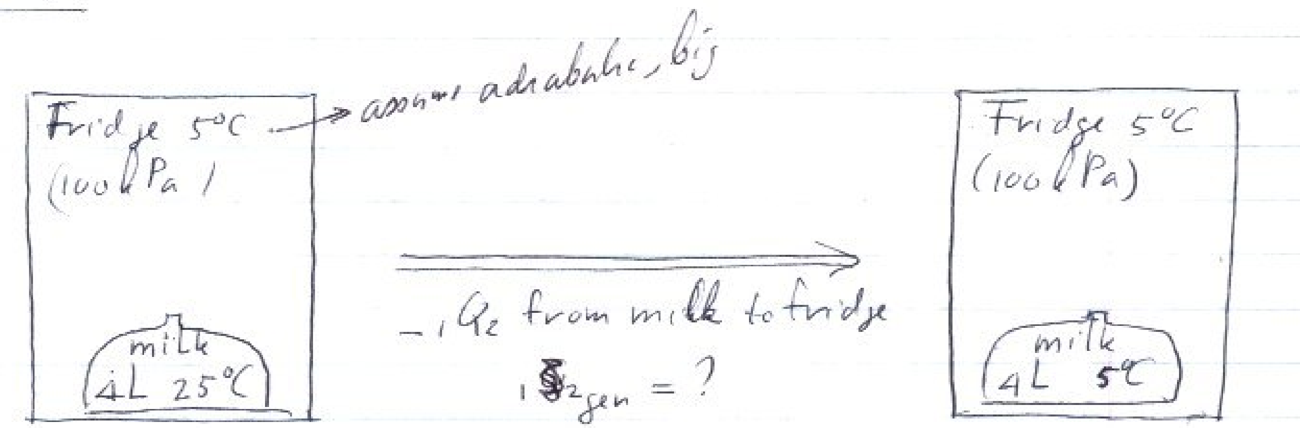
$$ds \approx C \frac{dT}{T}$$

$$\boxed{s_2 - s_1 \approx C \ln \frac{T_2}{T_1} \quad \text{for liquids and solids with } C \text{ constant}}$$

↓

(If you do not have tables)

p 0.77



Asked: entropy generated by this <u>irreversible</u> process

Answer: Since we will ignore heat conduction with the surroundings of the fridge, the entire system is adiabatic, so if it was reversible, $\Delta S_{total} = \int^2 \delta Q_{tot} / T_{tot}$ would be zero. But actually, the process is irreversible (the milk will not go from 5° to 25° in the fridge), so entropy will be generated.

$$ {}_1S_{2,gen} = S_{2tot} - S_{1tot} = (S_{2fridge} + S_{2milk}) - (S_{1fridge} + S_{1milk})$$
$$ = (S_{2fridge} - S_{1fridge}) + (S_{2milk} - S_{1milk})$$

Shorthand notation: $S_2 - S_1 \equiv \Delta S$, so

$$ {}_1S_{2gen} = \Delta S_{fridge} + \Delta S_{milk} \qquad \Delta S_{fridge} = \boxed{\Delta S_{surr} = \frac{-{}_1Q_2}{T_{surr}}}$$

~~Do milk first:~~

~~a) milk = water~~ ~~$m = \rho V = 997 \frac{kg}{m^3} 4L \frac{1 m^3}{1000 L} =$~~

~~b) use approximate formula for entropy change~~

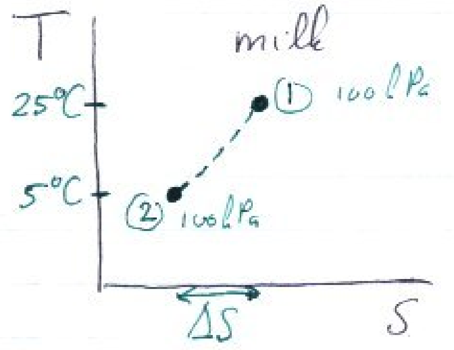
~~$\Delta S = m C \ln \frac{T_2}{T_1}$~~

Do milk first

SKIP

assumptions : a) milk = water
b) approximate formulae are good enough

Look at TS diagram first? Sure!



Note : Draw irreversible processes as broken lines.

The milk does not have a (single) temperature when it is cooling down : the inside will be hotter than the outside → so what is $\frac{\delta Q}{T}$??

The key to note is that entropy is a state variable
S_2 only depends on what state ② is, not how we got there

Approximate formula for entropy change :

$$\Delta S_{milk} = m\, C \ln \frac{T_2}{T_1} = \rho V C \ln \frac{T_2}{T_1}$$

(which was derived assuming a reversible process from ① to ②)

Using A.4

$$\Delta S_{milk} = \overset{A3,\,25^\circ C}{997}\,\frac{kg}{m^3}\, 4L\, \frac{1\,m^3}{1000L}\; \overset{A3,\,25^\circ C}{4.18}\,\frac{kJ}{kg\,K} \ln \frac{5+273}{25+273}$$

$$= -1.15\overset{75}{8}\,\frac{kJ}{K}$$

We also need the heal removed (to know what happens to the fridge). Use approximate formula

$$_1Q_2 = m\, C\, (T_2 - T_1) = 997\,\frac{kg}{m^3}\, 4L\, \frac{1m^3}{1000L}\; 4.18\,\frac{kJ}{kg\,K}\,(5-25)\,K$$

$$= -333.4\ kJ.$$

Now do the fridge.

From the milk we saw that 333.4 kJ of heat is transferred from milk to fridge.

Use the isothermal formula to find ΔS_{fridge}

$$({}_1Q_2)_{fridge} = mT(s_{2_{fridge}} - s_1)_{fridge} = T(S_{2fridge} - S_{1fridge})$$

$$= T\Delta S_{fridge}$$

$$333.4\text{ kJ} = (5+273)\text{K}\,\Delta S_{fridge}$$

$$\Delta S_{fridge} = 1.199\ \frac{\text{kJ}}{\text{K}}$$

(Again, this is correct even if the entire fridge is not all at 5°C during the heat exchange, since $S_{2_{fridge}}$ depends only on the final state, not how you got there)

Total:

$$ {}_1S_{2,gen} = \Delta S_{fridge} + \Delta S_{milk} = +1.199\ \frac{\text{kJ}}{\text{K}} - 1.150\ \frac{\text{kJ}}{\text{K}}$$

$$= \overset{0.04113}{0.041}\ \frac{\text{kJ}}{\text{K}} \quad \text{(positive as it should be)}$$

Better: use tables to do the milk: (will need to use saturated tables since $\underset{A-7}{B.1.4}$ stops at $\underset{5000}{500}$ kPa)

$$S_{2milk} - S_{1milk} = m(s_{2milk} - s_{1milk})$$

$$ {}_1Q_2 = U_2 - U_1 + {}_1W_2 = U_2 - U_1 + pV_2 - pV_1 = H_2 - H_1 = m(h_2 - h_1)$$

s_1, h_1 from B.1.1 @ 25°C

$h_2\ s_2$ " " @ 5°C

$$\left.\right\} \begin{array}{l} {}_1Q_2 = 334.2 \\ {}_1S_{2\,gen} = 0.042\overset{15}{}\ \frac{\text{kJ}}{\text{K}} \end{array}$$ (~~[illegible]~~)

3/24 9

§8.5 Thermodynamic property relations (Needed to do ideal gas s)

1st law $\delta q = du + p\,dv$

2nd law $\delta q_{rev} = T\,ds$

} combine : $T\,ds = du + p\,dv$

(Properties only: no longer a process needed.)

Can be rewritten in terms of h, since $u = h - pv$, so $du = dh - v\,dp - p\,dv$:

$$\boxed{\begin{array}{l} T\,ds = du + p\,dv \\ T\,ds = dh - v\,dp \end{array}}$$

"Gibbs equations"

"Thermodynamic property equations"

They can be used to compute s, e.g. for an ideal gas, or much else.

3/29 5

S5.7 Type formulae (S8.10) Entropy for ideal gases

For an ideal gas, entropy can be found using the Gibbs formulae:

$$\left.\begin{aligned} ds &= \frac{dh}{T} - \frac{v}{T}dp \\ dh &= c_p(T)\,dT \quad \frac{v}{T} = \frac{R}{p} \end{aligned}\right\} ds = c_p\frac{dT}{T} - R\frac{dp}{p}$$

$$s_2 - s_1 = \int_1^2 c_p(T)\frac{dT}{T} - R\ln\left(\frac{p_2}{p_1}\right)$$

The term $\int_1^2 \frac{c_p}{T}dT$ depends on temperature only, not on pressure. We can therefor use its value at 1 bar:

$$\boxed{s_2 - s_1 = s_T^0(T_2) - s_T^0(T_1) - R\ln\left(\frac{p_2}{p_1}\right)}$$

*Çengel does not use sub T

knowing

where s_T^0 is the entropy at 1 bar, as found in tables A7 and A8.

(NOTE: s_T^0 is an intensive variable equivalent to T)

Instead, if c_p constant, ($= c_{p\,ave}$, say), then $\int_1^2 \frac{c_p}{T}dT = c_p\ln\frac{T_2}{T_1}$, so

$$\boxed{s_2 - s_1 = c_p\ln\frac{T_2}{T_1} - R\ln\frac{p_2}{p_1} \quad \text{if } c_p, c_v, k = \frac{c_p}{c_v} \text{ constant}}$$

We may replace either T or p in these formulae by v using $p_2v_2/T_2 = p_1v_1/T_1$. For example:

$$c_p\ln\frac{T_2}{T_1} - R\ln\frac{p_2}{p_1} = c_p\ln\frac{p_2v_2}{p_1v_1} - R\ln\frac{p_2}{p_1} = (c_p - R)\ln\frac{p_2}{p_1} + c_p\ln\frac{v_2}{v_1}$$

where $c_p - R = c_v$:

$$\boxed{\begin{aligned} s_2 - s_1 &= c_v\ln\frac{p_2}{p_1} + c_p\ln\frac{v_2}{v_1} \quad \text{if } c_p, c_v, k \text{ constant} \\ s_2 - s_1 &= c_v\ln\frac{T_2}{T_1} + R\ln\frac{v_2}{v_1} \quad \text{"} \quad \text{"} \quad \text{"} \end{aligned}}$$

SKIP

what if volume ratio is to be computed or given?

SKIP

$$s_2 - s_1 = s_2^0 - s_1^0 - R\ln P_2/P_1$$

$$s_2 - s_1 = s_2^0 - s_1^0 - R\ln\left(\frac{T_2}{T_1}\frac{v_1}{v_2}\right)$$

$$= \underbrace{\left(s_2^0 - R\ln T_2\right)}_{s_2'} - \underbrace{\left(s_1^0 - R\ln T_1\right)}_{s_1'} + R\ln\frac{v_2}{v_1}$$

Instead define

$$s^0 \equiv R\ln P_r \qquad P_r = e^{s^0/R}$$

$$s' = -R\ln v_r \qquad v_r = e^{-s^0/R + \ln T} = \frac{T}{e^{s^0/R}} = \frac{T}{P_r}$$

$$s_2 - s_1 = R\ln P_{r2} - R\ln P_{r1} - R\ln P_2 + R\ln P_1$$

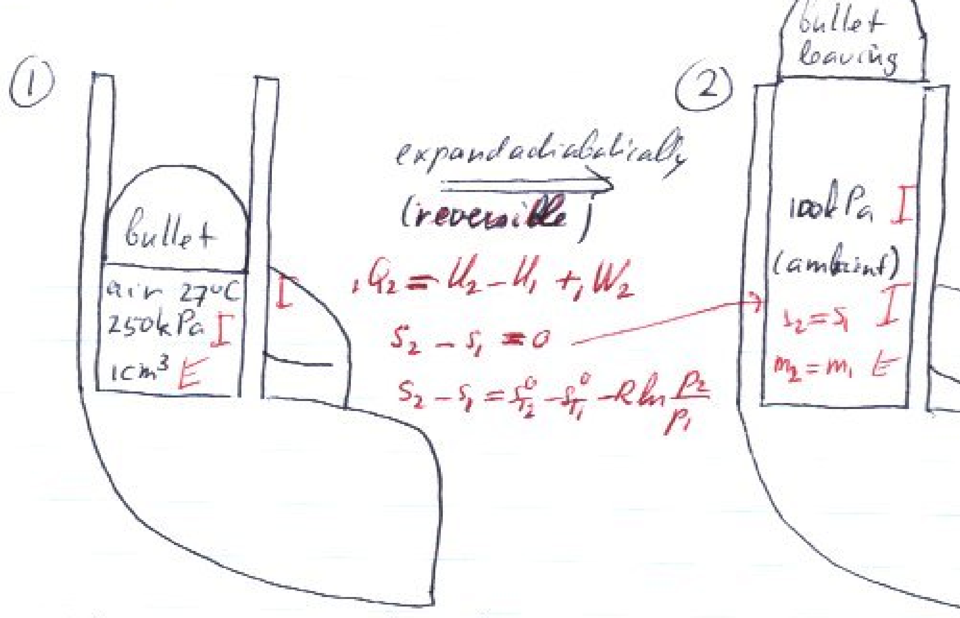
$$= -R\ln\frac{P_2}{P_{r2}}\frac{P_{r1}}{P_1} \qquad \text{isentropic } \frac{P_2}{P_1} = \frac{P_{r2}}{P_{r1}}$$

$$s_2 - s_1 = -R\ln v_{r2} + R\ln v_{r1} + R\ln v_2 - R\ln v_1$$

$$= R\ln\frac{v_2}{v_{r2}}\frac{v_{r1}}{v_1} \qquad \text{isentropic } \frac{v_2}{v_1} = \frac{v_{r2}}{v_{r1}}$$

3/24 6

<u>P8.90</u> Air gun.



$_1Q_2 = U_2 - U_1 + {}_1W_2$

$s_2 - s_1 = 0$

$s_2 - s_1 = s^0_{T_2} - s^0_{T_1} - R \ln \frac{p_2}{p_1}$

Asked: V_2 (determines how big the barrel must be), $_1W_2$ (determines how much energy the bullet receives.)

$$s_2 - s_1 = 0 = s_T^0(T_2) - s_T^0(T_1) - R \ln \frac{p_2}{p_1}$$

Table $\overset{A17}{A7.1}$, p660 @ $T_1 = 27 + 273\,K = 300\,K$: $\begin{cases} u_1 = 214.\overset{07}{36}\ kJ/kg \\ s_T^0(T_1) = s_{T_1}^0 = \underset{1.70203}{6.86926}\ \frac{kJ}{kg\,K} \end{cases}$

$$s_T^0(T_2) - \underset{1.70203}{6.86926}\ \frac{kJ}{kg\text{-}K} - 0.287\ \frac{kJ}{kg\text{-}K} \ln \frac{100\ kPa}{250\ kPa} = 0$$

$$\rightarrow s_{T_2}^0 = s_T^0(T_2) = \overset{1.43905}{6.60628}\ \frac{kJ}{kg\text{-}K}$$

lecture ended here ⟶

5 04

Table A.7.1, p660 @ $s_T^0 = \overset{1.43905}{6.60628}\ \frac{kJ}{kg\text{-}K}$ interpolated:

$$T_2 = \overset{230}{220}\,K + \frac{\overset{1.43905\ -\ 1.43557}{6.60628 - 6.55812}}{\underset{1.47824}{6.69535} - \underset{1.43557}{6.55812}}(240 - \overset{230}{220})K = \overset{230.81}{231.04}\,K$$

$$u_2 = \overset{164}{157.07} + \frac{6.60628 - 6.55812}{6.69535 - 6.55812}(\overset{171.13\ -\ 164}{171.38 - 157.07}) = 164.\overset{58}{97}\ \frac{kJ}{kg}$$

$$m = \frac{p_1 V_1}{R T_1} = \frac{250\ kPa\ 10^{-6}\ m^3}{.287\ \frac{kJ}{kg\text{-}K}\ 300\ K} = 2.903 \cdot 10^{-6}\ kg$$

$$V_2 = \frac{m R T_2}{p_2} = \frac{2.903 \cdot 10^{-6}\ kg\ .287\ \frac{kJ}{kgK}\ \overset{0.81}{231.04}\ K}{100\ kPa} = \underline{\underline{1.925\ cm^3}}$$

3/28 prob end ⟶

$$_1W_2 = {}_1Q_2 + U_1 - U_2 = 0 + 2.903 \cdot 10^{-6}\ kg\ (214.\overset{07}{36} - 164.\overset{58}{97})\frac{kJ}{kg} = \underline{\underline{0.14\overset{37}{3}\ J}}$$

$$s_2 - s_1 = c_v \ln \frac{p_2}{p_1} + c_p \ln \frac{v_2}{v_1} \xrightarrow[]{\overset{\text{if}}{s_2 = s_1}} \left(\frac{p_2}{p_1}\right) = \left(\frac{v_1}{v_2}\right)^{\frac{c_p}{c_v}}$$

3/29

Polytropic formulas for an ideal gas (S.P.11)

Polytropic $pV^n = \text{constant}$ $p_1 V_1^n = p_2 V_2^n$

When ~~polytropic~~ polytropic?

$\boxed{\text{Ideal gas + isothermal : } n = 1}$ (since $pv = RT = \text{const}$

i.e. $c_p = \text{const}$ or $c_v = \text{const}$

$\boxed{\text{Ideal gas + isentropic + } k = \text{constant} ; \ n = k}$

(since $s_2 - s_1 = 0 = c_v\left(\ln \frac{p_2}{p_1} + k \ln \frac{v_2}{v_1}\right) = c_v \ln \frac{p_2 v_2^k}{p_1 v_1^k}$)

If not polytropic, forget about this section

$$\boxed{\frac{P_2}{P_1} = \left(\frac{v_1}{v_2}\right)^n \overset{\uparrow}{=} \left(\frac{T_2}{T_1}\right)^{\frac{n}{n-1}}}$$

if an ideal gas

$$\boxed{\begin{array}{ll} {}_1w_2 = \dfrac{p_2 v_2 - p_1 v_1}{1-n} & \text{if } n \neq 1 \\ {}_1w_2 = pv \ln \dfrac{v_2}{v_1} & \text{if } n = 1 \\ \hline pv = RT \text{ if an ideal gas} & \end{array}}$$

(same as in Chapter 4; but here written in terms of specific variables.)

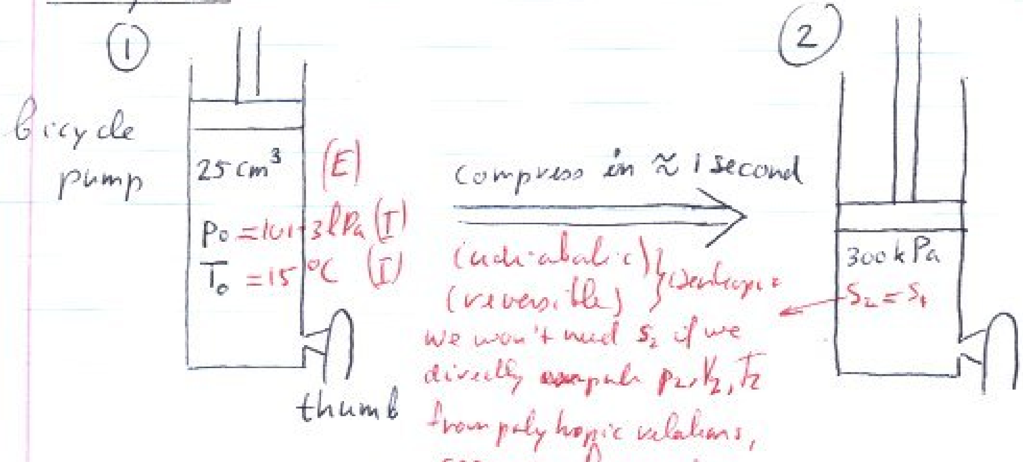
Notes: $\boxed{a = b^c \Longrightarrow a^{\frac{1}{c}} = b}$ (To get $\frac{v_1}{v_2}$ or $\frac{T_2}{T_1}$ if $\frac{p_2}{p_1}$ is known)

$$\boxed{\begin{array}{l} \ln(a) - \ln(b) = \ln\left(\frac{a}{b}\right) \\ \ln(a^b) = b \ln(a) \end{array}} \longrightarrow$$

(To compute exponents, e.g. n)

3/24 8

P 8.93 (1)



(adiabatic) } isentropic
(reversible) }

We won't need s_2 if we directly compute p_2, V_2, T_2 from polytropic relations, assuming k = constant

↳ otherwise like 8.90

Asked: $V_2, T_2 \{ {}_1W_2 \}$

Solution: "Normal" compressions of "normal" air typically adiabatic. We will also assume reversible ⟹ isentropic

Also, standard sea-level atmosphere: $p_0 = 101.3$ kPa, $T_0 = 15$°C

Problem is exactly same as 8.90! But here, we will assume that $k = 1.4$ (i.e. c_p and c_v constant, 25°C, values from table A.5)

Polytropic relationships:

$$\frac{p_2}{p_1}\left[=\left(\frac{v_1}{v_2}\right)^n\right]=\left(\frac{V_1}{V_2}\right)^n=\left(\frac{T_2}{T_1}\right)^{\frac{n}{n-1}} \quad \text{with } n = k = 1.4$$

$$\frac{300\text{ kPa}}{101.3\text{ kPa}}=\left(\frac{25\text{ cm}^3}{V_2}\right)^{1.4}=\left(\frac{T_2}{273+15\text{ K}}\right)^{\frac{1.4}{0.4}}$$

$$V_2=\left(\frac{101.3\text{ kPa}}{300.0\text{ kPa}}\right)^{\frac{1}{1.4}} 25\text{ cm}^3 = \underline{\underline{11.518}}\text{ cm}^3$$

$$T_2=\left(\frac{300\text{ kPa}}{101.3\text{ kPa}}\right)^{\frac{0.4}{1.4}}(273+15)\text{K} = 392.7\text{ K}$$
$$= \underline{\underline{119.7}}\text{ °C}$$

$$m = \frac{P_1V_1}{RT_1} = \frac{101.3\,\text{kPa}\ \ 0.25\ 10^{-6}\,\text{m}^3}{0.287\frac{\text{kJ}}{\text{kg K}}\ (273+15)\,\text{K}} = 30.639\ 10^{-6}\,\text{kg}$$

Can now compute work as ${}_1W_2 = \frac{P_2V_2 - P_1V_1}{1-n} = \underline{\underline{-2.307\ \text{J}}}$ 3/29 9

or as ${}_1W_2 = U_1 - U_2 = mc_v(T_2 - T_1) = \underline{\underline{2.300}}$ J

P 8.93 (2)

Same, except compress in about 1 hour instead of 1 second.

Solution: This slowly, the temperature will remain at 15°C, since any temperature difference has time to diffuse away.

$$\rightarrow T_2 = T_1 = \underline{\underline{15^\circ C}}$$

Isothermal is polytropic with n = 1:

$$\frac{P_2}{P_1} = \frac{V_1}{V_2} \quad \rightarrow V_2 = \frac{P_1}{P_2} V_1 = \underline{\underline{8.49}}\ \text{cm}^3$$

~~${}_1W_2 = P_1V_1 \ln$~~

$${}_1W_2 = P_1V_1 \ln\frac{V_2}{V_1} = + P_1V_1 \ln\frac{P_1}{P_2} = \underline{\underline{-2.75\ \text{J}}}$$

or using 1st law $\cancelto{0 \text{ if isothermal}}{U_2 - U_1} = {}_1Q_2 - {}_1W_2 \rightarrow$

$$\rightarrow {}_1W_2 = {}_1Q_2 = \overset{273+15}{T}(S_2 - S_1) = T m \left[\cancelto{0}{c_p \ln\frac{T_2}{T_1}} - R \ln\frac{P_2}{P_1}\right]$$

$$= \underline{\underline{-2.75\ \text{J}}}$$

3/29 1

Entropy generation (Replaces § 8.6 – 8.8)

$$\boxed{\text{Irreversible effects always act to increase total entropy}}$$

Assume: control mass CM

${}_1Q_2$ transferred to CM from surroundings at temperature T_{surr}

Then:

$$\boxed{\underset{\substack{\uparrow\\ \text{entropy}\\ \text{generated}\\ \text{by}\\ \text{irreversible}\\ \text{effects}}}{{}_1S_{2\,gen}} \equiv \underset{\substack{\uparrow\\ \text{total}\\ \text{change}\\ \text{in}\\ \text{entropy}}}{\Delta S_{net}} = \underbrace{S_2 - S_1}_{\substack{\uparrow\\ \text{entropy}\\ \text{change}\\ \text{of}\\ \text{CM}}} - \underset{\substack{\uparrow\\ \text{entropy}\\ \text{change}\\ \text{of}\\ \text{surroundings}}}{\frac{{}_1Q_2}{T_{surr}}}}\ \boxed{\geq 0}$$