Lecture 19, 10/30/07

GENERAL THERMODYNAMIC RELATIONS: THE JACOBIAN METHOD

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CLASIUS-CLAPEYRON RELATION

Maxwell relations

$$dU = TdS - PdV$$ $(T, \text{ and } -P)$ for dU

$$dH = TdS + VdP$$ $(T, \text{ and } V)$ for dH

$$dF = -SdT - PdV$$ $(-S, \text{and } -P)$ for dF

$$dG = -SdT + VdP$$ $(-S, \text{ and } V)$ for dG

$$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V$$
$$\left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P$$
$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$$
$$\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P .$$

Playing with the definitions

More such relations with the entropy!

1. From second law $\delta q_{rev} = TdS$

2. Total differential of entropy in terms of P and T $dS = \left(\frac{\partial S}{\partial T}\right)_P dT + \left(\frac{\partial S}{\partial P}\right)_T dP$

3. Constant pressure

$$dS_P = \left(\frac{\partial S}{\partial T}\right)_P dT$$

Playing with the definitions

4. Combining with

$$\delta q_{P,rev} = TdS_P = C_P dT$$

gives

$$T\left(\frac{\partial S}{\partial T}\right)_P dT = C_P dT$$

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

Relate specific heat with entropy

Playing with the definitions

1. Total differential of entropy in terms of V and T

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

2. Constant volume

$$dS_V = \left(\frac{\partial S}{\partial T}\right)_V dT$$

3. Combining with $\delta q_{V,rev} = T dS_V = C_V dT$

$$T\left(\frac{\partial S}{\partial T}\right)_V dT = C_V dT \Rightarrow C_V = T\left(\frac{\partial S}{\partial T}\right)_V$$

Functional relations to P and T

Showed functional dependence of entropy is related to heat capacities. Now convert thermodynamic quantities to functions of T and P

First step: Write dS and dV in terms of T and P

$$dS = \left(\frac{\partial S}{\partial T}\right)_P dT + \left(\frac{\partial S}{\partial P}\right)_T dP$$

$$dS = \left(\frac{C_P}{T} dT - V\alpha dP\right)$$

Functional relations to P and T

First step: Write dS and dV in terms of T and P

$$dV = \left(\frac{\partial V}{\partial T}\right)_P dT + \left(\frac{\partial V}{\partial P}\right)_T dP$$

Substituting

$$\alpha \equiv \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P \text{ and } \beta \equiv -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T$$

gives

$$dV = V\alpha dT - V\beta dP$$

Functional relations to P and T: U

Covert the four energy functions in terms of these quantities

$$dU = TdS - PdV$$

$$= T\left(\frac{C_P}{T}dT - V\alpha dP\right) - P\left(V\alpha dT - V\beta dP\right)$$

$$dU = \left(C_P - PV\alpha\right)dT + V\left(P\beta - T\alpha\right)dP$$

Functional relations to P and T: H

Writing the enthalpy H

$$dH = TdS + VdP$$

$$= T\left(\frac{C_P}{T}dT - V\alpha dP\right) + VdP$$

$$dH = C_P dT + V(1 - T\alpha)dP$$

Functional relations to P and T: F

Writing the Helmholtz free energy, F

$$dF = -SdT - PdV$$

$$\downarrow$$

$$= -SdT - P\left(V\alpha dT - V\beta dP\right)$$

$$\downarrow$$

$$dF = -\left(S + PV\alpha\right)dT + PV\beta dP$$

Functional relations to P and T

Writing the Gibbs free energy, G

$$dG = -SdT + VdP$$

$$dS = \left(\frac{C_P}{T}dT - V\alpha dP\right)$$
$$dV = V\alpha dT - V\beta dP$$
$$dU = (C_P - PV\alpha)\,dT + V\,(P\beta - T\alpha)\,dP$$
$$dH = C_P dT + V\,(1 - T\alpha)\,dP$$
$$dF = -\,(S + PV\alpha)\,dT + PV\beta dP$$
$$dG = -SdT + VdP$$

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General relations using the Jacobians

$$Z = Z(X, Y)$$

$$dZ = M\,dX + N\,dY \qquad M = \left(\frac{\partial Z}{\partial X}\right)_Y \qquad N = \left(\frac{\partial Z}{\partial Y}\right)_X$$

$$dX = \left(\frac{\partial X}{\partial P}\right)_T dP + \left(\frac{\partial X}{\partial T}\right)_P dT \qquad dY = \left(\frac{\partial Y}{\partial P}\right)_T dP + \left(\frac{\partial Y}{\partial T}\right)_P dT$$

$$X_P = \left(\frac{\partial X}{\partial P}\right)_T, \; Y_P = \left(\frac{\partial Y}{\partial P}\right)_T$$

$$dZ = M\left(X_T dT + X_P dP\right) + N\left(Y_T dT + Y_P dP\right)$$

$$dZ = \left(M X_T + N Y_T\right) dT + \left(M X_P + N Y_P\right) dP$$

General relations using the Jacobians

$$dZ = (MX_T + NY_T)\,dT + (MX_P + NY_P)\,dP$$

$$dZ = Z_T dT + Z_P dP$$

$$Z_T = MX_T + NY_T \qquad Z_P = MX_P + NY_P$$

$$M = \frac{\begin{vmatrix} Z_T & Y_T \\ Z_P & Y_P \end{vmatrix}}{\begin{vmatrix} X_T & Y_T \\ X_P & Y_P \end{vmatrix}} \qquad N = \frac{\begin{vmatrix} X_T & Z_T \\ X_P & Z_P \end{vmatrix}}{\begin{vmatrix} X_T & Y_T \\ X_P & Y_P \end{vmatrix}}$$

$$M = \frac{Z_T Y_P - Z_P Y_T}{X_T Y_P - X_P Y_T} \qquad N = \frac{Z_P X_T - Z_T X_P}{X_T Y_P - X_P Y_T}.$$

Example: S=S(T,V)

Step 1. Identify variables:

$$S = S(T, V)$$

Step 2. Write the differential form:

$$dS = M\,dT + N\,dV$$

Step 3. Convert dV using dV(P,T) from the summary:

$$dS = M\,dT + N\,(V\alpha dT - V\beta dP)$$

Step 4. Collect terms:

$$dS = (M + NV\alpha)\,dT - NV\beta dP$$

Step 5. Obtain dS(P,T) from the summary and compare to dS we just derived:

$$dS = \left[\frac{C_p}{T}\right] dT - V\alpha dP$$

Example: S=S(T,V)

Step 4. Collect terms:

$$dS = (M + NV\alpha)\, dT - NV\beta dP$$

Step 5. Obtain $dS(P,T)$ from the summary and compare to dS we just derived:

$$dS = \left[\frac{C_p}{T}\right] dT - V\alpha dP$$

The coefficients are equal to each other so:

$$\frac{C_p}{T} = M + NV\alpha$$

and

$$V\alpha = NV\beta$$

Step 6. Since the algebra is simple we can just use elimination of N.

$$N = \frac{\alpha}{\beta} = \left(\frac{\partial S}{\partial V}\right)_T$$

and $$M = \frac{C_p}{T} - \frac{\alpha^2}{\beta}V = \left(\frac{\partial S}{\partial T}\right)_V$$

Example: S=S(T,V)

$$dS = \left(\frac{C_p}{T} - \frac{\alpha^2}{\beta}V\right)dT + \frac{\alpha}{\beta}dV$$

S=S(P,V)

Step 1. Identify variables:

$$S = S(P, V)$$

Step 2. Write the differential form:

$$dS = MdP + NdV$$

Step 3. Convert dV using dV(P,T) from the summary:

$$dS = MdP + N\left(V\alpha dT - V\beta dP\right)$$

Step 4. Collect terms:

$$dS = \left(M - NV\beta\right)dP + NV\alpha dT$$

Step 5. Obtain dS(P,T) from the summary and compare to dS we just derived:

$$dS = \left[\frac{C_P}{T}\right]dT - V\alpha dP$$

S=S(P,V)

Step 4. Collect terms:

$$dS = (M - NV\beta)\, dP + NV\alpha dT$$

Step 5. Obtain $dS(P,T)$ *from the summary and compare to* dS *we just derived:*

$$dS = \left[\frac{C_p}{T}\right] dT - V\alpha dP$$

The coefficients are equal to each other so:

$$\frac{C_p}{T} = NV\alpha$$

and

$$-V\alpha = M - NV\beta$$

Step 6. Since the algebra is simple again we can just use elimination of N.

$$N = \frac{C_p}{VT\alpha} = \left(\frac{\partial S}{\partial V}\right)_P$$

and $$M = \frac{C_p\beta}{T\alpha} - V\alpha = \left(\frac{\partial S}{\partial P}\right)_V$$

$$dS = \left(\frac{C_p\beta}{T\alpha} - V\alpha\right) dP + \frac{C_p}{VT\alpha} dV$$

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F=F(P,V)

$$dF = -\frac{S\beta}{\alpha}dP - (\frac{S}{V\alpha} + P)dV$$

H=H(S,V)

Step 1. Identify variables:

$$H = H(S, V)$$

Step 2. Write the differential form:

$$dH = MdS + NdV$$

Step 3. Convert dS and dV using dS(P,T) and dV(P,T) from the summary:

$$dH = M\left(\frac{C_P}{T}dT - V\alpha dP\right) + N\left(V\alpha dT - V\beta dP\right)$$

Step 4. Collect terms:

$$dH = -\left(MV\alpha + NV\beta\right)dP + \left(M\frac{C_P}{T} + NV\alpha\right)dT$$

Step 5. Obtain dH(P,T) from the summary and compare to dH we just derived:

$$dH = C_P dT + V\left(1 - T\alpha\right)dP$$

$H=H(S,V)$

Step 4. Collect terms:

$$dH = -\left(MV\alpha + NV\beta\right)dP + \left(M\frac{C_P}{T} + NV\alpha\right)dT$$

Step 5. Obtain $dH(P,T)$ from the summary and compare to dH we just derived:

$$dH = C_P dT + V\left(1 - T\alpha\right)dP$$

The coefficients are equal to each other so:

$$V\left(1 - T\alpha\right) = -\left(MV\alpha + NV\beta\right)$$

and

$$C_P = \left(M\frac{C_P}{T} + NV\alpha\right)$$

$$M = \frac{\begin{vmatrix} H_T & V_T \\ H_P & V_P \end{vmatrix}}{\begin{vmatrix} S_T & V_T \\ S_P & V_P \end{vmatrix}}$$

$$N = \frac{\begin{vmatrix} S_T & H_T \\ S_P & H_P \end{vmatrix}}{\begin{vmatrix} S_T & V_T \\ S_P & V_P \end{vmatrix}}$$

$H=H(S,V)$

$$M = \frac{\begin{vmatrix} H_T & V_T \\ H_P & V_P \end{vmatrix}}{\begin{vmatrix} S_T & V_T \\ S_P & V_P \end{vmatrix}} = \frac{H_T V_P - H_P V_T}{S_T V_P - S_P V_T}$$

$$= \frac{-C_P V\beta - V(1-T\alpha)V\alpha}{-\frac{C_P}{T}V\beta + V\alpha V\alpha}$$

$$= \frac{-C_P\beta - \left(V\alpha - TV\alpha^2\right)}{-\frac{C_P}{T}\beta + V\alpha^2}$$

$$= \frac{\beta\left(C_P + \frac{V\alpha}{\beta} - \frac{TV\alpha^2}{\beta}\right)}{\frac{\beta}{T}\left(C_P - \frac{TV\alpha^2}{\beta}\right)}$$

$$M = \frac{T\left(C_P + \frac{V\alpha}{\beta} - \frac{TV\alpha^2}{\beta}\right)}{\left(C_P - \frac{TV\alpha^2}{\beta}\right)}$$

$$M = \frac{T}{C_V}\left(C_V + \frac{V\alpha}{\beta}\right) = \left(\frac{\partial H}{\partial S}\right)_V$$

H=H(S,V)

$$N = \frac{\begin{vmatrix} S_T & H_T \\ S_P & H_P \end{vmatrix}}{\begin{vmatrix} S_T & V_T \\ S_P & V_P \end{vmatrix}} = \frac{S_T H_P - S_P H_T}{S_T V_P - S_P V_T} = \frac{-C_P}{\beta C_V}.$$

P is a dependent variable: P(S,F)

First we identify variables: $P = P(S,F)$

Next we rewrite our master equation since in this case the dependent variable is pressure P.

$$S = S(P,F)$$

We can then write the Jacobians for the partials directly:

$$\left(\frac{\partial S}{\partial P}\right)_F = \frac{\left(\frac{\partial S}{\partial T}\right)_P\left(\frac{\partial F}{\partial P}\right)_T-\left(\frac{\partial S}{\partial P}\right)_T\left(\frac{\partial F}{\partial T}\right)_P}{\left(\frac{\partial P}{\partial T}\right)_P\left(\frac{\partial F}{\partial P}\right)_T-\left(\frac{\partial P}{\partial P}\right)_T\left(\frac{\partial F}{\partial T}\right)_P} \longrightarrow \left(\frac{\partial S}{\partial P}\right)_F = \frac{\left(\frac{\partial S}{\partial T}\right)_P\left(\frac{\partial F}{\partial P}\right)_T-\left(\frac{\partial S}{\partial P}\right)_T\left(\frac{\partial F}{\partial T}\right)_P}{0\left(\frac{\partial F}{\partial P}\right)_T-1\left(\frac{\partial F}{\partial T}\right)_P}$$

$$= \frac{-\left(\frac{\partial S}{\partial T}\right)_P\left(\frac{\partial F}{\partial P}\right)_T}{\left(\frac{\partial F}{\partial T}\right)_P} + \left(\frac{\partial S}{\partial P}\right)_T$$

$$\left(\frac{\partial S}{\partial F}\right)_P = \frac{\left(\frac{\partial P}{\partial T}\right)_P\left(\frac{\partial S}{\partial P}\right)_T-\left(\frac{\partial P}{\partial P}\right)_T\left(\frac{\partial S}{\partial T}\right)_P}{\left(\frac{\partial P}{\partial T}\right)_P\left(\frac{\partial F}{\partial P}\right)_T-\left(\frac{\partial P}{\partial P}\right)_T\left(\frac{\partial F}{\partial T}\right)_P} \longrightarrow \left(\frac{\partial S}{\partial F}\right)_P = \frac{0\left(\frac{\partial S}{\partial P}\right)_T-1\left(\frac{\partial S}{\partial T}\right)_P}{0\left(\frac{\partial F}{\partial P}\right)_T-1\left(\frac{\partial F}{\partial T}\right)_P} = \frac{\left(\frac{\partial S}{\partial T}\right)_P}{\left(\frac{\partial F}{\partial T}\right)_P}$$

P is a dependent variable: P(S,F)

$$\left(\frac{\partial S}{\partial P}\right)_F = \frac{\left(\frac{\partial S}{\partial T}\right)_P\left(\frac{\partial F}{\partial P}\right)_T - \left(\frac{\partial S}{\partial P}\right)_T\left(\frac{\partial F}{\partial T}\right)_P}{0\left(\frac{\partial F}{\partial P}\right)_T - 1\left(\frac{\partial F}{\partial T}\right)_P}$$
$$= \frac{-\left(\frac{\partial S}{\partial T}\right)_P\left(\frac{\partial F}{\partial P}\right)_T}{\left(\frac{\partial F}{\partial T}\right)_P} + \left(\frac{\partial S}{\partial P}\right)_T$$

$$\left(\frac{\partial S}{\partial F}\right)_P = \frac{0\left(\frac{\partial S}{\partial P}\right)_T - 1\left(\frac{\partial S}{\partial T}\right)_P}{0\left(\frac{\partial F}{\partial P}\right)_T - 1\left(\frac{\partial F}{\partial T}\right)_P} = \frac{\left(\frac{\partial S}{\partial T}\right)_P}{\left(\frac{\partial F}{\partial T}\right)_P}$$

Now that we have general expressions for the partials (we could substitute in for the various partials from the summary of thermodynamic relations, but we'll refrain from that here) we can write our total differential:

$$dS = MdP + NdF$$

and rearranging gives

$$dP = \frac{dS}{M} - \frac{NdF}{M}$$
$$dP = \left[\left(\frac{\partial S}{\partial P}\right)_F\right]^{-1} dS - \left[\left(\frac{\partial S}{\partial P}\right)_F\right]^{-1}\left[\frac{\left(\frac{\partial S}{\partial T}\right)_P}{\left(\frac{\partial F}{\partial T}\right)_P}\right] dF$$

Useful simplification

Notice that when I have the partials of one state function with respect to another at either a constant temperature or constant pressure that this partial becomes just the ratio of the two partials with respect to T or P (which ever is not held constant). That is

$$\left(\frac{\partial X}{\partial Y}\right)_P = \frac{\left(\frac{\partial P}{\partial T}\right)_P\left(\frac{\partial X}{\partial P}\right)_T - \left(\frac{\partial P}{\partial P}\right)_T\left(\frac{\partial X}{\partial T}\right)_P}{\left(\frac{\partial P}{\partial T}\right)_P\left(\frac{\partial Y}{\partial P}\right)_T - \left(\frac{\partial P}{\partial P}\right)_T\left(\frac{\partial Y}{\partial T}\right)_P}$$

which simplifies by

$$\left(\frac{\partial X}{\partial Y}\right)_P = \frac{0\left(\frac{\partial X}{\partial P}\right)_T - 1\left(\frac{\partial X}{\partial T}\right)_P}{0\left(\frac{\partial Y}{\partial P}\right)_T - 1\left(\frac{\partial Y}{\partial T}\right)_P}$$

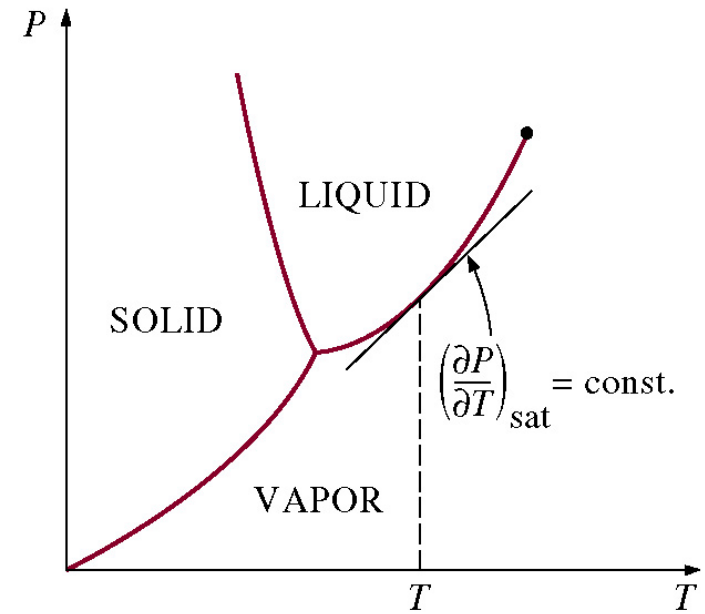
so that

$$\left(\frac{\partial X}{\partial Y}\right)_P = \frac{\left(\frac{\partial X}{\partial T}\right)_P}{\left(\frac{\partial Y}{\partial T}\right)_P}$$

Clapeyron equation

- Lets look at a phase transition (e.g. the water-vapor transition).

$$dG = -SdT + VdP$$

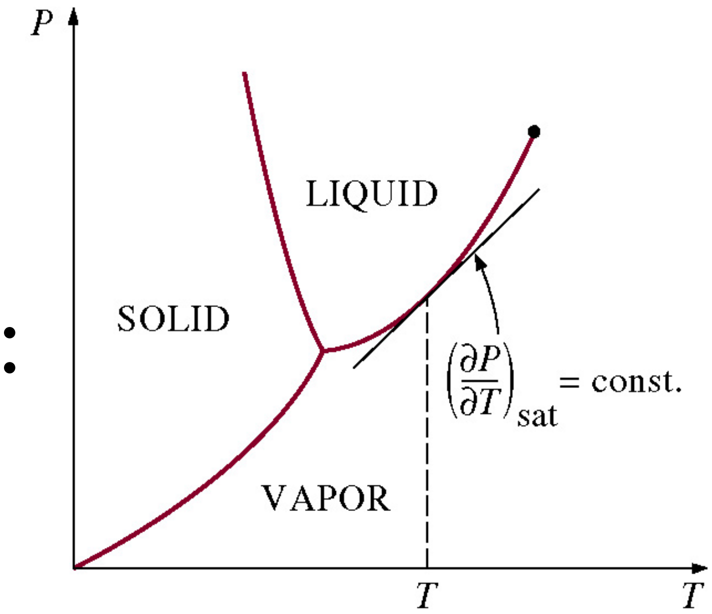


- During phase transition: dG=0 (equilibrium condition)

$$\Delta G = \Delta H - T\Delta S = 0 \Rightarrow \Delta S = \frac{\Delta H}{T}$$

Clapeyron equation

$$s_{fg} = \frac{h_{fg}}{T}$$



- From the Maxwell relation:

$$\frac{\partial S}{\partial V}\Big|_T = \frac{\partial P}{\partial T}\Big|_V = \frac{dP}{dT}\Big|_{sat}$$

- There is no V dependence here.

$$\frac{\partial s}{\partial v}\Big|_T = \frac{\partial P}{\partial T}\Big|_v = \frac{dP}{dT}\Big|_{sat} = \frac{s_g - s_f}{v_g - v_f} \Rightarrow$$

$$\boxed{\frac{dP}{dT}\Big|_{sat} = \frac{h_g - h_f}{T(v_g - v_f)}}$$

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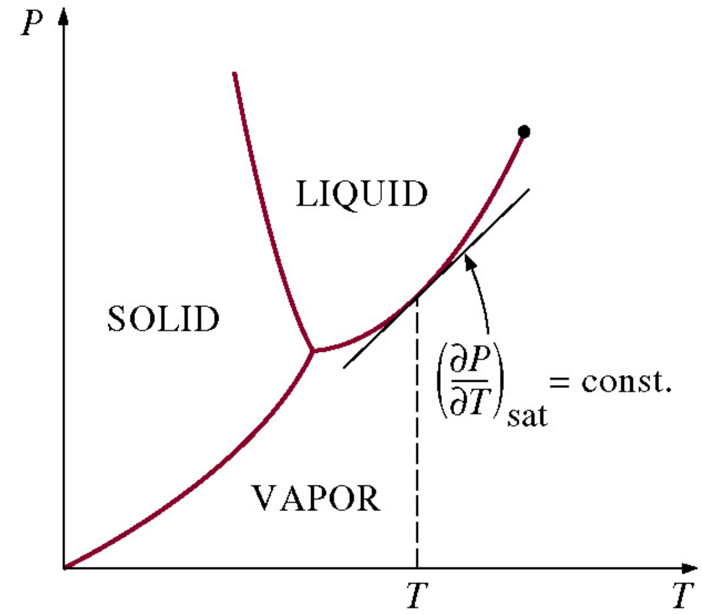
Clausius-Clapeyron equation

$$\frac{dP}{dT}\Big|_{sat} = \frac{h_g - h_f}{T(v_g - v_f)}$$



- Assume $v_g \gg v_f$ and that ideal gas conditions apply:

$$v_g = \frac{RT}{P}$$

- Then: $$\frac{dP}{dT}\Big|_{sat} = \frac{h_g - h_f}{T(v_g - v_f)} = \frac{h_{fg}}{RT^2/P} \Rightarrow$$

$$\frac{d\ln P}{dT}\Big|_{sat} = \frac{h_{fg}}{RT^2} \Rightarrow$$

$$\ln\frac{P_2}{P_1} = \frac{h_{fg}}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

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