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PROJECT TITLE: "Equilibrium and Volumetric Data and Model
Development of Coal Fluids"

PROJECT PERIOD: January 1, 1992 to March 31, 1992

SUMMARY

During the present reporting period, the solubility of
carbon monoxide in naphthalene was measured at $212\,°F$ ($100\,°C$)
and $302\,°F$ ($150\,°C$) at pressures to 227.9 bar (3305 psia).
These new data can be described with root mean square (RMS)
errors within 0.001 in mole fraction by the Soave-Redlich-
Kwong (SRK) and Peng-Robinson (PR) equations of state with
one interaction parameter, C_{ij}, and they can be described
within 0.0005 RMS errors in mole fraction with two
interaction parameters, C_{ij} and D_{ij}.

DISCLAIMER

EQUILIBRIUM AND VOLUMETRIC DATA AND MODEL
DEVELOPMENT OF COAL FLUIDS

Report for the Period

January 1, 1992 to March 31, 1992

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EQUILIBRIUM AND VOLUMETRIC DATA AND MODEL
DEVELOPMENT OF COAL FLUIDS

ABSTRACT

The proper design, operation, and optimization of coal conversion and utilization processes depend heavily on knowledge of phase behavior of the mixtures encountered in these processes. Frequently quoted statistics suggest that in conventional chemical plants 70% of the capital and 90% of the operating expenses are associated with phase separations. Since multiple fluid phases occur in almost all stages of coal conversion process - from feed preparation through conversion reactions to product separation - the proper description of phase behavior is important in each step of these processes.

The long term goal of our efforts is to develop accurate predictive methods for description of equilibrium phase properties for a variety of types of mixtures and operating conditions. The specific objectives of the work specified herein include:

(1) development of an experimental facility having the capability to provide data on equilibrium phase compositions (solubilities) and liquid densities, and doing so with greater accuracy and speed than our previous facility,

(2) measurement of equilibrium phase properties for systematically-selected mixtures - specifically those containing important solute gases (such as

hydrogen, carbon monoxide, carbon dioxide, methane, ethane, carbonyl sulfide, ammonia) in a series of heavy paraffinic, naphthenic and aromatic solvents (e.g., n-decane, n-eicosane, n-octacosane, n-hexatriacontane, cyclohexane, Decalin, perhydrophenanthrene, perhydropyrene, benzene, naphthalene, phenanthrene, pyrene),

(3)   testing/development of correlation frameworks for representing the phase behavior of fluids of the type encountered in coal conversion processes, and

(4)   generalization of parameters in the correlation frameworks to enable accurate predictions for systems of the type studied, permitting predictions to be made for systems and conditions other than those for which experimental data are available.

During the present reporting period, the solubility of carbon monoxide in naphthalene was measured at $212°F$ ($100°C$) and $302°F$ ($150°C$) at pressures to 227.9 bar (3305 psia). These new data can be described with root mean square (RMS) errors within 0.001 in mole fraction by the Soave-Redlich-Kwong (SRK) [1] and Peng-Robinson (PR) EOS [2] with one interaction parameter, C_{ij}, and they can be described within 0.0005 RMS errors in mole fraction with two interaction parameters, C_{ij} and D_{ij}.

INTRODUCTION

Essentially all state of the art models for phase behavior contain one [1,2], two [3] or three [4] interaction parameters to account for unlike molecular pair interactions. These parameters, in general, cannot be predicted a priori from existing theory, but can be established from experimental measurements on the binary pairs which form the system of interest. These "empirical" interaction parameters have a dramatic effect on the predicted properties of mixtures and are thus required for accurate predictions. In most instances, successful modeling of the behavior of complex multicomponent mixtures requires accurate information on the pure compounds and on the binary interactions that exist between the different molecular species.

Experimental measurements made on systematically chosen mixtures can be used to evaluate interaction parameters and, more importantly, furnish the basis for generalization of the parameters to allow interpolation (and perhaps extrapolation) to other solvents in the same homologous series. Toward this end, we have previously reported and analyzed data on the solubility of carbon dioxide, ethane, methane, and carbon monoxide in a series of hydrocarbons [5-12]. In the present report, we complement our solubility, x, (or equivalently, bubble point pressure, p) measurements for carbon monoxide with data for the system carbon monoxide + naphthalene. The uncertainty in measured bubble point pressure, which depends on the p-x profile for each isotherm, is of the order of 0.4

bar (6 psia).

The carbon monoxide used in this study was supplied by Matheson Gas Products with a stated purity of 99.99%. Naphthalene was supplied by Aldrich Chemical Company and had a stated purity of 99+%. No further purification of the chemicals was attempted.

DISCUSSION OF TECHNICAL RESULTS

The experimental data (presented in Table I) have been correlated using the SRK [1] and PR [2] equations of state. Optimum binary interaction parameters were obtained by minimizing the sum of squares of pressure deviations from the experimental values. Detailed procedures for data reduction are given elsewhere [9]. The input parameters for the pure components (acentric factors, critical temperatures and critical pressures) required by the SRK and PR equations of state, together with the literature sources, are presented in Table II.

Figure 1 shows the effect of temperature and pressure on carbon monoxide solubility (liquid phase mole fraction of carbon monoxide) in naphthalene. For a given total pressure, solubility of the gas increases with increasing temperature. This behavior is the same as observed for carbon monoxide in Benzene [11].

The equation of state representations of the solubilities for the system under study are documented in Table III. In general, the SRK and PR equations are capable

of describing the data with RMS errors of 0.001 in mole

fraction when a single interaction parameter, C_{ij}, is used

over the complete temperature range. Improvements in

equation of state predictions are realized (RMS = 0.0003)

when an additional parameter, D_{ij}, is introduced. The

results given in Table III indicate that the PR EOS fits the

data somewhat better than the SRK EOS, when either one or two

interaction parameters are used over the complete temperature

range (RMS errors of 0.0005 for PR EOS compared to 0.0007 for

SRK EOS, using only C_{ij}). When one interaction parameter,

C_{ij}, is fitted to each isotherm, the RMS errors are less than

0.0006 and the two equations of state give comparable

representations of the data.

Figures 2 and 3 illustrate the quality the of fit

obtained using the SRK and PR EOS. The solubility deviation

plots were generated by comparing SRK equation of state

predictions with the experimental measurements. Interaction

parameters, C_{ij} and D_{ij}, employed in the equation of state

predictions were obtained by fitting our data to the isotherm

under study.

Due to the absence of published data on this binary

system, a direct comparison with literature data is not

possible; however, our results illustrate both the ability of

the equations of state and the precision of our reported

data.

CONCLUSION

New data have been obtained for the solubility of carbon monoxide in naphthalene at temperatures of 373.2 K (212 °F) and 423.2 K (302 °F) at pressures to 227.9 bar (3305 psia). These data are well described by the SRK and PR equations of state. These results will be of value in establishing equation-of-state interaction parameters for light gases in aromatic solvents.

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TABLE I

SOLUBILITY DATA OF CARBON MONOXIDE IN NAPHTHALENE

Mole Fraction Carbon Monoxide	Bubble point pressure bar	(psia)
--------- 373.15 K (100.0°C, 212.0°F) ---------		
0.0239	47.9	(694)
0.0267	53.7	(778)
0.0395	81.4	(1180)
0.0489	102.4	(1486)
0.0605	129.9	(1884)
0.0671	146.9	(2131)
0.0767	169.8	(2463)
0.0984	227.9	(3305)
--------- 423.15 K (150.0°C, 302.0°F) ---------		
0.0269	48.2	(700)
0.0297	53.6	(777)
0.0380	68.8	(998)
0.0482	89.2	(1294)
0.0506	93.9	(1361)
0.0615	115.8	(1680)
0.0663	125.6	(1821)
0.0746	142.4	(2066)
0.0942	184.6	(2677)

TABLE II

CRITICAL PROPERTIES AND ACENTRIC FACTORS USED IN THE SRK AND PR EQUATION OF STATE

Component	Pressure bar	Temperature K	Acentric Factor	Reference
Carbon Monoxide	34.960	132.9	0.049	13
Naphthalene	40.516	748.4	0.302	14

TABLE III

SRK AND PR EQUATION-OF-STATE REPRESENTATIONS OF
SOLUBILITY OF CARBON MONOXIDE IN NAPHTHALENE

| Temperature K (°F)	Soave Parameters (PR Parameters)		Errors in Mole Fraction (Using PR Equation)	
	C_{ij}	D_{ij}	RMS	|MAX|
373.2 (212.0)	0.0120	0.0214	0.0002	0.0004
	(0.0542)	(0.0211)	(0.0001)	(0.0004)
	0.1252		0.0004	0.0006
	(0.1506)		(0.0004)	(0.0006)
423.2 (302.0)	−0.0760	0.0384	0.0001	0.0003
	(0.0138)	(0.0305)	(0.0001)	(0.0003)
	0.1357		0.0005	0.0009
	(0.1557)		(0.0004)	(0.0008)
373.2, 423.2	−0.0563	0.0345	0.0003	0.0004
	(0.0262)	(0.0274)	(0.0002)	(0.0004)
	0.1281		0.0007	0.0011
	(0.1521)		(0.0005)	(0.0009)
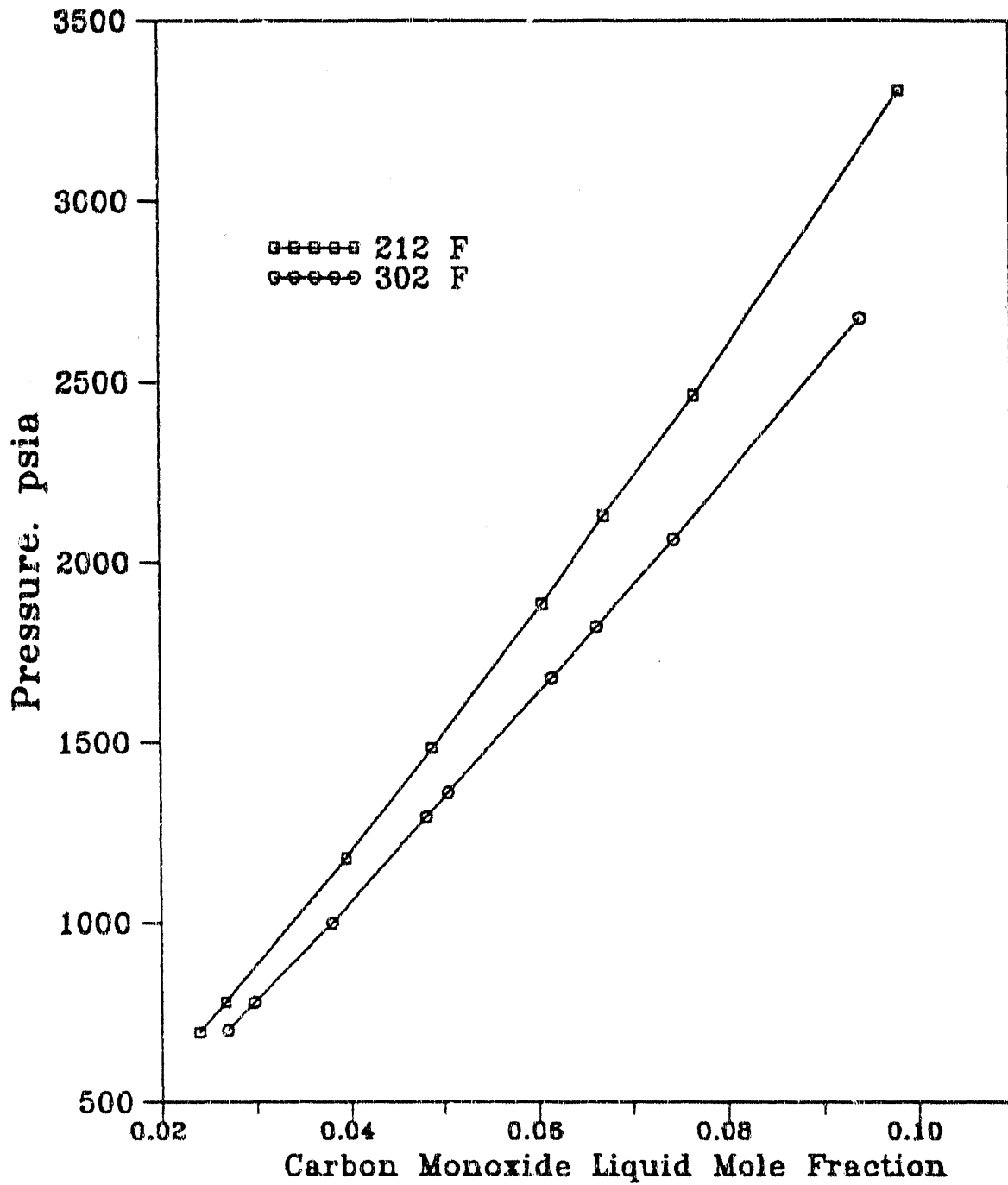
Figure 1. Bubble Point Pressure Data for
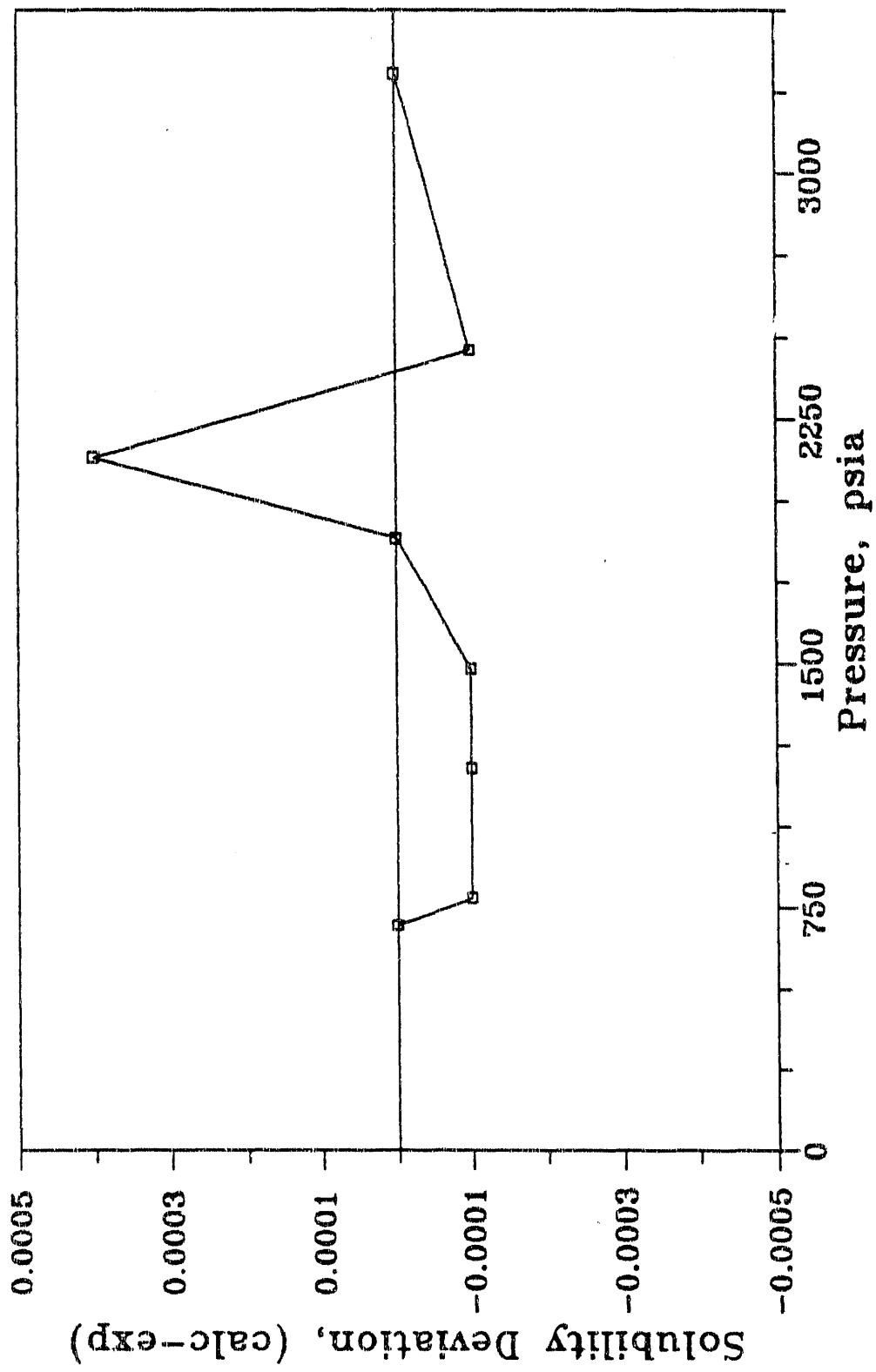Carbon Monoxide + Naphthalene

Figure 2. Deviations of solubilities of Carbon Monoxide in Naphthalene at 212 F
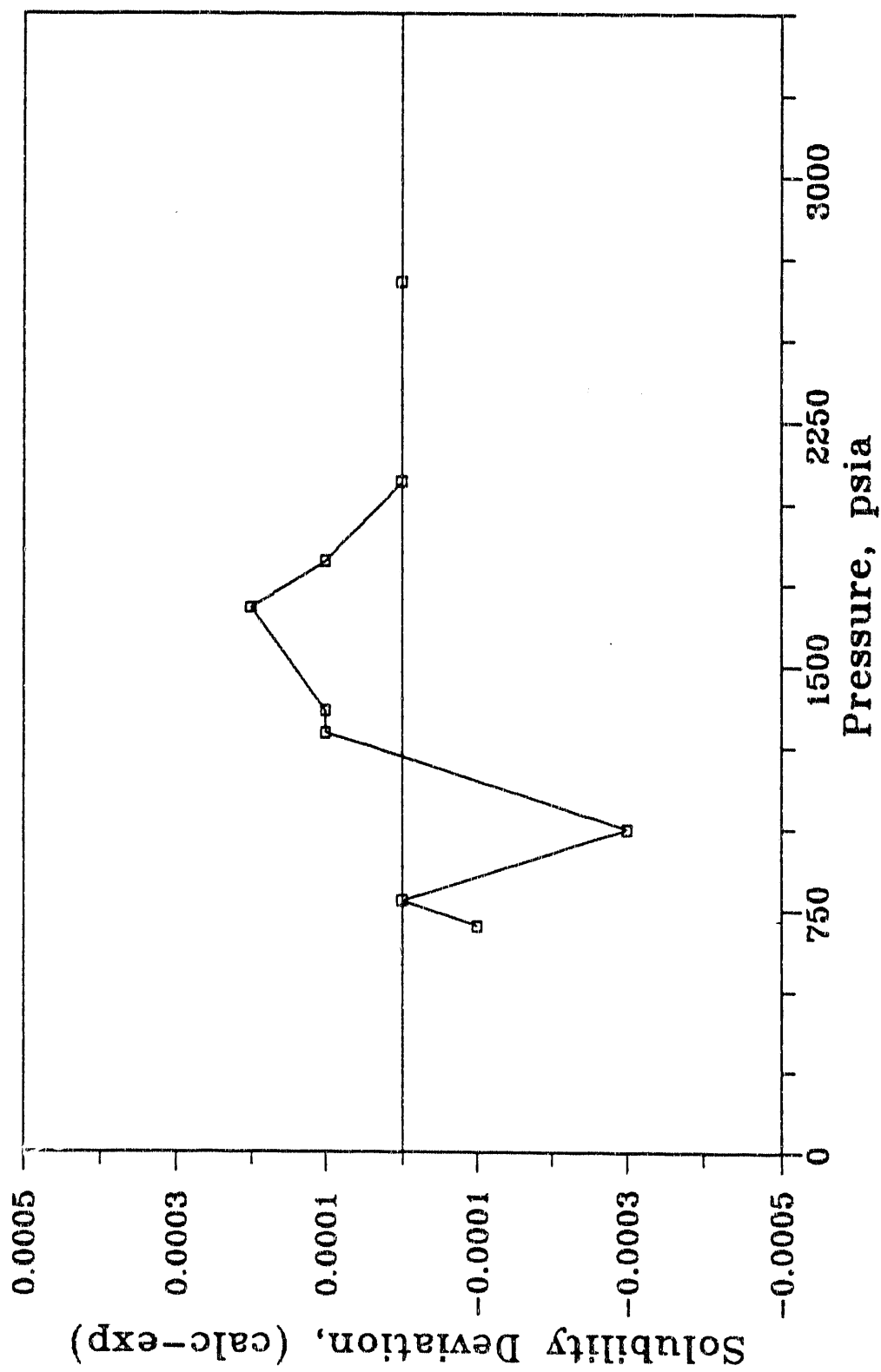
Figure 3. Deviations of solubilities of Carbon Monoxide in Naphthalene at 302 F

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