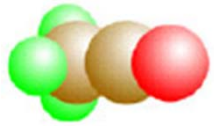
열역학 물성 연구회
2003년 10월 13일 발표자료



고려대학교

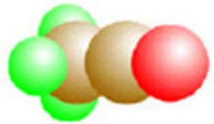
열역학 물성 연구 동향 및 KDB 응용 프로그램의 개발

고려대학교

화공생명공학과

강정원

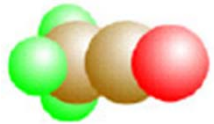
발표 내용



고려대학교

- 열역학 물성 관련 연구동향
  - CAPEC, Technical University of Denmark 센터 소개
  - 열역학 물성 분야의 표준화 방향
- KDB 응용 프로그램의 개발
  - KDB 응용 프로그램 개발 현황 및 문제점
  - 향후 개발 방향

CAPEC, DTU 소개



고려대학교

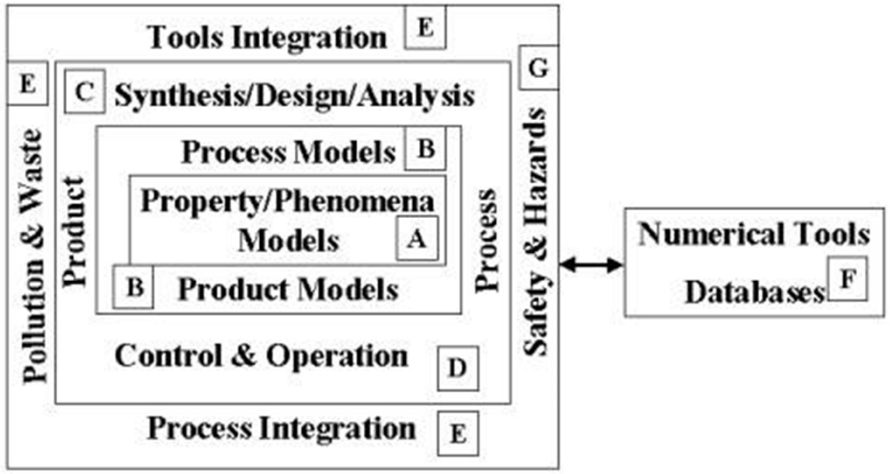
- Computer Aided Process Engineering Center
  - Professor Rafiqul Gani
  - Professor Sten Bay Jorgensen
  - Professor Jens Abildskov
  - Professor Niels Jens
- Research Area
  - Program A : Physical Properties
  - Program B : Process Modeling, Simulation and Idetification
  - Program C : Process Synthesis, Product / Process Design and Analysis
  - Program D : Process Control and Operation
  - Program E : Numerical and Computational Aspects
  - Program F : Safety and Risk Analysis

CAPEC

DTU

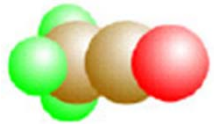
Research Activities

- List of Softwares
  - ICAS : Integrated computer aided system
  - TML : Thermodynamic Model Library
  - ProPred : Property Prediction
  - TMS : Thermodynamic Model Selection
  - PDS : Process Design Studio
  - PROCAMD : Computer Aided Molecular Design
  - MoT : Model Testbed



CAPEC

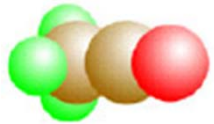
Collaboration



고려대학교

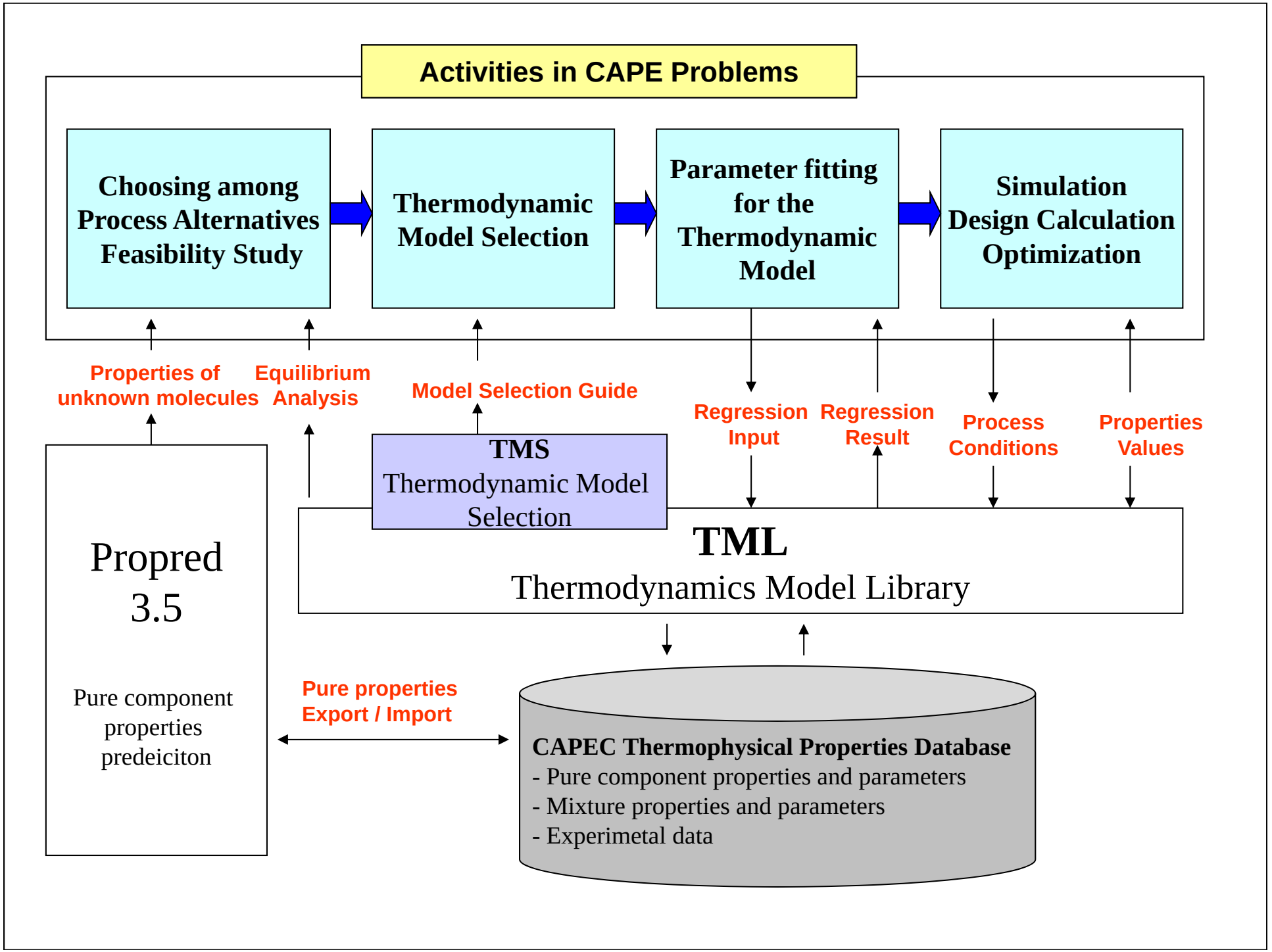
- Consortium
  - FMC , USA
  - Bayer , Germany
  - Mitsubishi, Japan
  - ICI , UK
  - Syngenta , UK
  - Novo Nordisk , Denmark
  - PDC, Germany
  - Danisco Ingredient , Denmark
  - and many more… (About 20)
- Academic
  - Prof. J. P. O'Connel (Univ. of Virginia)
  - …

Tools for Thermodynamic Properties and Phase Equilibrium

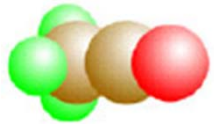


고려대학교

- Thermodynamic Properties Database
- TML (Thermodynamic Model Library)
- TMS (Thermodynamic Model Selection)
- ProPred 3.5 (Pure component property prediction Too)
- ProCAMD (Computer-Aided Molecular Design Software)


Activities in CAPE Problems
Choosing among Process Alternatives Feasibility Study
Thermodynamic Model Selection
Parameter fitting for the Thermodynamic Model
Simulation Design Calculation Optimization
Properties of unknown molecules
Equilibrium Analysis
Model Selection Guide
Regression Input
Regression Result
Process Conditions
Properties Values
TMS
Thermodynamic Model Selection
TML
Thermodynamics Model Library
Propred 3.5
Pure component properties predeiciton
Pure properties Export / Import
CAPEC Thermophysical Properties Database
- Pure component properties and parameters
- Mixture properties and parameters
- Experimetal data

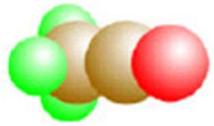
Research



고려대학교

- Development of 2nd order UNIFAC method
  - KT-UNIFAC 1st order and 2nd order
  - New parameters Matrix
- Development of KT-UNIFAC Utility Program
- Phase equilibrium for surfactant solution

Development of UNIFAC Method



고려대학교

- Uncertainties for prediction using current GC method are quite high
- Current GC methods are generally unable to distinguish isomers and reflect effects of adjacent groups
- Second order UNIFAC can overcome deficiencies of current GC methods

$$\ln \gamma_i = \ln \gamma_i^C + \ln \gamma_i^R + w_{R2} \ln \gamma_i^{R2}$$

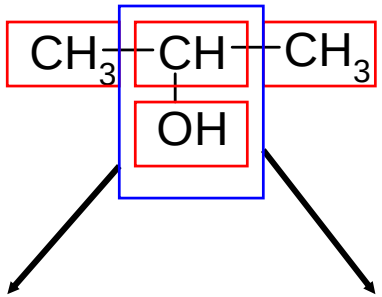
First oder contribution **Second order contribution**

Development of new UNIFAC method

고려대학교

- Example of group decomposition of molecules

2-Propanol



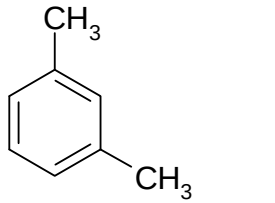
First-order groups

2 CH3
1 CH
1 OH

Second-order groups

1 CHOH

M-Xylele



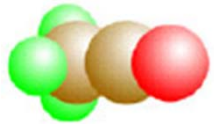
First-order groups

4 ACH
2 AC-CH3

Second-order groups

1 ARS1S3

KT-UNIFAC, Model Description



고려대학교

Combinatorial Term

$$\ln \gamma_i^C = \ln \gamma_{i,FH}^C + \ln \gamma_{i,SG}^C$$

$$\ln \gamma_{i,FH}^C = 1 - J_i + \ln J_i$$

$$\ln \gamma_{i,SG}^C = -\frac{Z}{2} q_i \left(1 - \frac{J_i}{L_i} + \ln \frac{J_i}{L_i} \right)$$

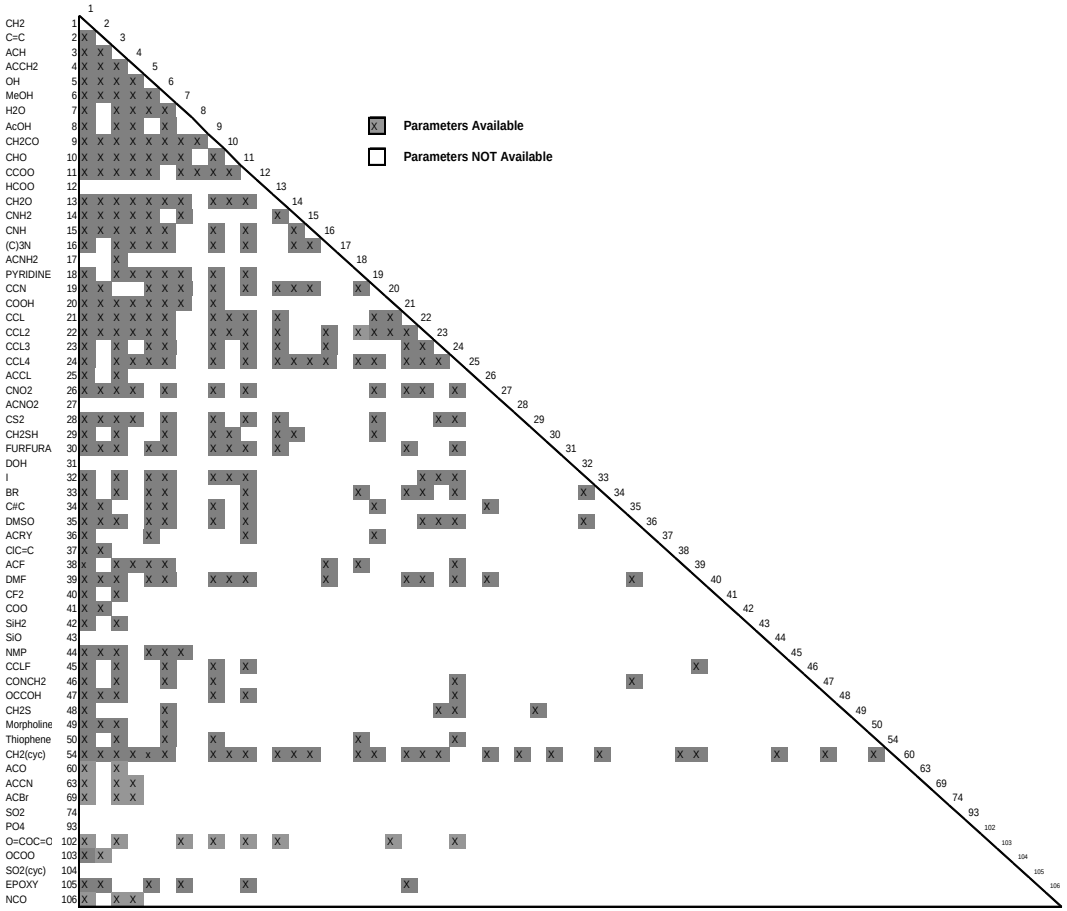
Residual Term

$$\ln \gamma_i^R = q_i (1 - \ln L_i) - \sum_k^{NMG} \left(\frac{s_{ki}}{\eta_k} - G_{ki} \ln \frac{s_{ki}}{\eta_k} \right)$$

Second-Order Term

$$\ln \gamma_i^{R2} = \sum_j^{NSOG} \sum_{m \in j}^{NSG} \sum_{n \neq m}^{NSG} \left[\frac{\delta u_{m'n,j}}{RT} \left(\left(G_{m'i} \vartheta_n - \vartheta_{m'} V_{ni} \right) \frac{\tau_{mn}}{\eta_n} - G_{m'i} G_{ni} \frac{\tau_{mn}}{s_{ni}} \right) + \frac{\delta u_{nm',j}}{RT} \left(\left(G_{ni} \vartheta_{m'} - \vartheta_n V_{m'i} \right) \frac{\tau_{nm}}{\eta_m} - G_{ni} G_{m'i} \frac{\tau_{nm}}{s_{mi}} \right) \right]$$

New parameters for 1st order groups



T dependency is similar to Linear UNIFAC (Hansen et al.)

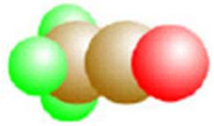
$$\tau_{mk} = \exp(-\Delta u_{mk} / T)$$

$$\Delta u_{mk} = a_{mk,1} + a_{mk,2}(T - T_0)$$

First order parameters were obtained from 4413 Data Sets (*VLE*, H^E, γ^{inf})

New groups were included (Nitriles, epoxy,...)

New parameters for 2nd order



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- Second Order Group Parameters were fitted from 842 experimetal data sets (***VLE***, H^E, γ^{inf})

Property	UNIFAC		Modified UNIFAC		New Method			
					First Order		Second Order	
	AAE	ARE (%)	AAE	ARE (%)	AAE	ARE (%)	AAE	ARE (%)
P	3.50	3.47	4.09	3.89	1.95	2.69	1.78	1.99
y_1	0.0153	3.64	0.0147	3.60	0.0129	3.04	0.0112	2.79
H^E	388.82	192.03	476.62	1167.60	137.94	20.33	115.79	20.20
γ^{inf}	89.53	39.41	68.07	58.81	134.96	25.78	124.97	25.11

Comparison of calculated result

고려대학교

Improved prediction due to new groups

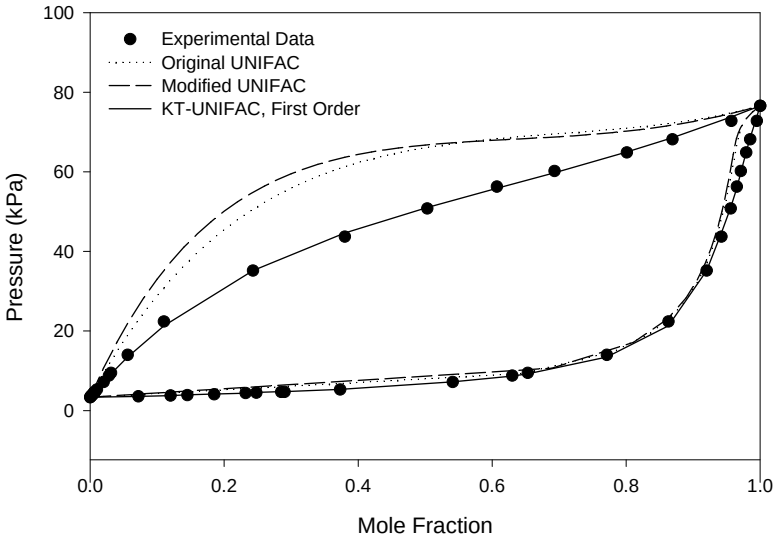


Figure 3. Comparison of experimental and predicted result for VLE (hexane + methoxy benzene (anisole) at 333.25 K)

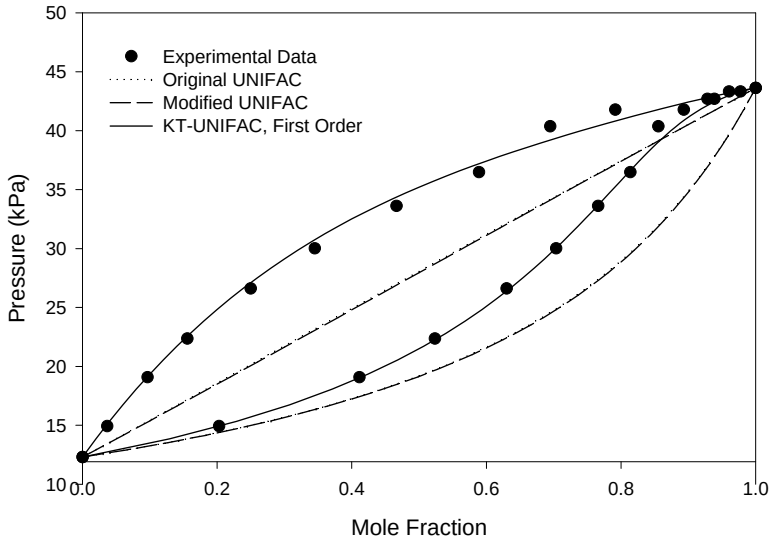


Figure 4.Experimental and predicted result for VLE (1,2-epoxybutane + n-heptane at 313.15 K)

Comparison of calculated result

고려대학교

Improved prediction due to second order group

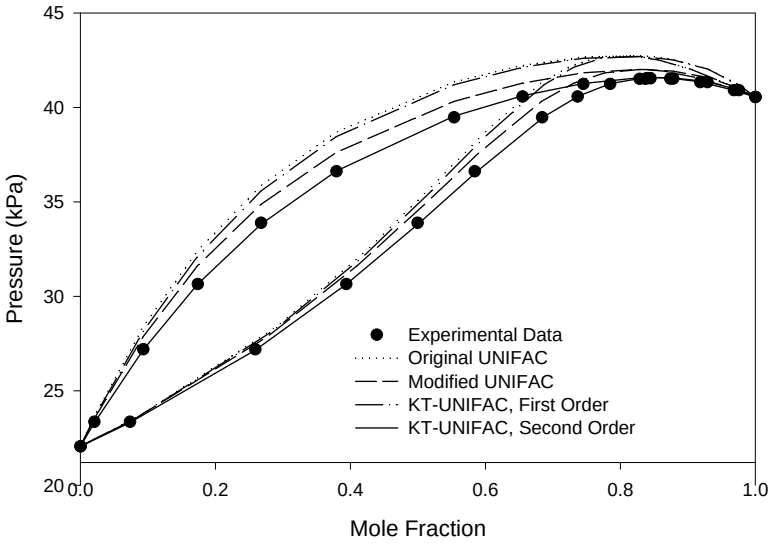


Figure 7. Experimental and predicted result for VLE
(Hepatne + 2-Methyl-Isobutyl-Ketone at 348.15 K)

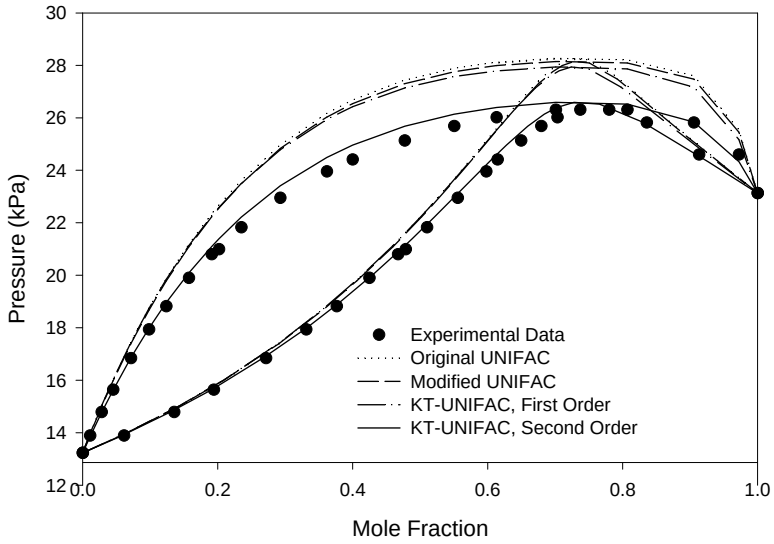


Figure 8. Experimental and predicted result for VLE
(hepatne + 2-methyl-2-butanol at 328.15 K)

Comparison of calculated result

고려대학교

Improved prediction due to second order group

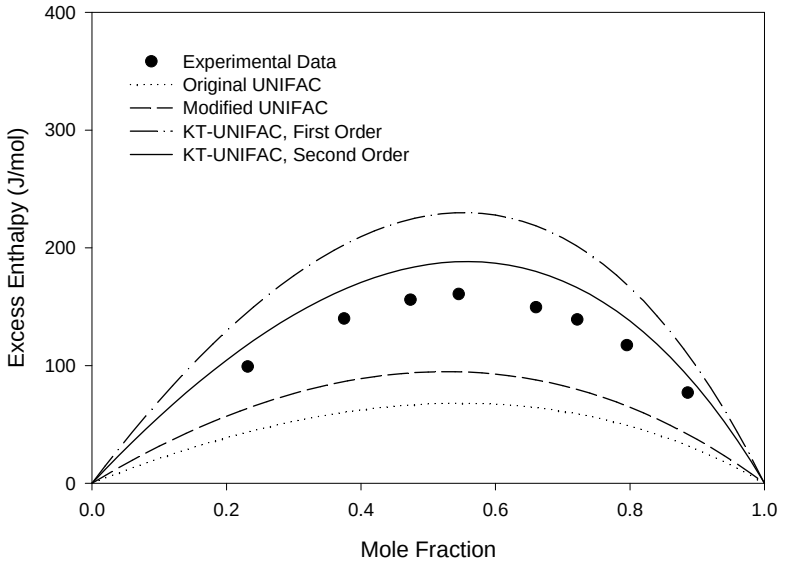


Figure 10. Experimental and predicted result for HE (benzene + 1,2,3,4-tetrahydronaphthalene at 298.15 K)

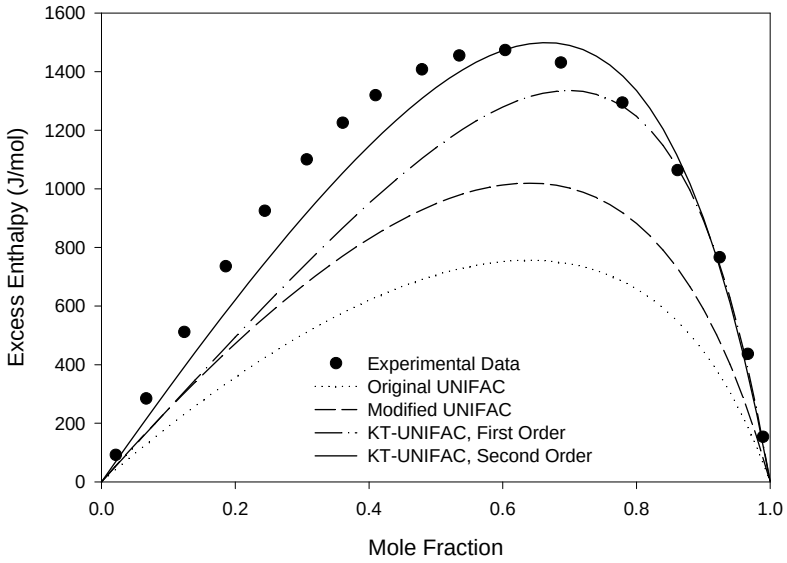
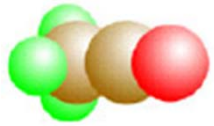


Figure 11. Experimental and predicted result for Excess Enthalpy (benzene + isopropanol at 308.15 K)

UNIFAC Utility

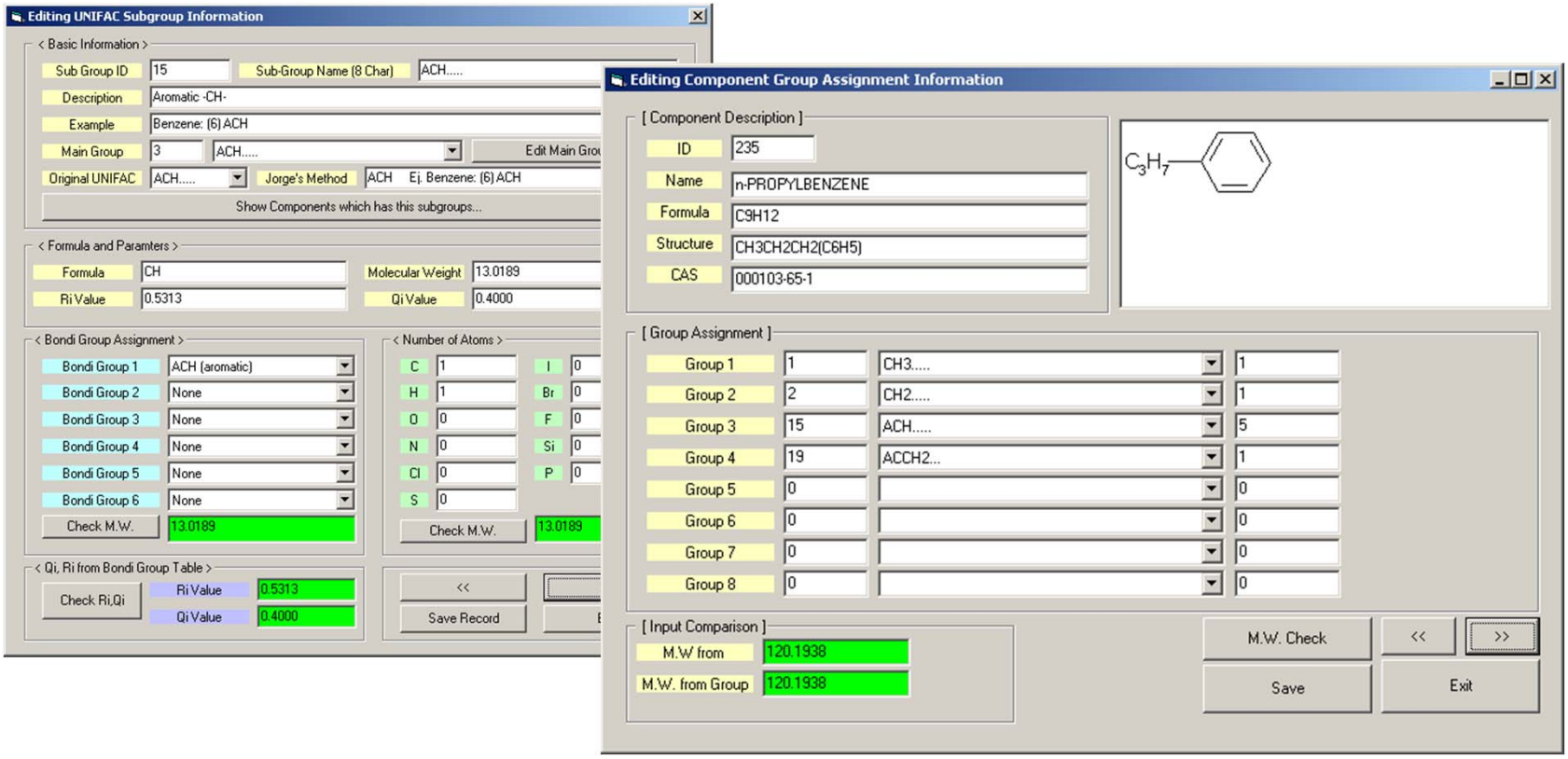


고려대학교

- Database Management Tools
  - UNIFAC Groups and Group Assignment Tables
  - UNIFAC Interaction Parameters
  - VLE Experimental Data

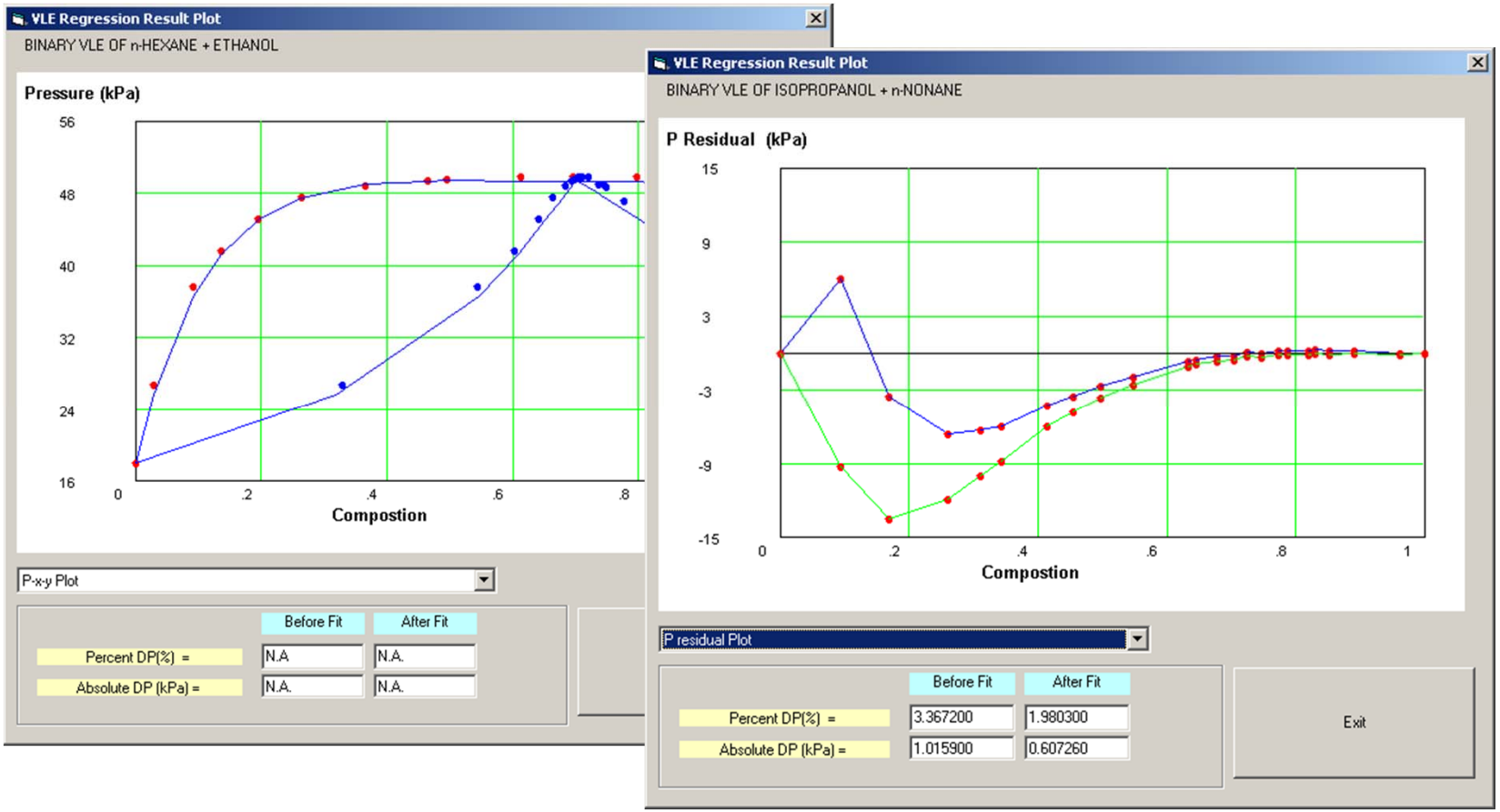
    (CAPEC DB and User Database)
- Parameter Regression and Analysis Tool

UNIFAC Group Data Management Tools

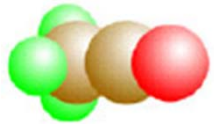


Regression Analysis Tool

고려대학교



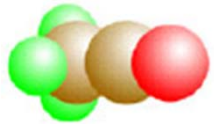
Software Demo…



고려대학교

- CAPEC Tools
- UNIFAC Utility

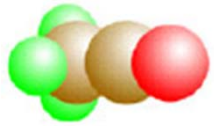
열역학 물성 관련 연구동향



고려대학교

- 자료의 표준화 (Standardization)
  - 효율적인 정보의 공유와 유통을 위하여 필수적임
- 자료의 검증 (Validation)
  - 적절한 절차를 통하여 검증된 정포를 포함해야 함
- QM/MM 기반의 물성 DB
- 상업화 , 대형화, 집중화

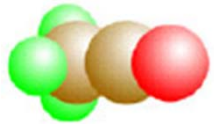
Standardization Efforts



고려대학교

- PDXI (Properties Data eXchange) by AIChE
  - Move on to CAPE-OPEN
- CAPE-OPEN (European Committee)
  - Too abstract
  - COM Model
- Self-ML (CODATA Group, Kehiaian)
  - Project ended (funding too !)
- CML (Chemical Mark-up language) – Chemical Structure
- matML (Material Mark-up language, NIST)
- ThermoML (TRC, NIST)
  - Collaboration with J. Chem. Eng. Data

Why XML ?



고려대학교

- Minimum specification
  - small set of rules (easily understood)
- Formats and actual data are integrated
- Don’t have to worry about data structure
- Extensible
- Easily portable to RDBMS structure

XML 처리 과정

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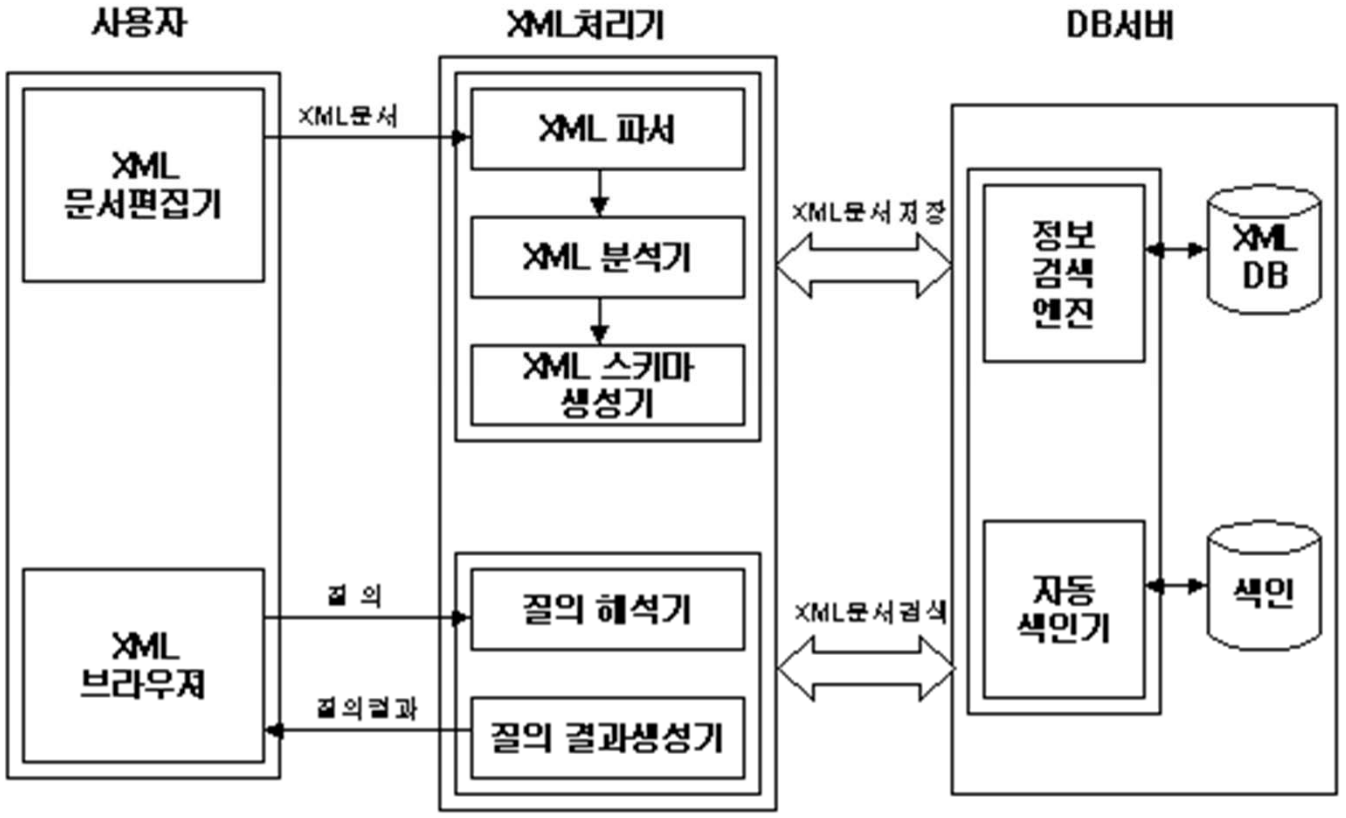
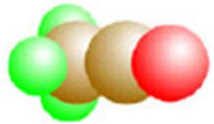
XML의 문서 처리 과정



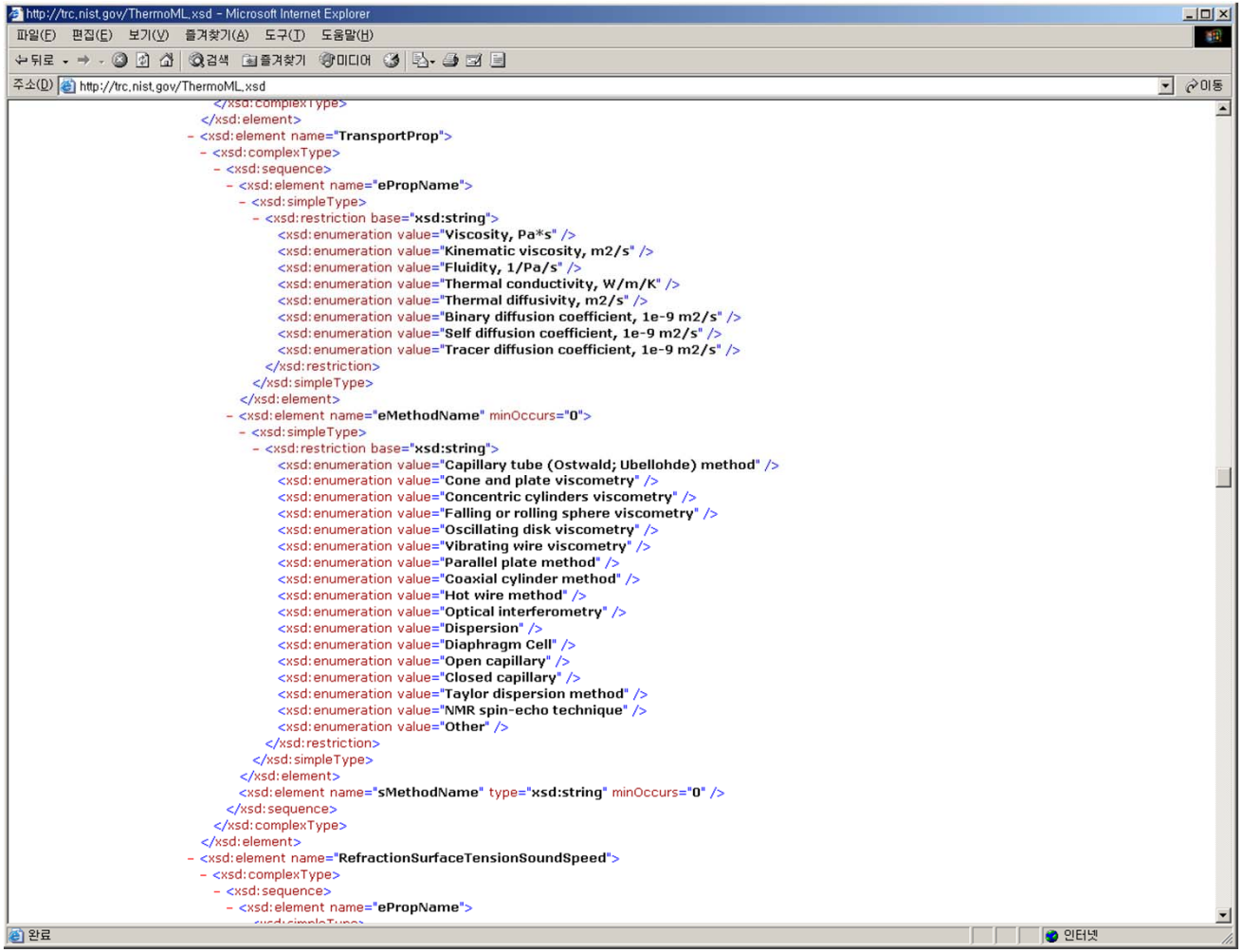
ThermoML



고려대학교

- M. Frenkel et al., J. Chem. Eng. Data, 48, 2 (2003)
- Specification
  - Experimentally measurable physical properties and transport properties data (120 properties)
  - Mixture phase equilibrium and reaction data
- Cooperative data processing between J. Chem. Eng. Data and TRC

Example


http://trc.nist.gov/ThermoML.xsd - Microsoft Internet Explorer
파일(F) 편집(E) 보기(V) 즐겨찾기(A) 도구(T) 도움말(H)
주소(D) http://trc.nist.gov/ThermoML.xsd
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- <xsd:complexType>
- <xsd:sequence>
- <xsd:element name="ePropName">
- <xsd:simpleType>
- <xsd:restriction base="xsd:string">
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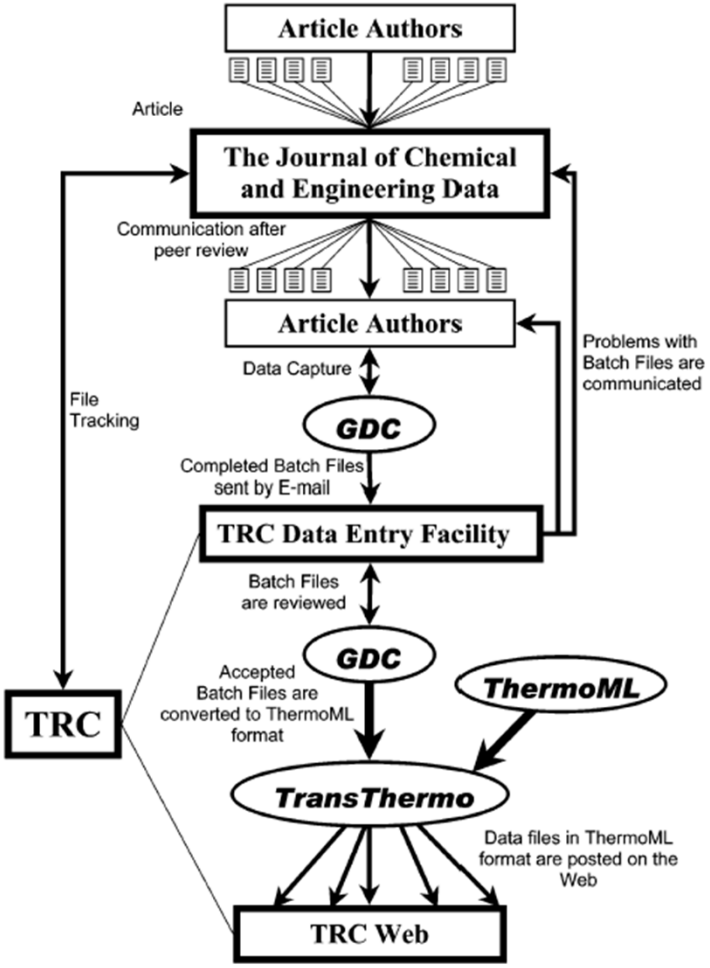
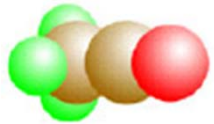
- <xsd:element name="ePropName">
완료
인터넷

Information flow architecture



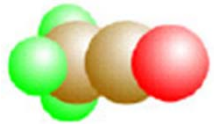
국내 연구 동향



고려대학교

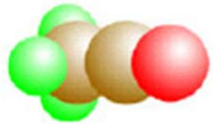
- KISTI
  - Accepted ThemoML as a new standard

KDB 연구연구 개발 동향



- KDB 현황
  - 웹 버전으로 개발되어 서비스 중
  - 현재 화학공학연구정보센터에서 서비스 중
  - 매월 8000여 사용자
  - 지속적인 업데이트가 어려운 실정임

KDB 연구연구 개발 동향



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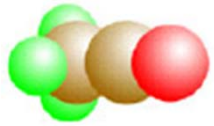
- 현재 KDB의 문제점
  - 자료와 계산 프로그램이 별도로 운영되고 있음
  - 많은 양의 자료를 효과적으로 교육 및 연구에 활용하기에 불편함이 많음
  - 지속적인 사업을 하기 위한 예산 확보의 어려움
  - 효과적인 홍보 전략이 필요할 것으로 보임

열 물성 데이터베이스의 교육용 소프트웨어 개발의 사례



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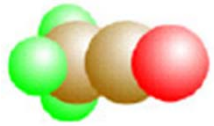
- ICAS 5.0 – CAPEC, DTU
- Phase – W. Chapman , Rice University

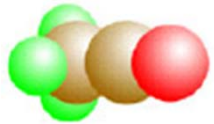
문제점 해결방안 - 1



고려대학교

- KDB의 활용
  - 열역학 및 분리공정 과목 등의 학생교육에 활용
  - DDB 및 KDB를 통합한 인터페이스를 개발하여 연구 목적으로 활용
    - 모델의 개발 (G-NLF-HB EOS)
    - 기타 물성 그룹 기여 방법개발 등
- 해결 전략
  - VB .NET 를 활용한 통합 인터페이스 및 응용 프로그램의 개발
  - KDB 및 DDB의 표준화 (ThermoML의 표준 도입)

KDB work in progress…



고려대학교

- DB Format conversion (Incorporating ThermoML)
- Thermodynamic calculation methods
  - EOS : SRK/PR/NLF-HB
  - Activity : NRTL, UNIQUAC, UNIFAC
- Calculations
  - VLE / SLE / LLE /SVE
- Regressions
  - Pure component properties
  - VLE regression
  - Group Contribution regression
- Planning to finish before the end of ***November*** …

KDB-Thermo LAB