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Thermodynamic Modeling of Liquid-Liquid Extraction (LLE) Equilibria for the System TBP-HNO_3-UO_2-H_2O-Diluent

by

Carlos F. Jové Colón

Harry K. Moffat

Rekha R. Rao

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- # Introduction

  - ## Liquid-Liquid Extraction (LLE) of metals

    - Most widely adopted industrial-scale actinide separation and/or recovery technology (e.g., PUREX, TRUEX)
    - Relatively large number of LLE studies and data sets
      - Actinides, lanthanides, common metals
    - Thermodynamic models have been used to represent LLE:
    - Thermodynamic approaches to LLE are **NOT NEW!!!**
    - Use of existing (geo)chemical speciation codes to model LLE
    - Ability to model chemical equilibria of multi-component multi-phase systems

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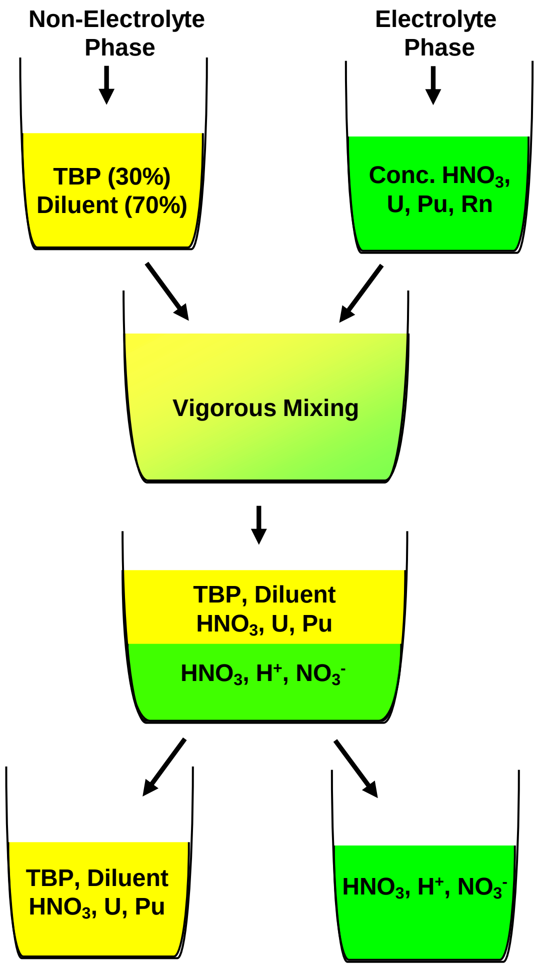
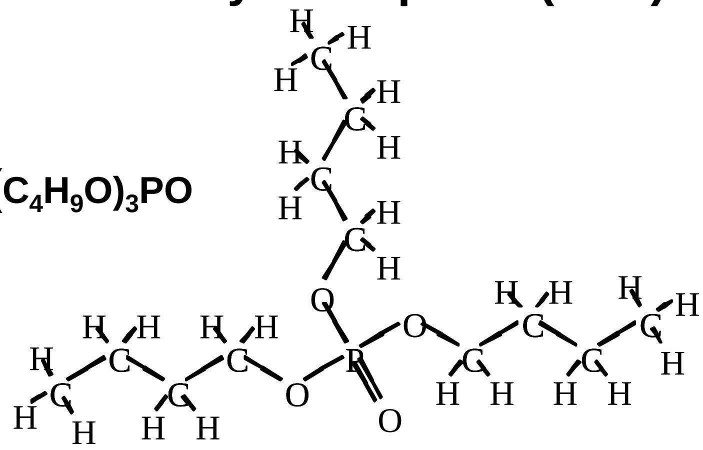
PUREX Process (Mixer – Settler)

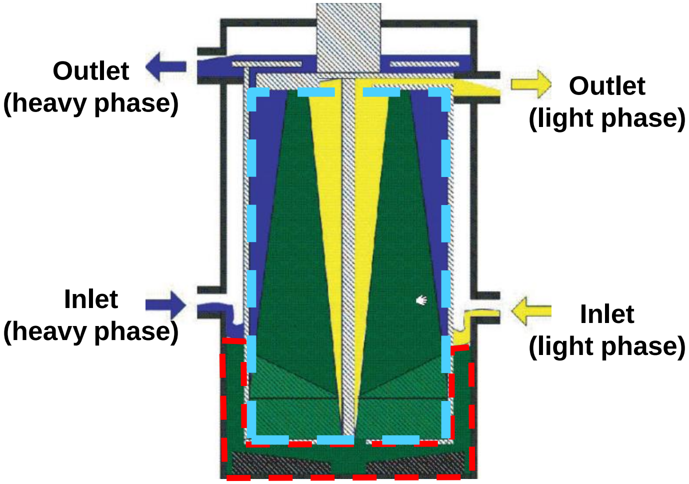


Tri-n-butyl Phosphate (TBP)

$(C_4H_9O)_3PO$



Centrifugal Contactor



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- Development of Thermodynamic Parameters for Model Inputs:
  - Compilation of thermodynamic data $\Rightarrow \Delta G^\circ_f, \Delta H^\circ_f, S^\circ_{298}$
    - Retrieval of Gibbs energies $\Rightarrow$ $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$
    - Handbook Data, Scientific Literature
    - K_{eq} or equilibrium constants relevant species:
      - LLE extraction data:
        - e.g., $(TBP)_2 \bullet UO_2(NO_3)_{2(org)} \rightleftarrows UO_2^{++} + 2NO_3^- + 2TBP_{org}$
  - Ionic strength corrections in the aqueous phase:
    - **Pitzer (aqueous phase)** $\Rightarrow$ **adopted in this work**
      - UO_2^{++} - NO_3^- (Kim and Frederick, 1988)
      - H^+ - NO_3^- (Marion, 2002)
    - Debye-Hückel (valid for relatively dilute solutions) $\Rightarrow$ **not considered in this work**
- Density and volumetric data for the electrolyte and organic liquid phases

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- **Methodology:**
  - **Comprehensive compilation for the extraction of nitric acid (HNO_3), U(VI), Pu(IV), and other metals in the aqueous phase by TBP(org).**
  - **Computer codes:**
    - **EQ3/6 (LLNL; Wolery & Jarek, 2003) ⇒ Mass Action Law Equations**
    - **Cantera (Caltech & SNL; D. Goodwin (Caltech) & H. Moffat (SNL) ⇒ Gibbs Energy Minimization**
      - **Cantera: Open Source OO software tools ⇒ http://code.google.com/p/cantera/**
    - **Thermodynamic databases: Yucca Mountain Project (YMP) databases for EQ3/6 (data0.R5, Pitzer, SPEQ06.dat, and modifications of these); Cantera thermodynamic databases**
  - **Code calculations:**
    - **EQ3/6 and Cantera code calculations on the aqueous system HNO_3 – H_2O and HNO_3 – $UO_2(NO_3)_2$ – H_2O → from dilute to concentrated solutions.**
    - **Modeling of HNO_3 – $UO_2(NO_3)_2$ – H_2O aqueous Mixtures: Test comparisons between predicted and experimental data for equilibrium HNO_3(g) partial pressures in HNO_3 – $UO_2(NO_3)_2$ – H_2O aqueous solutions.**
  - **Implementation of HNO_3 and $UO_2(NO_3)_2$ extraction reactions and fitting data to generate K_{eq} values from extraction isotherms using EQ3/6 and Cantera.**
  - **Assumption: unit activity for all TBP species in the organic liquid phase.**
    - **Retrieved K_{eq} values from extraction isotherms are considered apparent**

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- **Estimates of Gibbs energy of formation for TBP(org) :**
  - $\Delta H°_f$ for TBP(org) = -1458.54 ±12.35 kJ/mol (Starostin et al. 1966).
  - S° for TBP(org) = 558.994 J/K mol ⇒ Obtained from volumetric-based thermodynamic correlations for organic liquids by Glasser and Jenkins (2004).
  - $\Delta S°$ for TBP(org) = $S°_{TBP} - \Sigma\, S°_{elem}$ = -1725.44 J/K mol.
  - $\Delta G°_f$ for TBP(org) = $\Delta H°_{f,TBP} - T\, \Delta S°_{TBP}$ = -944.103 kJ/mol.
  - ○ Estimate $\Delta G°_{rxn} = -RT\, LnK_{eq}$ ⇒ Apparent K_{eq} obtained from fitting extraction isotherms

$$K_{eq} = \prod_i a_i^{\upsilon_i} = \prod_i (\gamma_i m_i)^{\upsilon_i}$$

$$(TBP)_2 \bullet UO_2(NO_3)_{2(org)} \rightleftarrows UO_2^{++} + 2NO_3^- + 2TBP_{org}$$

$$K_{eq} = \frac{a_{UO_2^{++}} a^2_{NO_3^-} a^2_{TBP_{org}}}{a_{(TBP)_2 \bullet UO_2(NO_3)_{2(org)}}} = \frac{a_{UO_2^{++}} a^2_{NO_3^-} M^2_{TBP_{org}}}{M_{(TBP)_2 \bullet UO_2(NO_3)_{2(org)}}} \bullet \boxed{\frac{\gamma^2_{TBP_{org}}}{\gamma_{(TBP)_2 \bullet UO_2(NO_3)_{2(org)}}}}$$

Activity coefficient ratio assumed to be constant

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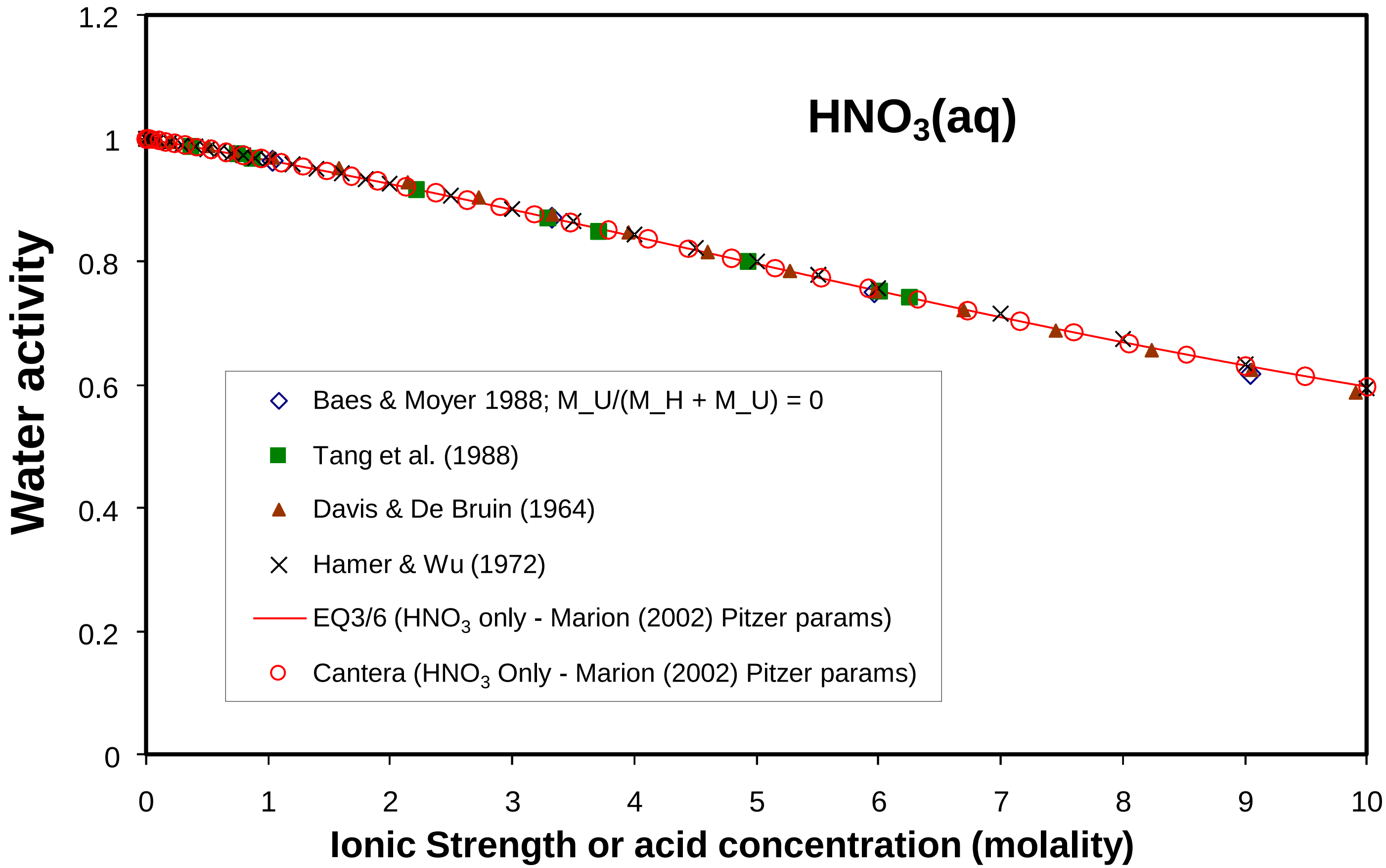

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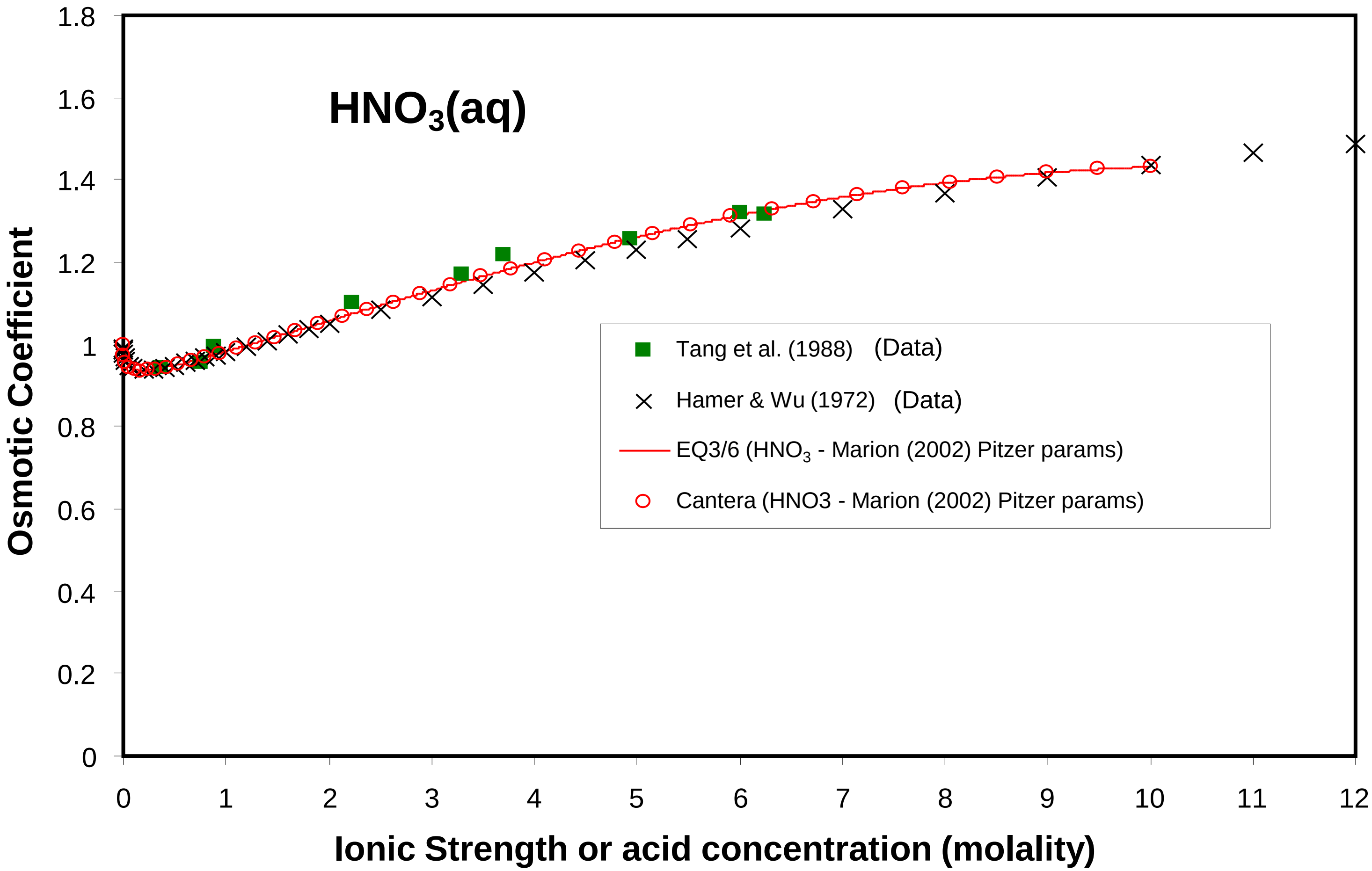

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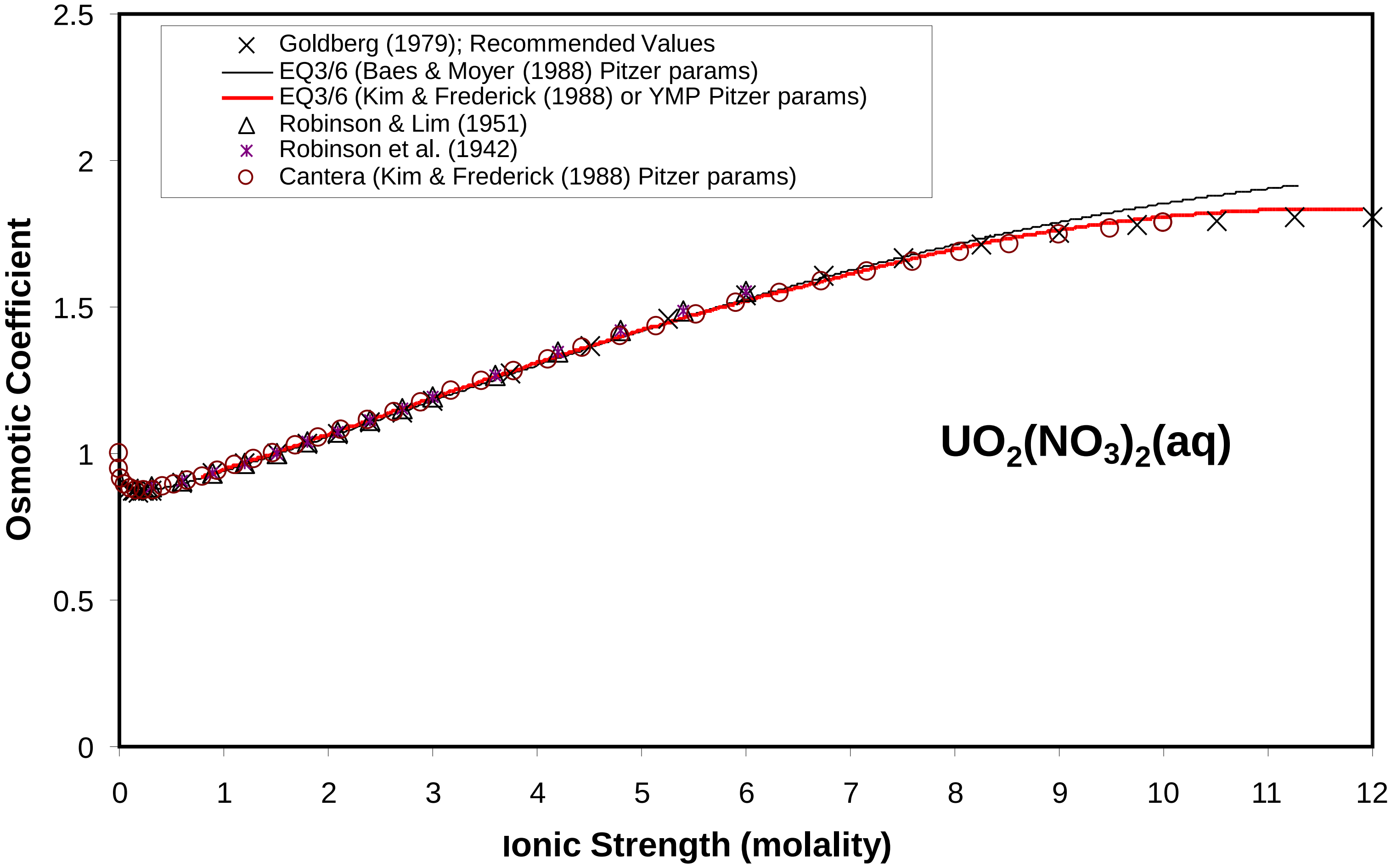

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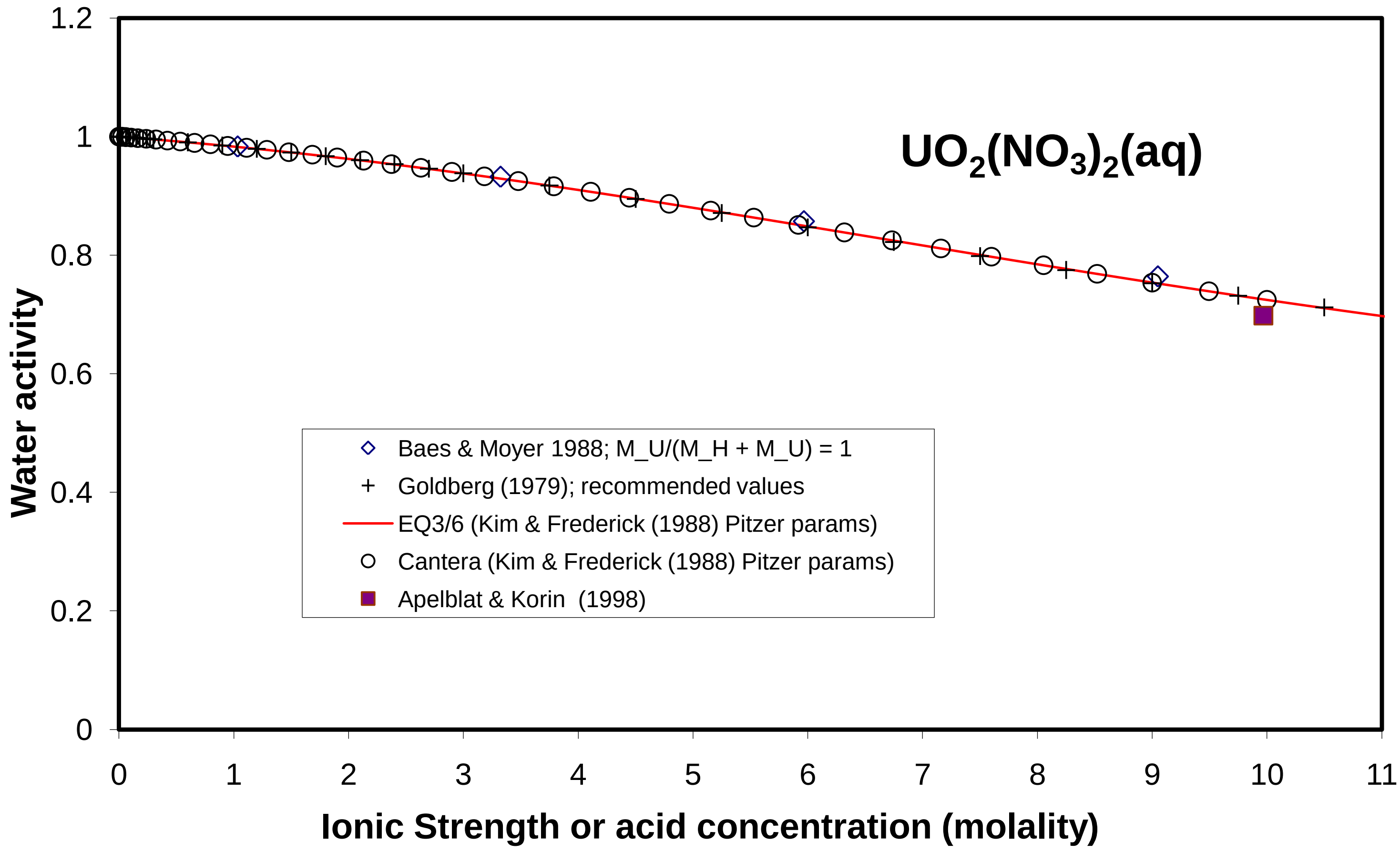

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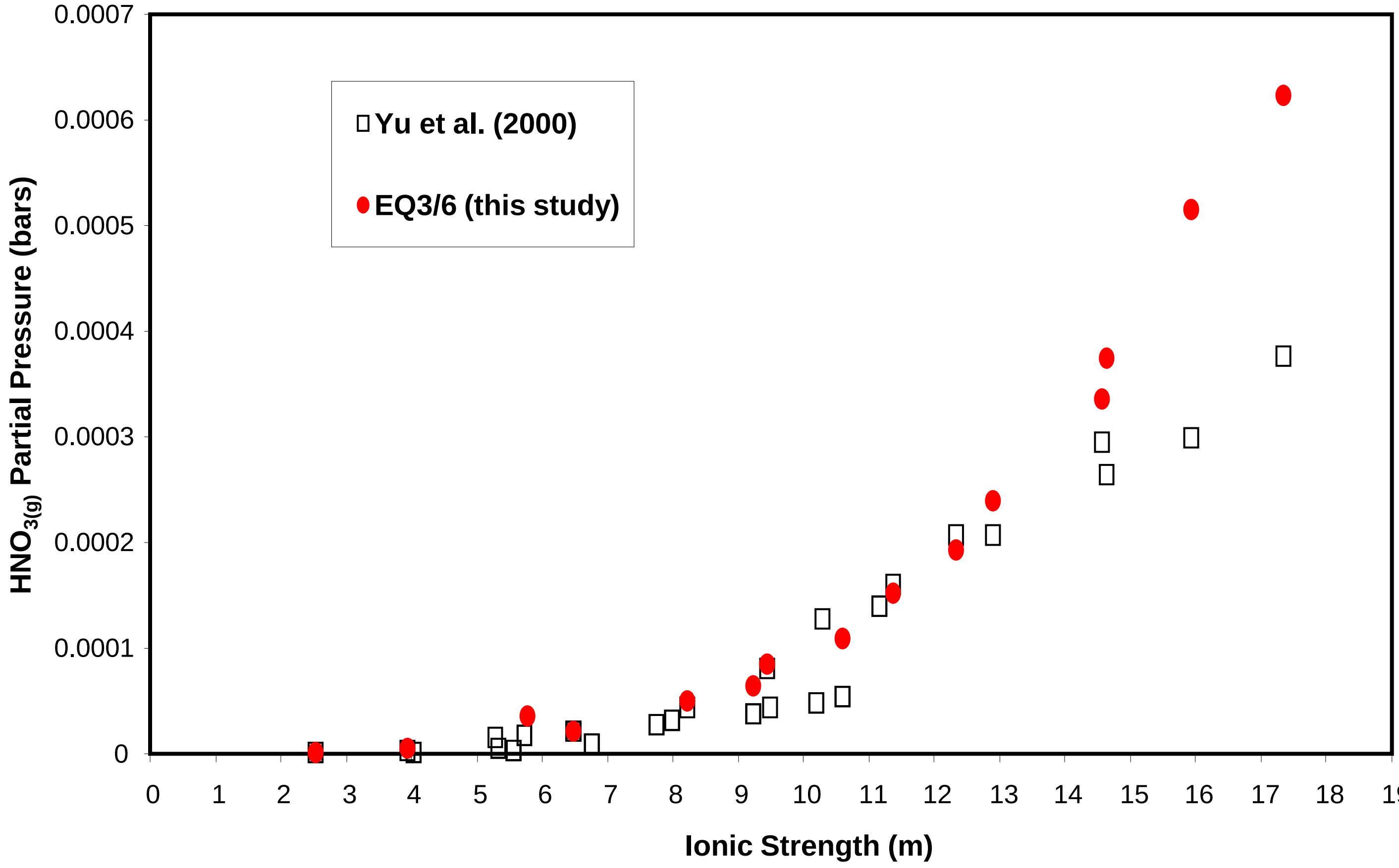

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- Reaction set considered for the HNO_3-UO_2-H_2O-TBP-AMSCO Diluent system. Log K constants obtained in this work from extraction and solubility data:

$$TBP \bullet HNO_{3(org)} \rightleftarrows H^+ + NO_3^- + TBP_{org} \quad \text{Log K} = 0.0228$$

$$(TBP)_2 \bullet HNO_{3(org)} \rightleftarrows H^+ + NO_3^- + 2TBP_{org} \quad \text{Log K} = -0.9$$

$$TBP_{aq} \rightleftarrows TBP_{org} \quad \text{Log K} = 2.8097$$

$$TBP \bullet H_2O_{(org)} \rightleftarrows TBP_{org} + H_2O \quad \text{Log K} = -0.5539$$

$$(TBP)_{2org} \rightleftarrows 2TBP_{org} \quad \text{Log K} = 1.4089$$

$$(TBP)_2 \bullet UO_2(NO_3)_{2(org)} \rightleftarrows UO_2^{++} + 2NO_3^- + 2TBP_{org} \quad \text{Log K} = -3.4232$$

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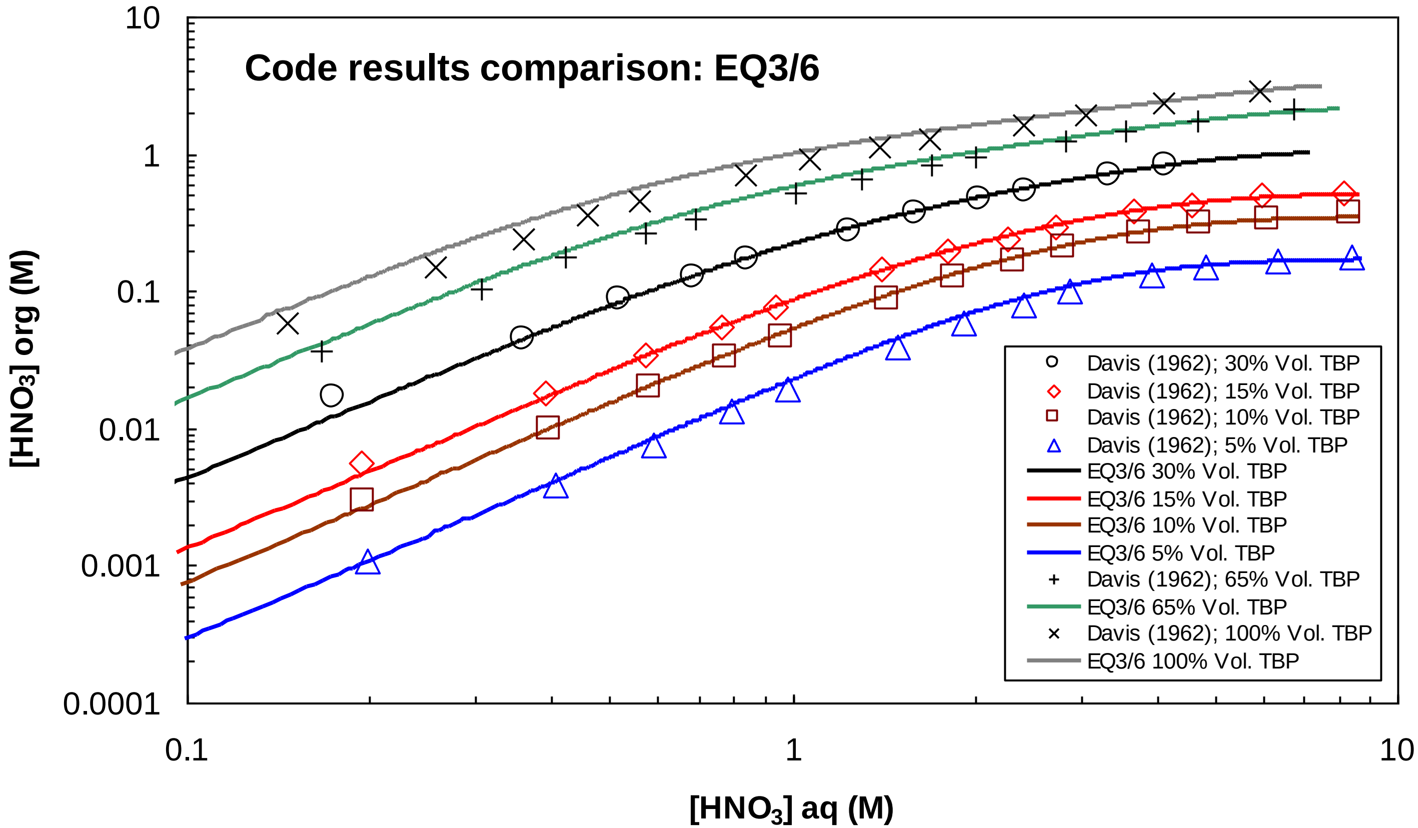

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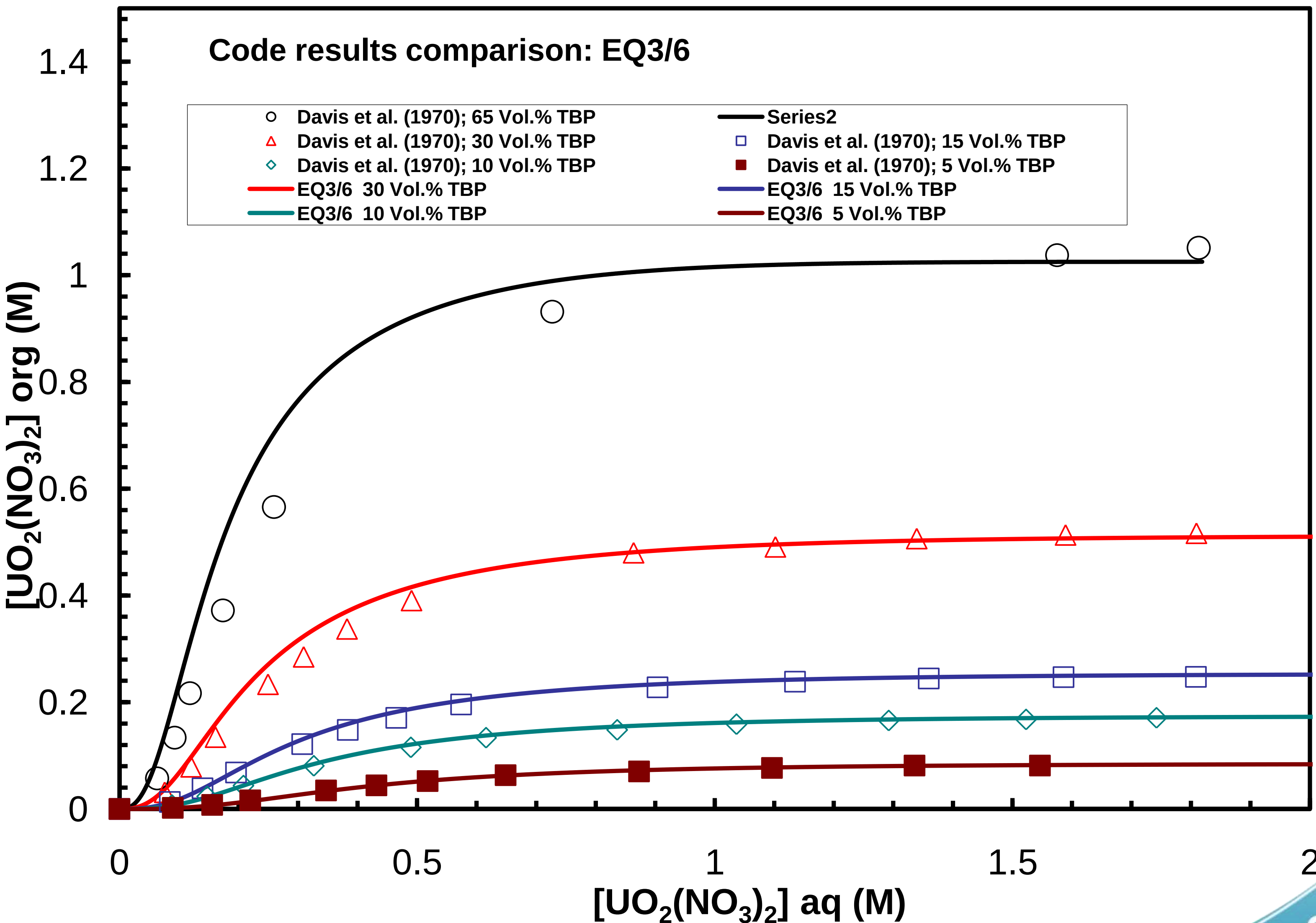

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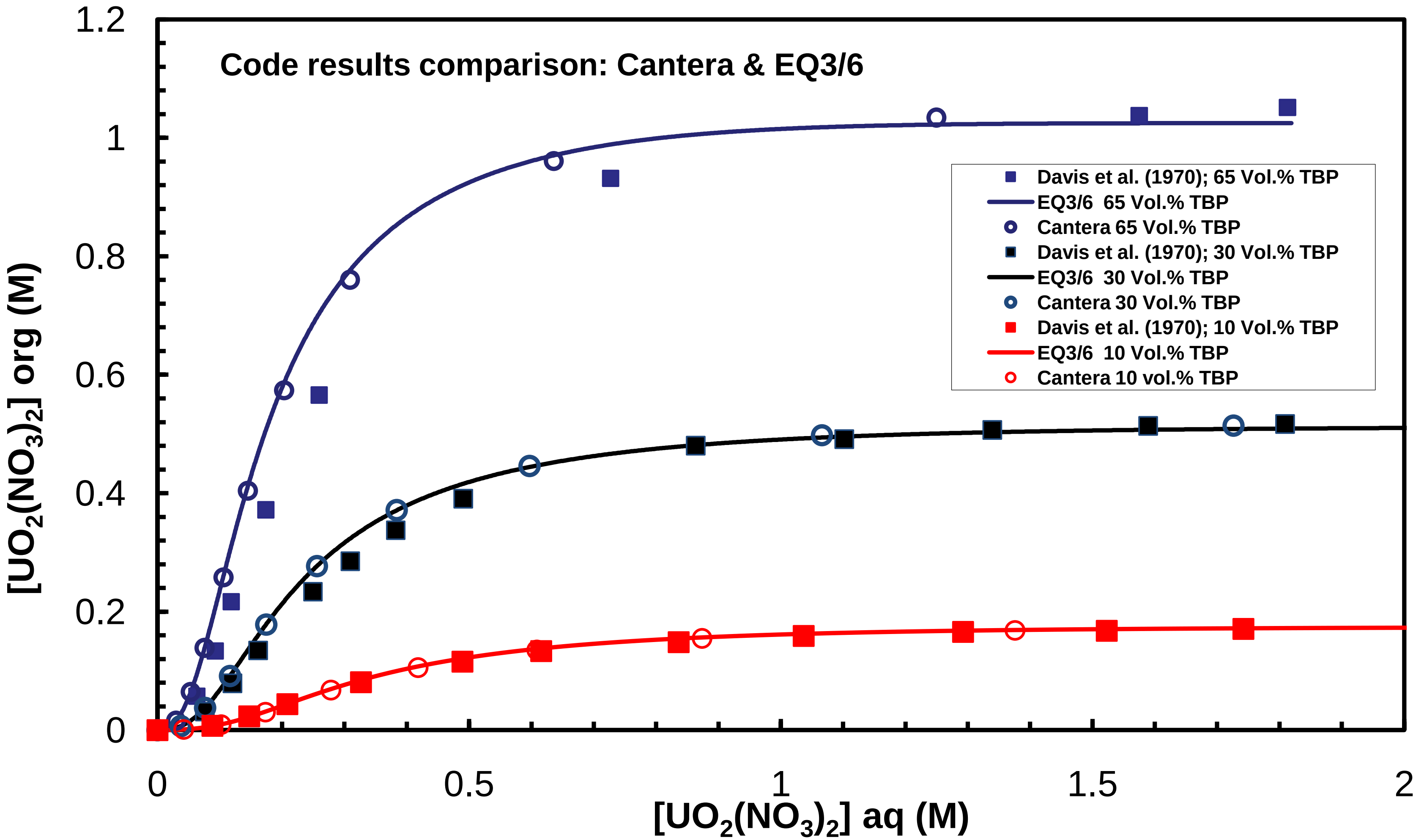

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EXTRA SLIDE

Thermodynamic Modeling of Liquid-Liquid Extraction (LLE) Equilibria for the System TBP-HNO_3-UO_2-H_2O-Diluent

- **Examples of Thermodynamic Modeling of LLE**
  - $UO_2(NO_3)_2$ Extraction $\Rightarrow$ Rozen et al. (1951)
  - HNO_3–$UO_2(NO_3)_2$ Extraction $\Rightarrow$ Davis et al. (1962-1970)
  - HNO_3 Extraction $\Rightarrow$ Chaiko and Vandegrift (1988)
  - HNO_3–$UO_2(NO_3)_2$ Extraction $\Rightarrow$ Moyer et al. (2001)