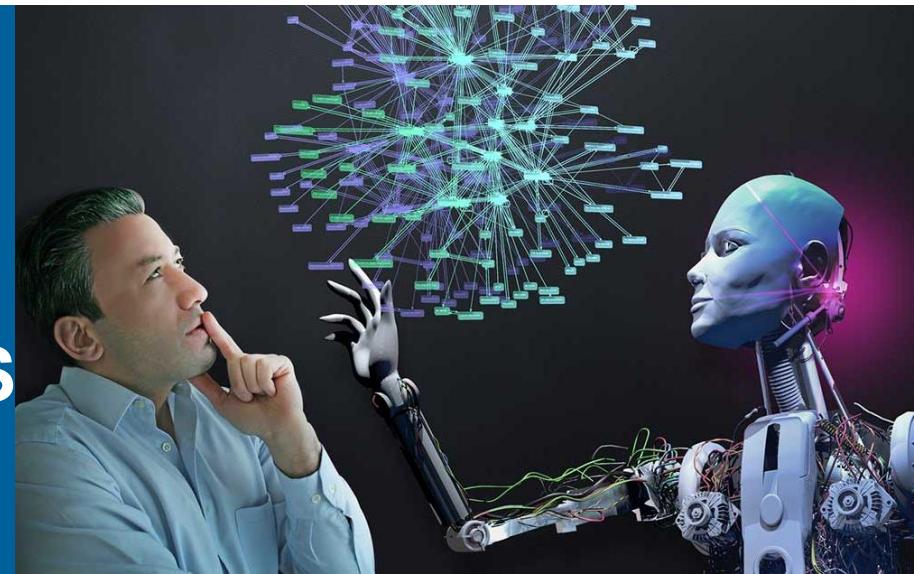


ATPESC 2017

St, Charles, IL
Aug. 5, 2017

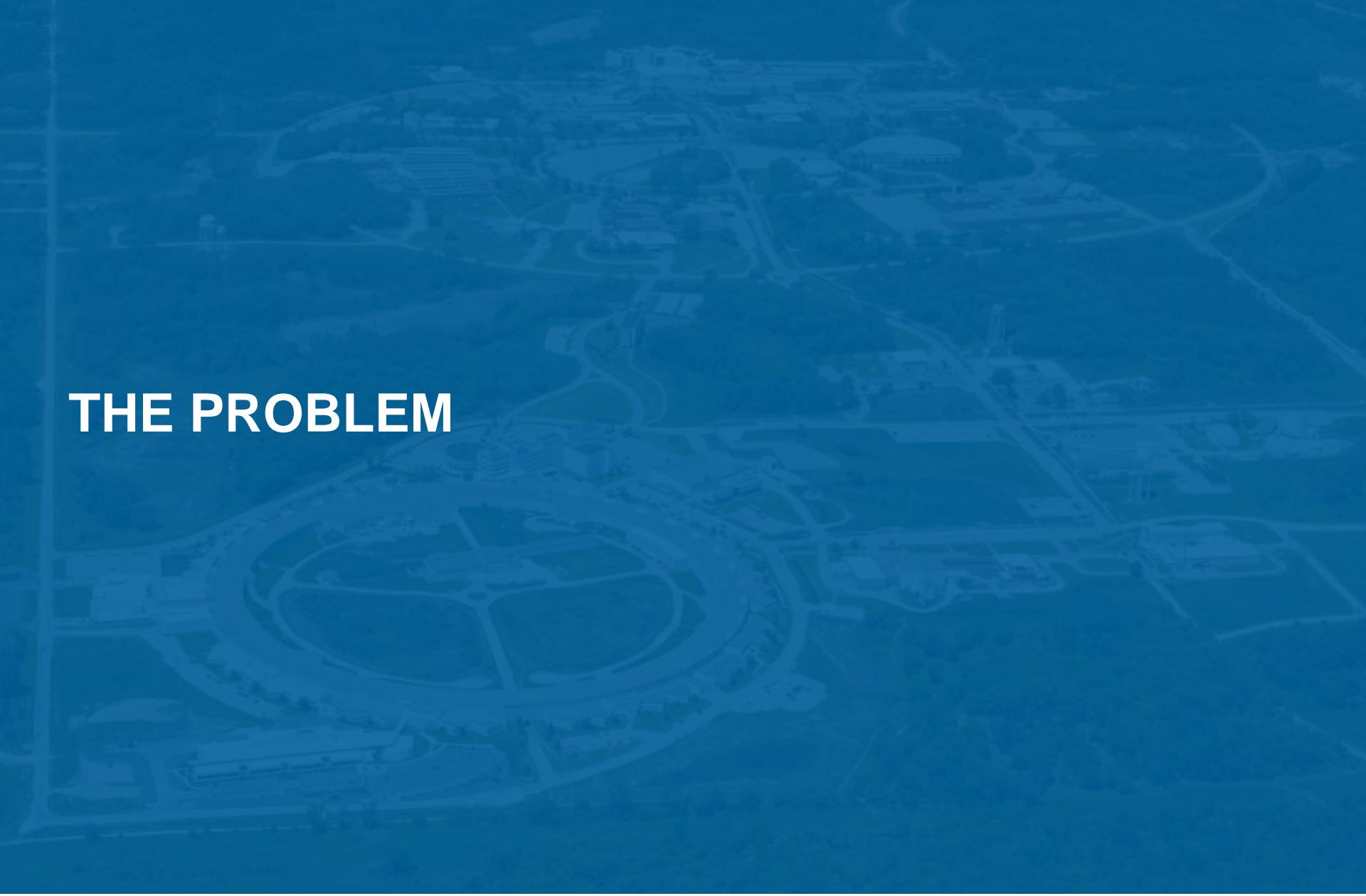
Argonne
NATIONAL LABORATORY

UNCERTAINTY OF THERMODYNAMIC DATA: HUMANS AND MACHINES



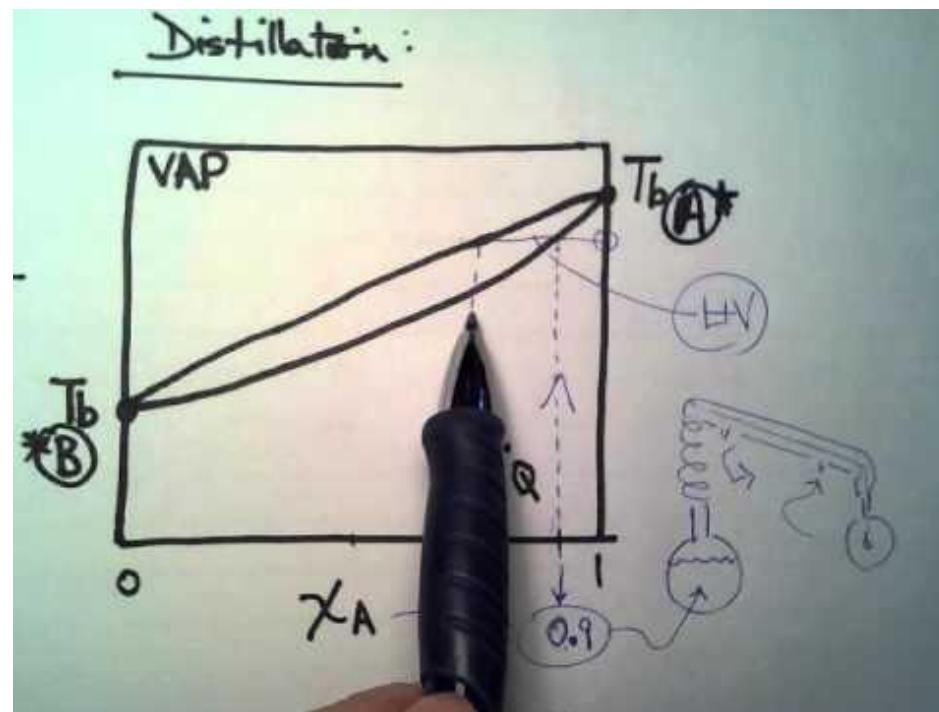
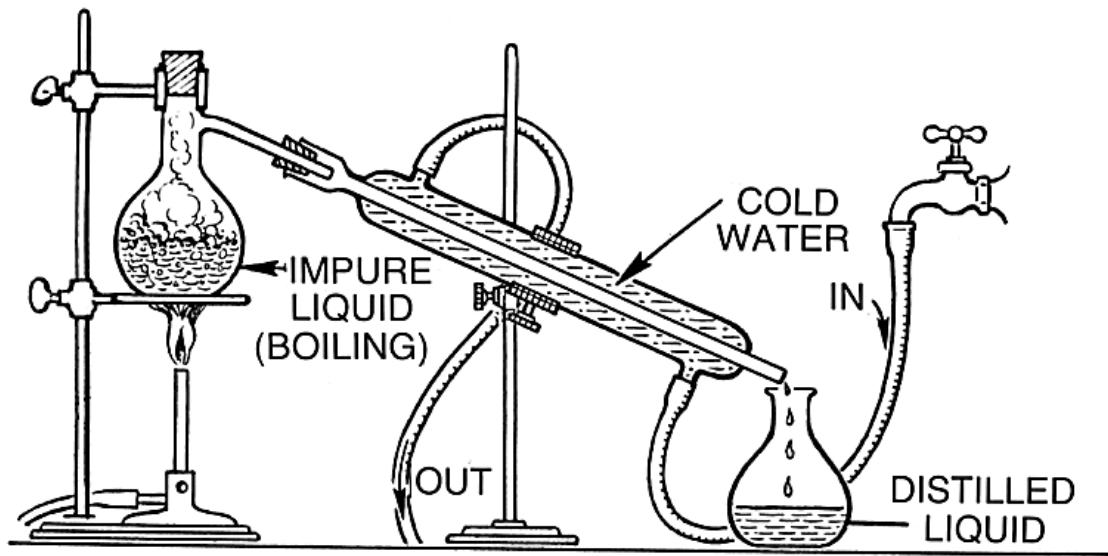
MARIUS STAN

Senior Scientist and Group Leader
Complex Physical Systems
Systems Security Center
ANL

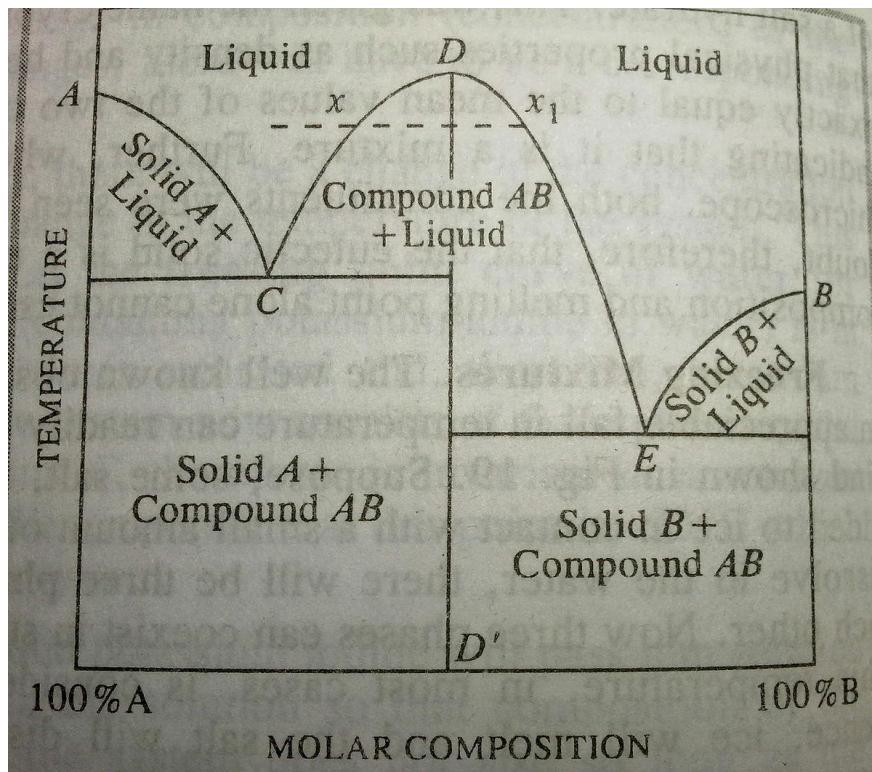
An aerial photograph of the Argonne National Laboratory complex. The image shows a large, sprawling research facility with numerous buildings, roads, and green spaces. In the foreground, there is a large, circular, open-area construction or industrial site. The surrounding area includes fields and other parts of the laboratory grounds.

THE PROBLEM

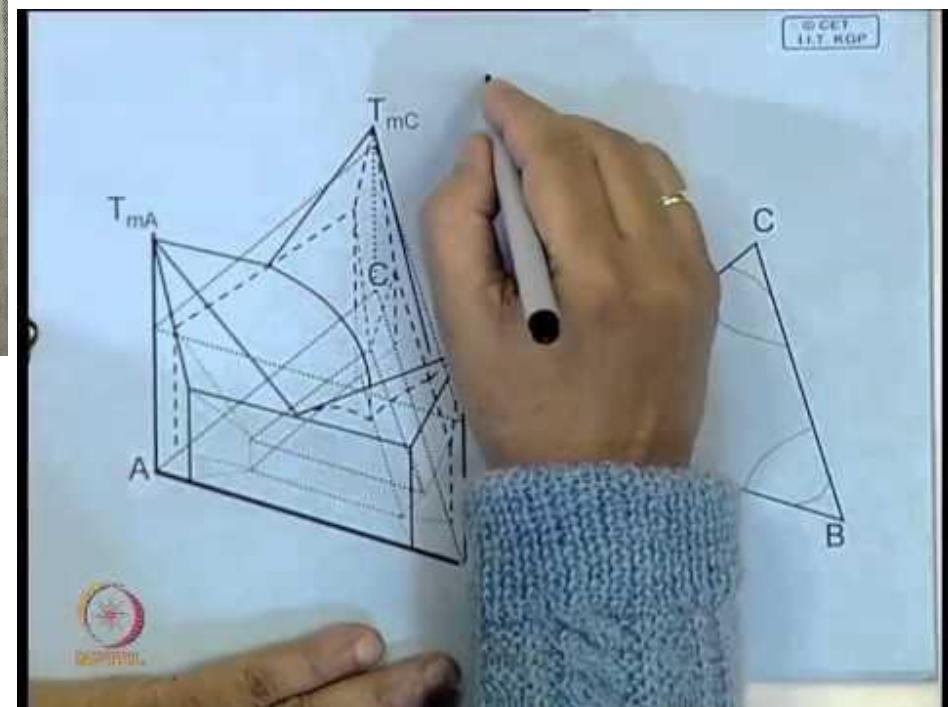
Temperature-composition phase diagrams



Humans can draw simple diagrams



Binary diagram



Ternary diagram

An aerial photograph of the Argonne National Laboratory campus, showing a large, sprawling complex of buildings and green spaces. The image is heavily desaturated, giving it a blue-toned, almost monochromatic appearance.

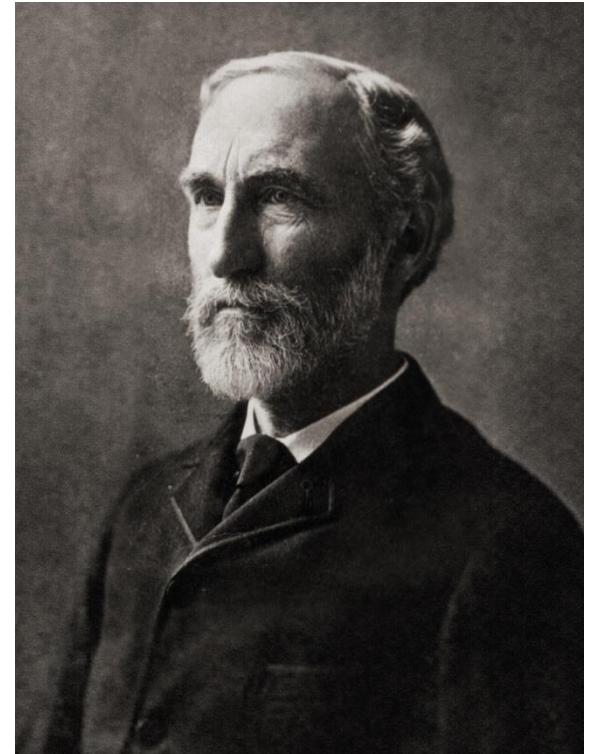
HUMANS ONLY

The Gibbs rule

At thermodynamic equilibrium, the chemical potential of each component A, B, C ... must be the same in all phases $\alpha, \beta, \gamma \dots$

$$\mu_A^\alpha(T, P, x^\alpha) = \mu_A^\beta(T, P, x^\beta)$$

$$\mu_B^\alpha(T, P, x^\alpha) = \mu_B^\beta(T, P, x^\beta)$$



Josiah Willard Gibbs
(1839-1903)

Calculating equilibrium binary phase diagrams

Free energy of components A, B, C ...
in phases $\alpha, \beta, \gamma \dots$

$$G_{A,B,C\dots}^{\alpha,\beta,\gamma\dots}(T,P,x)$$

Chemical potentials

$$\mu_A^\alpha(T,P,x) = G^\alpha(T,P,x) - x \left[\frac{\partial G^\alpha(T,P,x)}{\partial x} \right]_{T,P}$$

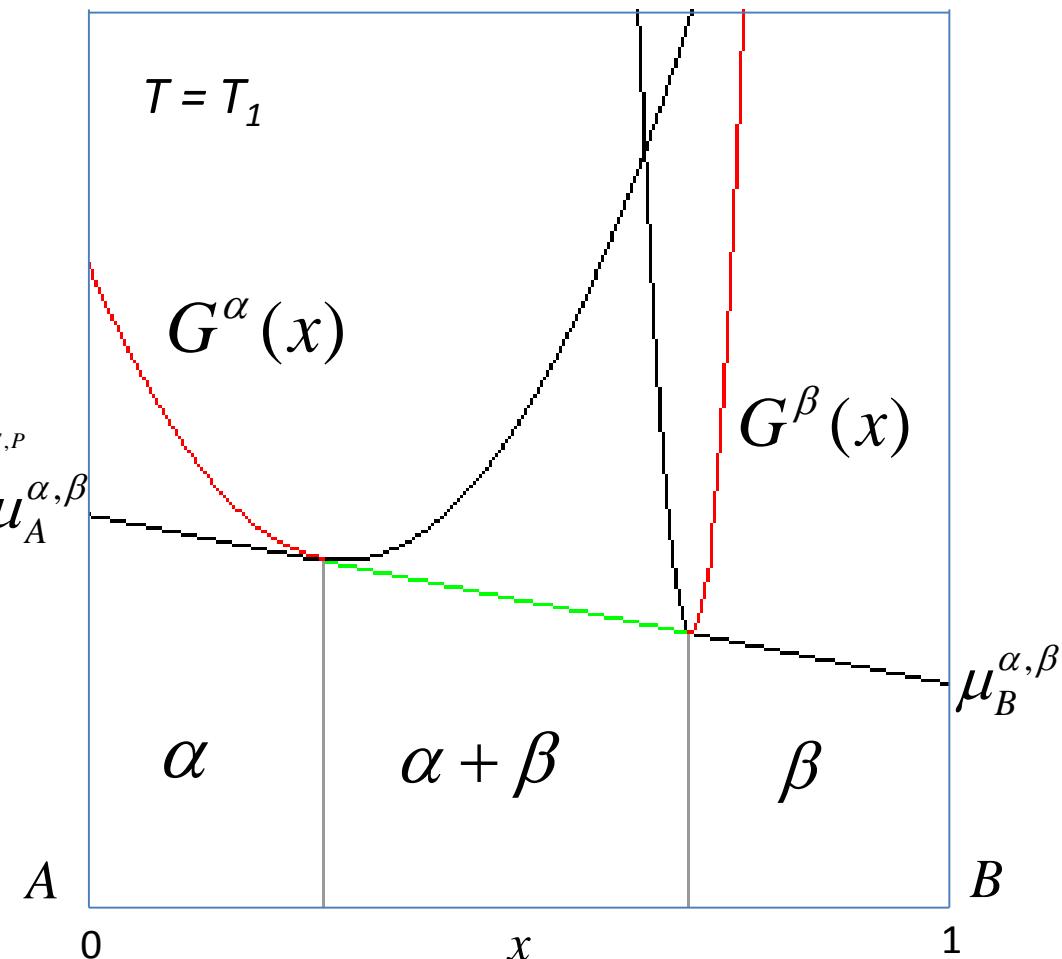
$$\mu_B^\alpha(T,P,x) = G^\alpha(T,P,x) + (1-x) \left[\frac{\partial G^\alpha(T,P,x)}{\partial x} \right]_{T,P}$$

Thermodynamic equilibrium
(Gibbs' rule)

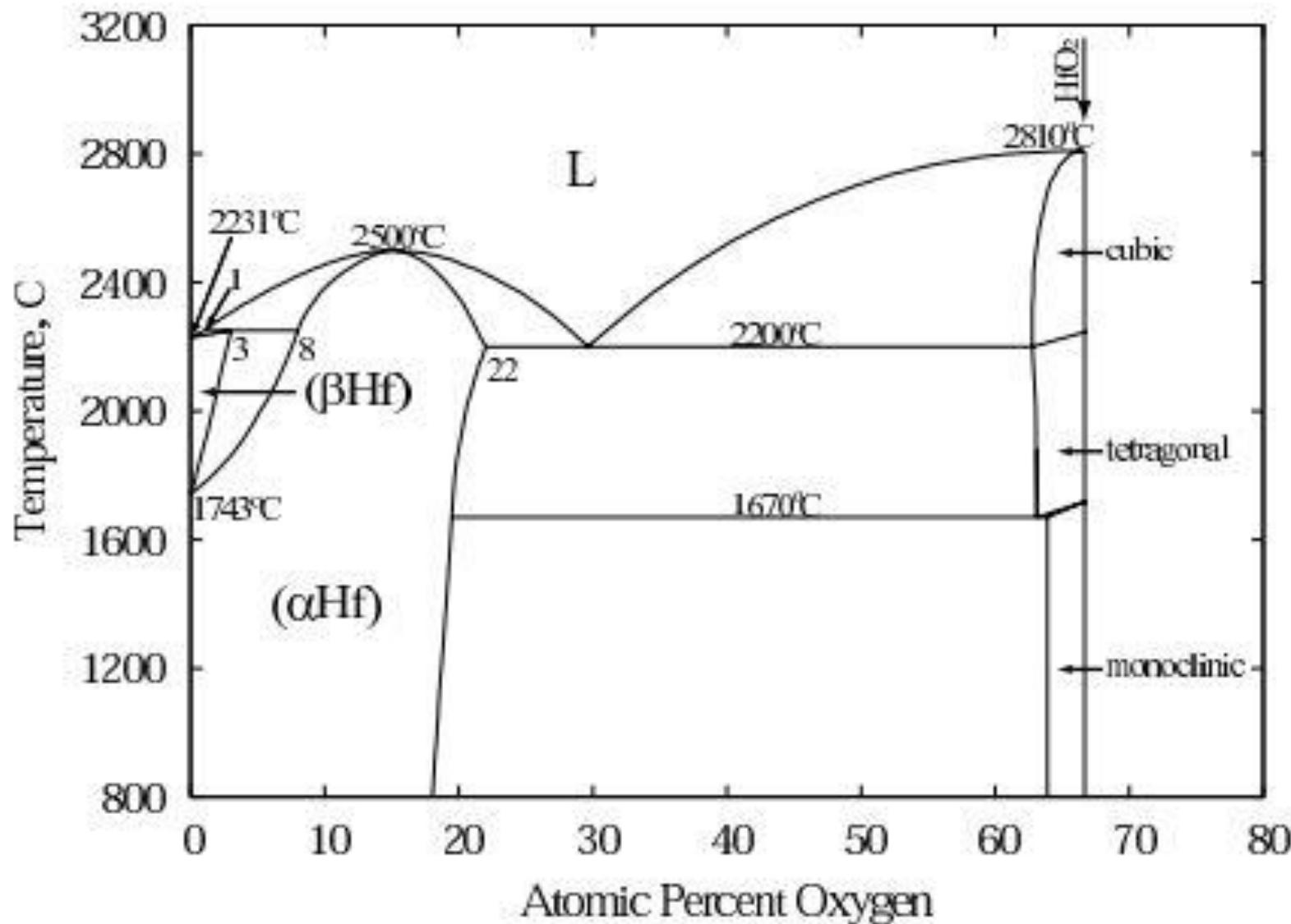
$$\mu_A^\alpha(T,P,x^\alpha) = \mu_A^\beta(T,P,x^\beta)$$

$$\mu_B^\alpha(T,P,x^\alpha) = \mu_B^\beta(T,P,x^\beta)$$

Phase diagram



The Hf-O Phase Diagram



HUMANS AND MACHINES

Melting via Molecular Dynamics



Enthalpy $H^L = f(T, P, x)$
 $H^S = f(T, P, x)$

Predicting the equilibrium phase diagrams from atomistic simulations

Free energy of components A, B, C ...
in phases α, β, γ ...by thermal integration^{1,2}

$$\frac{G(T, P, x)}{T} = \frac{G^{ref}(T^{ref}, P, x)}{T^{ref}} - \int_{T^{ref}}^T \frac{H(T', P, x)}{T'^2} dT'$$

↓

Chemical potentials by
composition derivation

$$\mu_A^\alpha(T, P, x) = G^\alpha(T, P, x) - x \left[\frac{\partial G^\alpha(T, P, x)}{\partial x} \right]_{T, P}$$

$$\mu_B^\alpha(T, P, x) = G^\alpha(T, P, x) + (1-x) \left[\frac{\partial G^\alpha(T, P, x)}{\partial x} \right]_{T, P}$$

↓

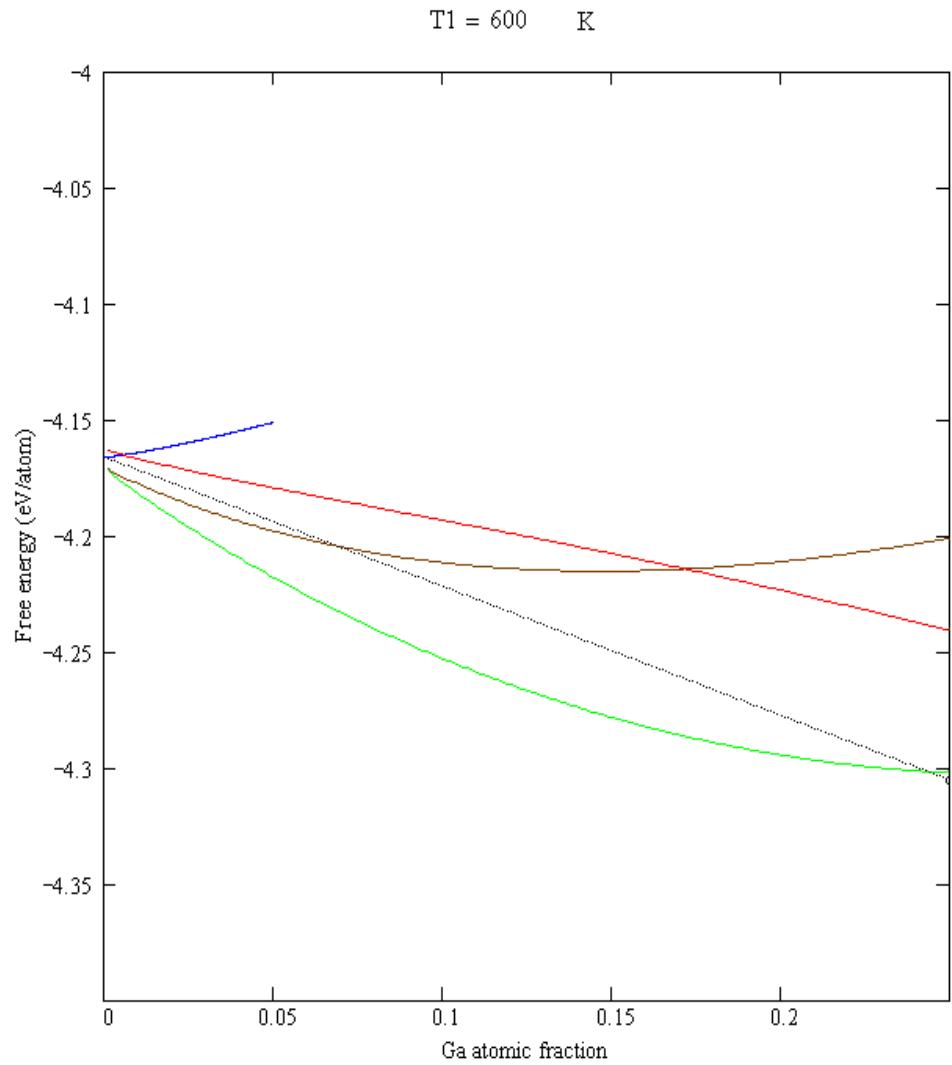
Thermodynamic equilibrium
(Gibbs' rule)

$$\mu_A^\alpha(T, P, x^\alpha) = \mu_A^\beta(T, P, x^\beta)$$

$$\mu_B^\alpha(T, P, x^\alpha) = \mu_B^\beta(T, P, x^\beta)$$

↓

Phase diagram



¹M. I. Baskes, K. Muralidharan, M. Stan, S. M. Valone, and F. J. Cherne, JOM, 55 (2003) 41-50.

²M. I. Baskes and M. Stan, Metall. Mater. Trans. 34A (2003) 435-39

LEARNING MACHINES

The Bayesian Method¹

Take a guess → Acquire info → Improve model

$$\sigma(M_j | D) = \frac{P(D | M_j)P(M_j)}{\sum_{i=1}^N P(D | M_i)P(M_i)}$$

Prior
↓
Posterior



Reverend Thomas Bayes
(1702-1761)

That is how Humans and Machines learn

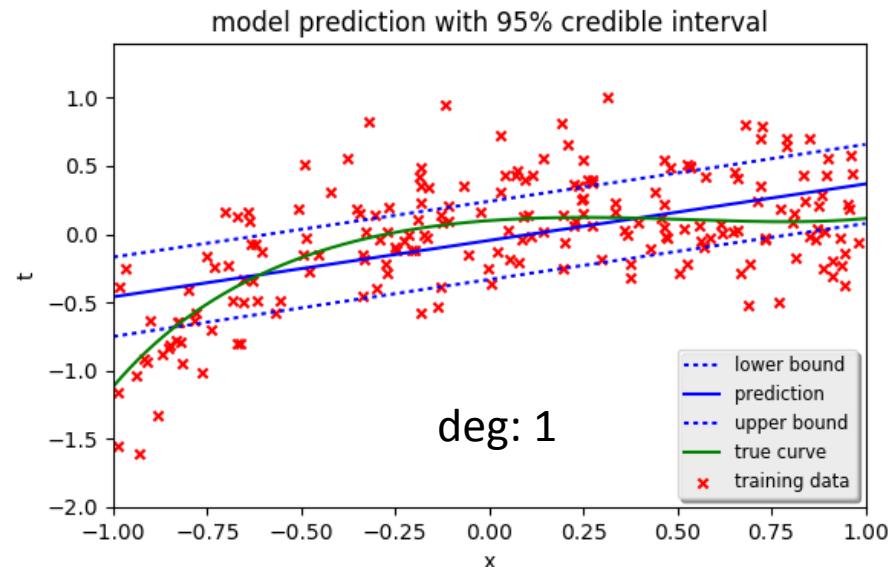
¹Philosophical Transactions of London, 53 (1763) 370 (free on Google Books).

Bayesian Polynomial Regression

Bayes Rule:

$$p(\mathbf{w}|\mathbf{X}, \mathbf{t}) \propto p(\mathbf{t}|\mathbf{X}, \mathbf{w})p(\mathbf{w})$$

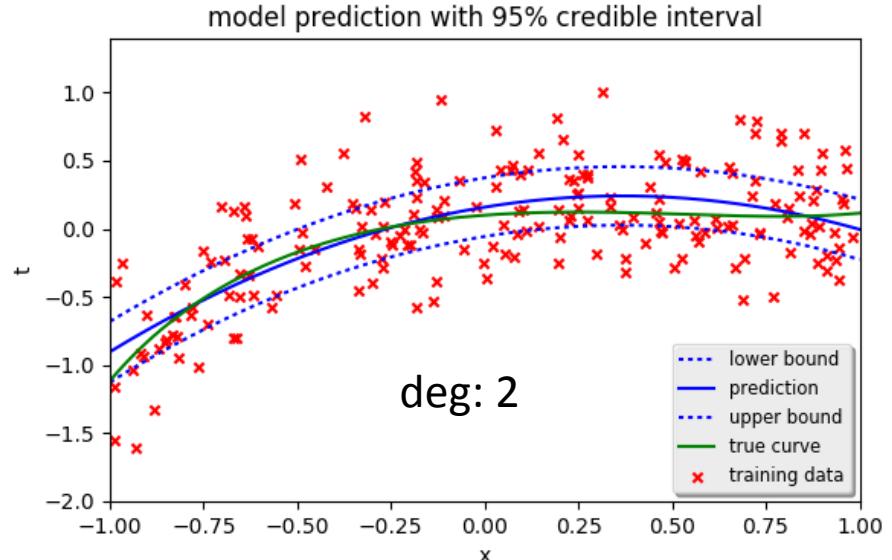
posterior likelihood prior



predictive distribution:

$$p(\mathbf{t}|\mathbf{x}, \mathbf{X}, \mathbf{t}) = \int p(\mathbf{t}|\mathbf{x}, \mathbf{w}) p(\mathbf{w}|\mathbf{X}, \mathbf{t}) d\mathbf{w}$$

likelihood posterior



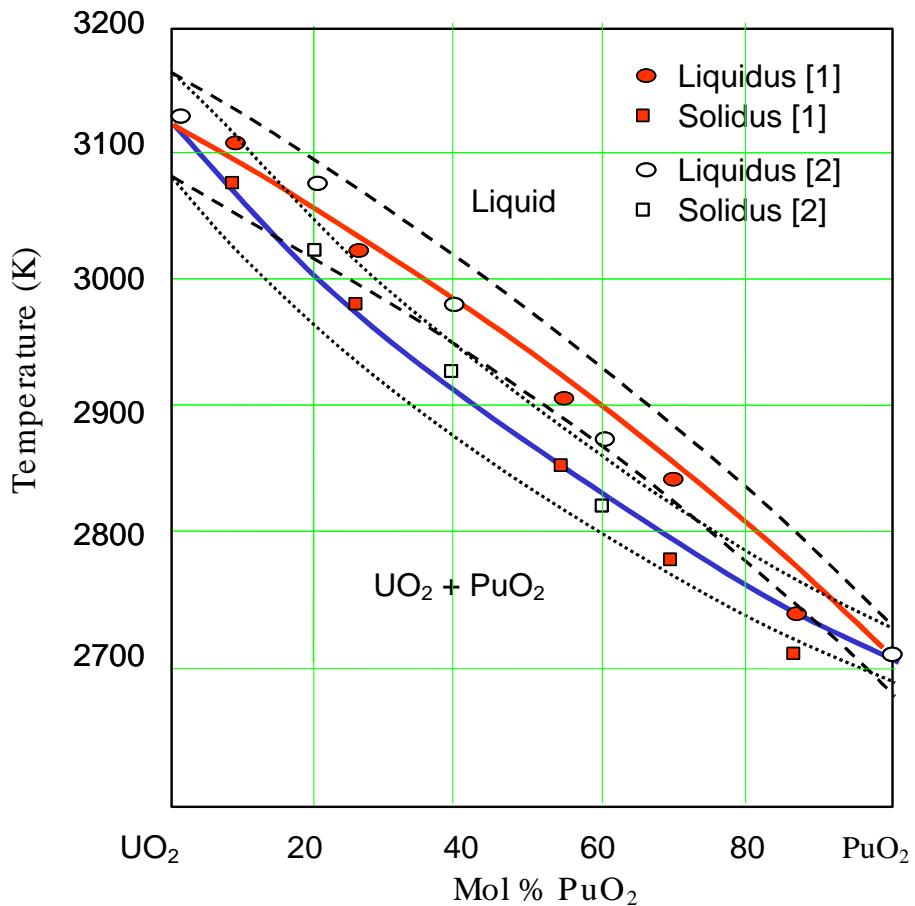
$\mathbf{w}^{(l)}$ samples using MCMC (Metropolis-Hastings algorithm)

Uncertainty Quantification of Phase Diagrams

- Uncertainty in fuel thermo-mechanical properties is often >10%
- Uncertainty of chemical properties (free energy) can be 10-15 %

Example:

- Uncertainty quantification the $\text{UO}_2\text{-PuO}_2$ phase diagram*. $\Delta T = \pm 50\text{K}$, $\delta c = 5\%$
- Bayesian analysis of 15 data sets (melting temperatures , transformation enthalpies, ...).
- Optimization via a genetic algorithm.



* M. Stan and B. J. Reardon, *CALPHAD*, **27** (2003) 319-323.

[1] M. G. Adamson, E. A. Aitken, and R. W. Caputi, *J. Nucl. Mater.*, **130** (1985) 349-365.

[2] T. D. Chikalla, *J. Am. Ceram. Soc.*, **47** (1964) 309-309.

Bayesian Analysis

Diagram line model

$$x^L = f(T, \Delta H_A^L, \Delta H_B^L, T_A^m, T_B^m)$$

$$x^S = f(T, \Delta H_A^S, \Delta H_B^S, T_A^m, T_B^m)$$

Model parameter vector

$$M = (\Delta H_A^M, \Delta H_B^M, T_A^M, T_B^M)^T$$

Data vector

$$D = (D_1, D_2, \dots, D_N)^T$$

Bayes' Theorem

$$\sigma(M_j | D) = \frac{P(D | M_j) P(M_j)}{\sum_{i=1}^N P(D | M_i) P(M_i)}$$

The mean model

$$\langle M \rangle = \sum_i M_i \sum_j \sigma(M_j | D_j)$$

Posterior covariance matrix

$$C = \sum_i M_i M_i^T \sigma(M_i | D) - \langle M \rangle \langle M \rangle^T$$

Standard deviation

$$STD = \sqrt{C_{ll}}$$

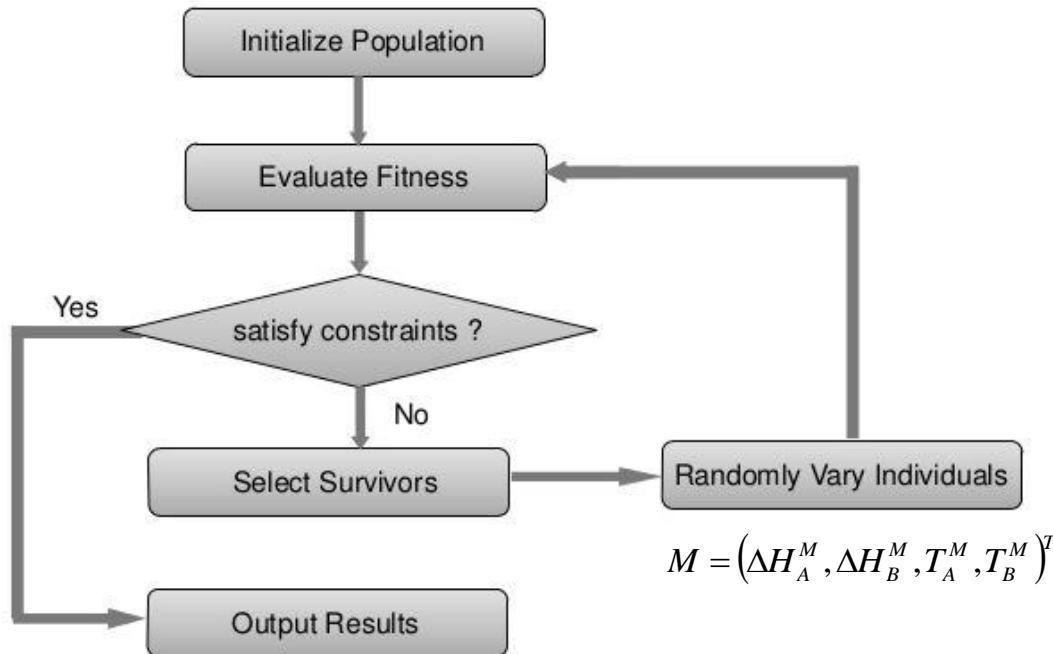
Correlation matrix

$$R_{lm} = \frac{C_{lm}}{\sqrt{C_{ll}} \sqrt{C_{mm}}}$$

Evolutionary (Genetic) Algorithms

$$D = (D_1, D_2, \dots, D_N)^T$$

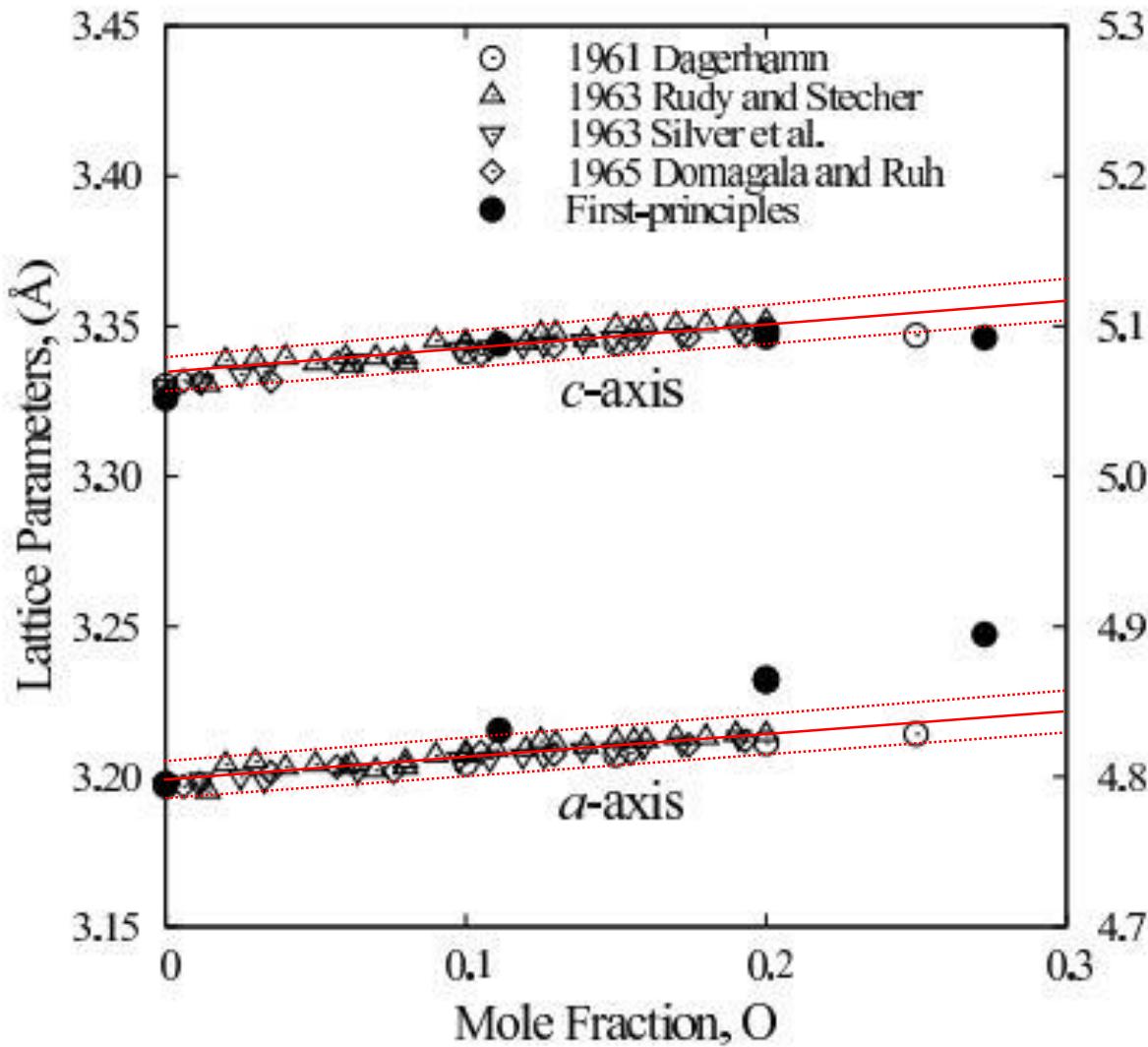
$$M = (\Delta H_A^M, \Delta H_B^M, T_A^M, T_B^M)^T$$



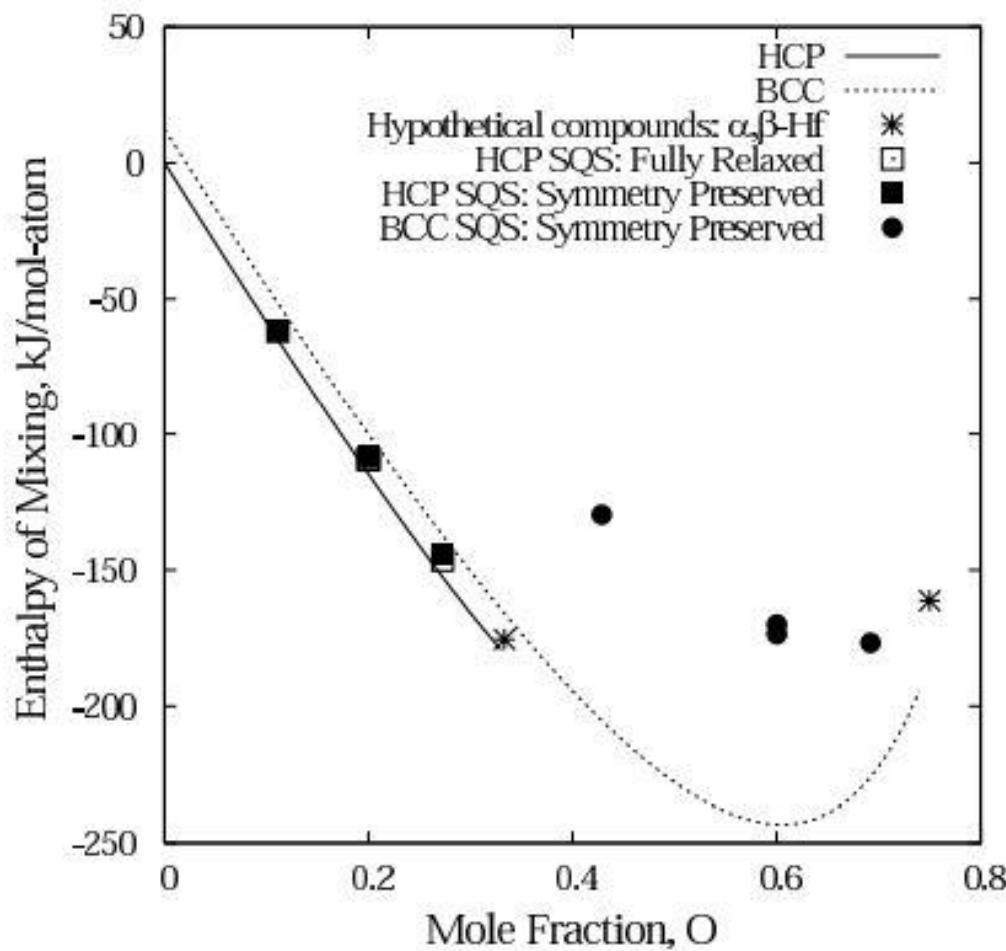
$$M = (\Delta H_A^M, \Delta H_B^M, T_A^M, T_B^M)^T$$

$$\begin{aligned}x^L &= f(T, \Delta H_A^L, \Delta H_B^L, T_A^m, T_B^m) \\x^S &= f(T, \Delta H_A^L, \Delta H_B^L, T_A^m, T_B^m)\end{aligned}$$

Uncertainty of Hf-O Lattice Parameters

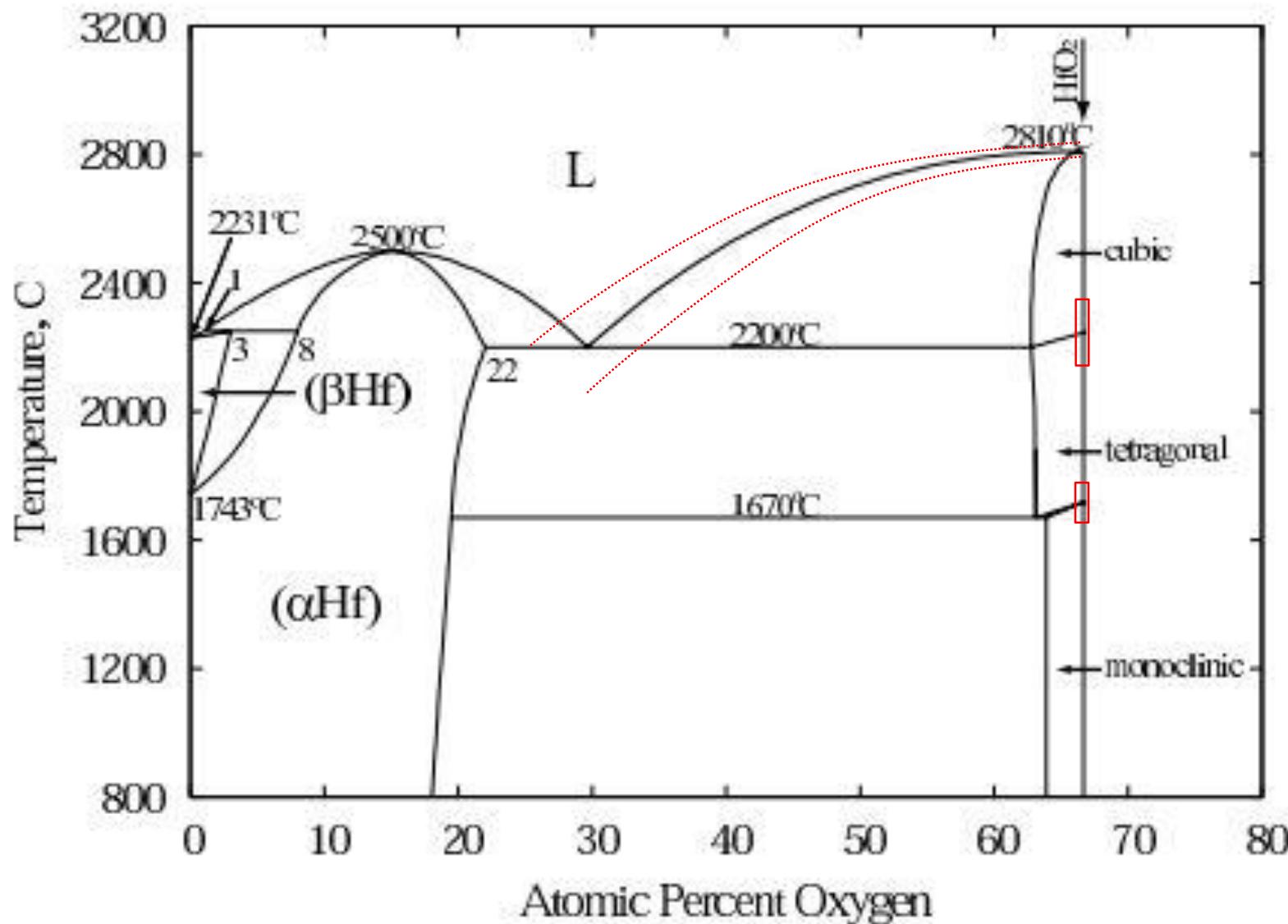


Thermodynamics of Hf-O¹



¹D. Shin, R. Arroyave, Z.K. Liu, CALPHAD, 30 (2006) 375-386

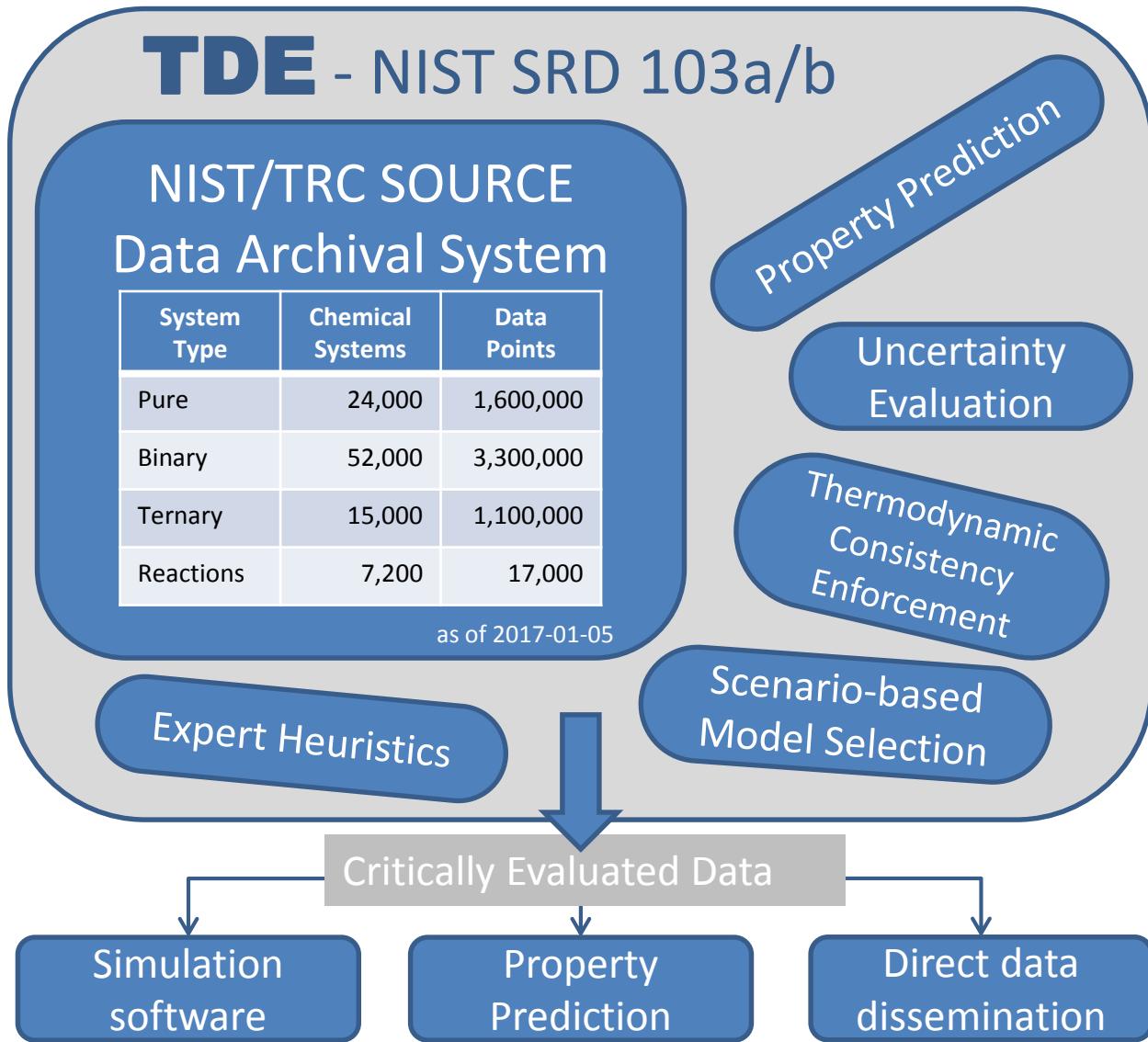
Uncertainty of the Hf-O Phase Diagram



THERMODYNAMIC DATA

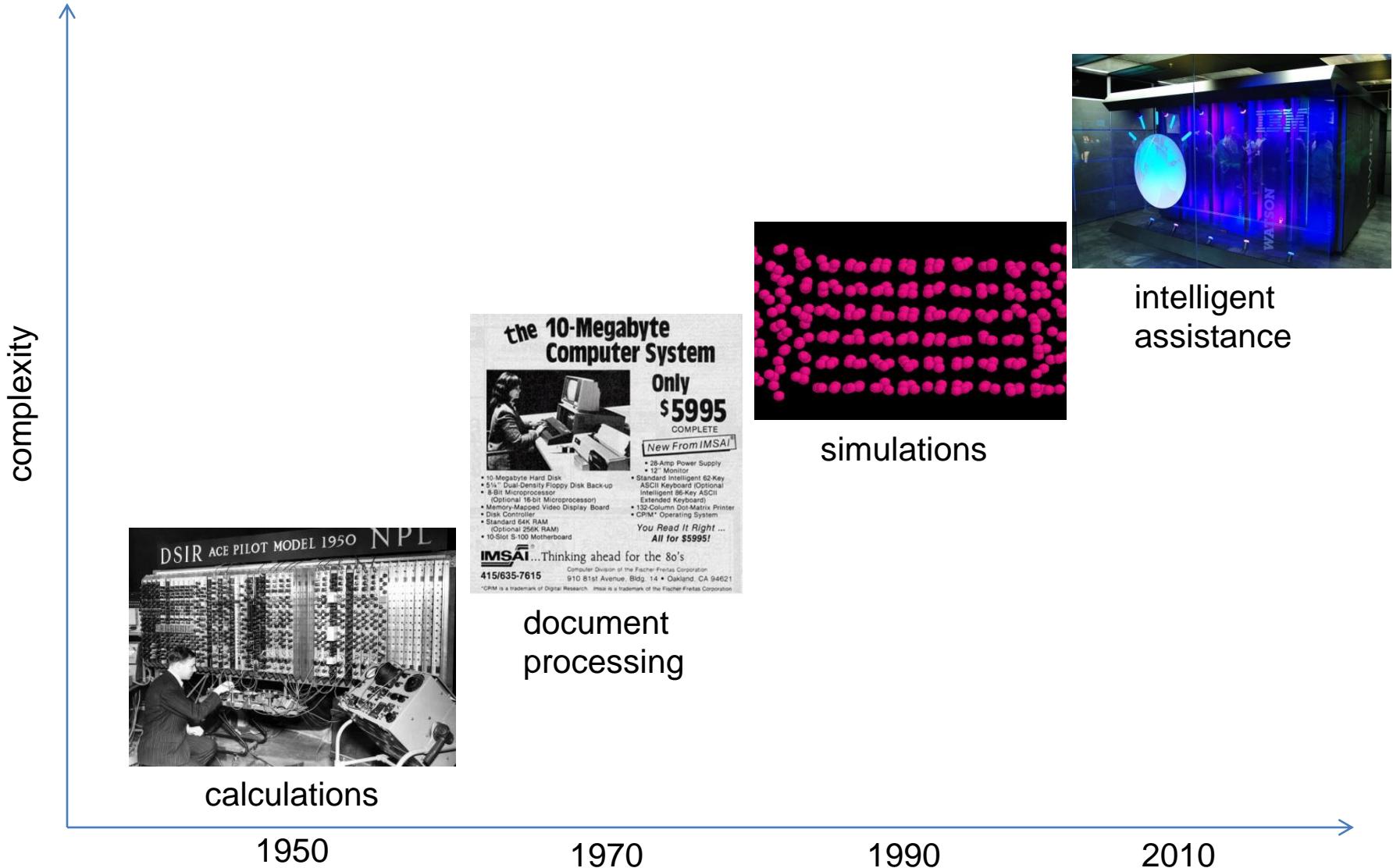
NIST ThermoData Engine (TDE)

- Requires
 - Knowledge Base: A trusted data archive with full, machine-interpretable metadata
 - Inference Engine: software developed via systematic, test-driven analysis of real data systems with a team of subject experts
- Delivers
 - A virtual data expert backed by a well-curated library for engineers



OUTLOOK

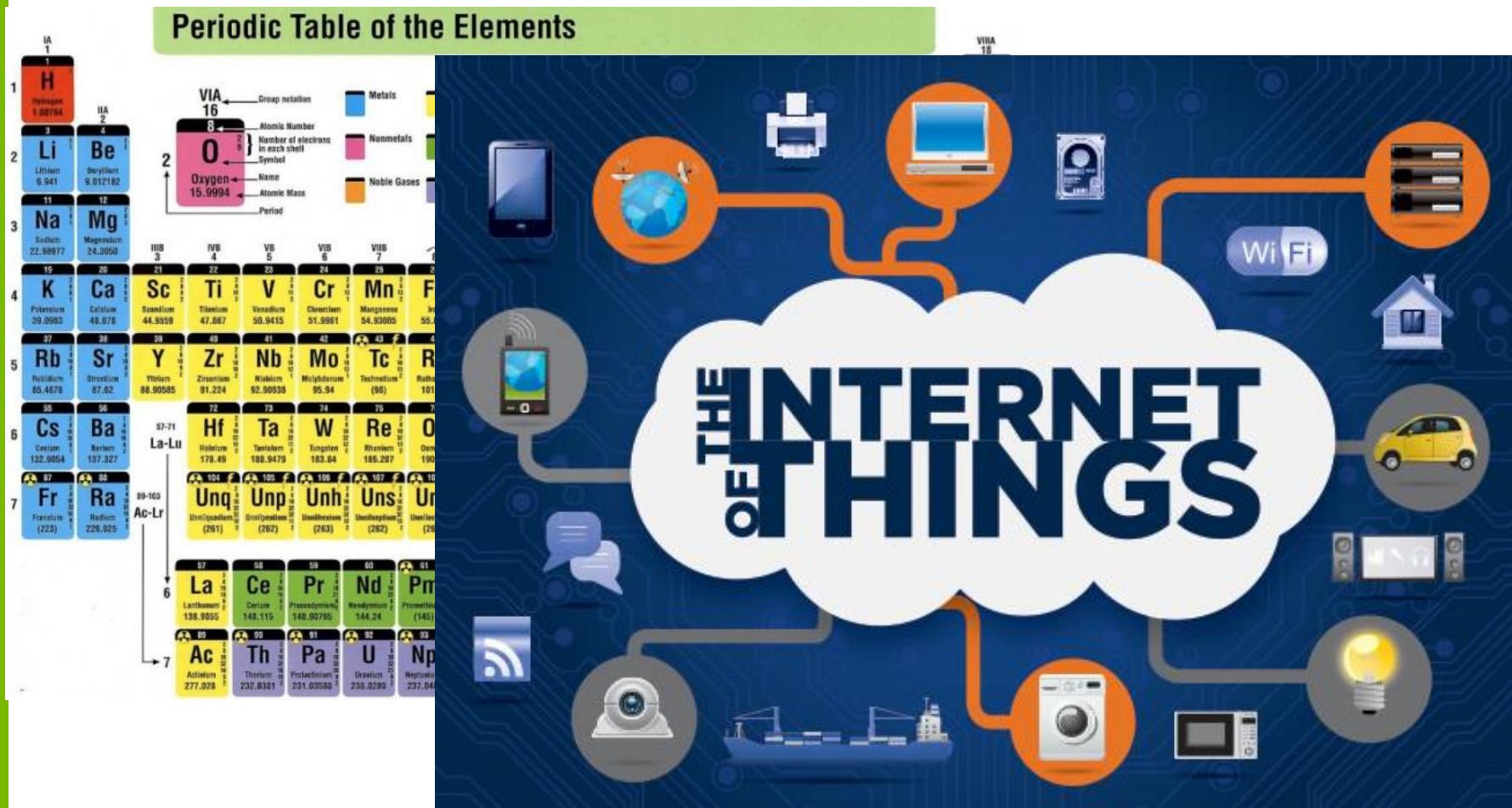
The role of computation is changing



Impact on Science and Technology

MATERIAL GENOME INITIATIVE

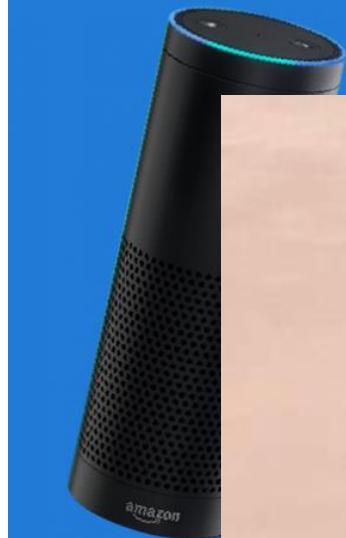
*Create a multi-dimensional Periodic Table of
multi-component, multi-phase materials*



Impact on You

Immersive visualization

Personal assistance



Augmented reality

