Phase Diagram Modelling of Cast Energetic Materials

Kevin M. Jaansalu
Department of Chemistry and Chemical Engineering
Royal Military College of Canada

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Outline

- Approach and Thermodynamic Basis
- Pure Components
  - TNT, RDX, HMX
- Binary Phase Diagrams
  - TNT – RDX & HMX – RDX Systems
- Summary

Approach

- Apply the principles of phase diagram modelling to systems involving energetic materials
- Determine what information is important in these systems

Thermodynamic Basis

- With the solid and the liquid of a pure compound in equilibrium:

$$\Delta G = \Delta H_m - T_m \, \Delta S_m = 0$$

$$\Delta S_m = \frac{\Delta H_m}{T_m}$$

- Once state variables fixed, the difference as a function of temperature is:

$$\Delta G_{s \to l} = \Delta H_m - T \, \Delta S_m$$

Thermodynamic Basis

- Problem: previous equation embodies differences
- Heat capacity, Cp, is measured directly
- Generalise for a specific phase: liq, α, ..

$$G = \Delta H_f^0 + \int_{T_{ref}}^{T} C_p dT - T\left(S_{ref}^0 + \int_{T_{ref}}^{T} \frac{C_p}{T} dT \right)$$

- Preserve differences in the ΔG
  - *Implicitly defined a reference phase*

Thermodynamic Basis - Binary Systems

- At constant temperature, equilibrium between two phases, α and β, occurs when the partial molar Gibbs energy of each of the two components A and B are equal in both phases:

$$\overline{G_A}^{\alpha} = \overline{G_A}^{\beta} \quad \text{and} \quad \overline{G_B}^{\alpha} = \overline{G_B}^{\beta}$$

- The Gibbs energy of a solution is described by:

$$\begin{aligned} G = {} & x_A G_A^{ref} + x_B G_B^{ref} + x_A G_A^{\Delta phase} + x_B G_B^{\Delta phase} \\ & + RT\left(x_A \ln x_A + x_B \ln x_B\right) \\ & + x_A x_B (p_0 + p_1 x_B + p_2 x_B^2 + ..p_n x_B^n ..) \end{aligned}$$

Computational Tools

- Partial molar Gibbs energy determined numerically
- Computations repetitive and onerous
- Use specific software written for the purpose:
  - Here, FactSage 6.4 and Fact 2.2

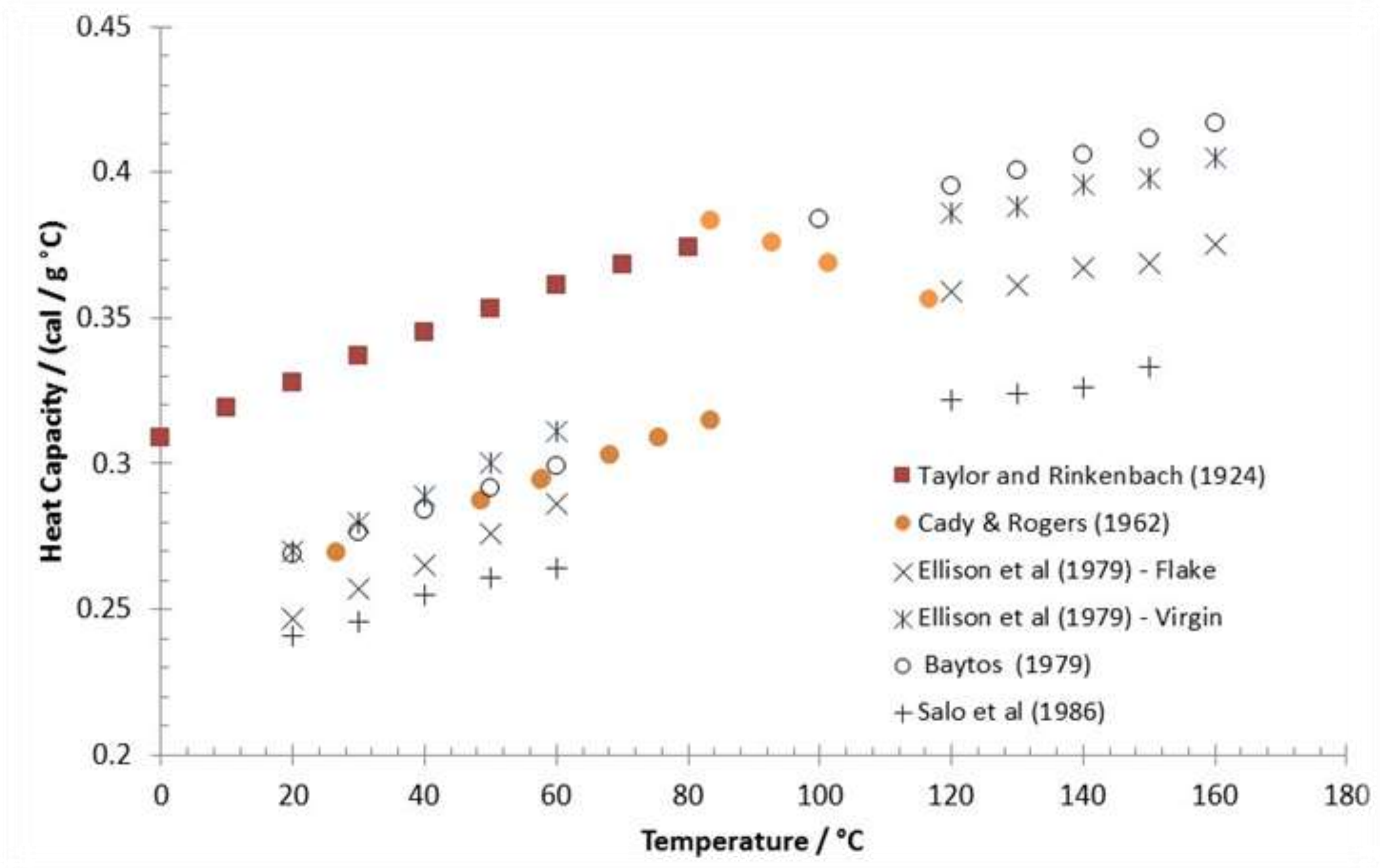
Pure Compound: TNT

- T_m= 80.8°C (393.95 K)
- $\Delta_{fus}h°$=23.5 cal g^{-1} (5250 cal mol^{-1})
- Heat capacity (cal $mol^{-1}K^{-1}$):

$$C_P^{solid} = 11.174 + 0.17035T \text{ and}$$

$$C_P^{liquid} = 140.61 + 0.12488T$$

Pure Compound: TNT



Heat capacity of TNT as a function of temperature.

Pure Compound: RDX

- T_m= 205.3°C (478.45 K)
- $\Delta_{fus}h°$ = 7356 cal mol^{-1}
- Heat capacity:

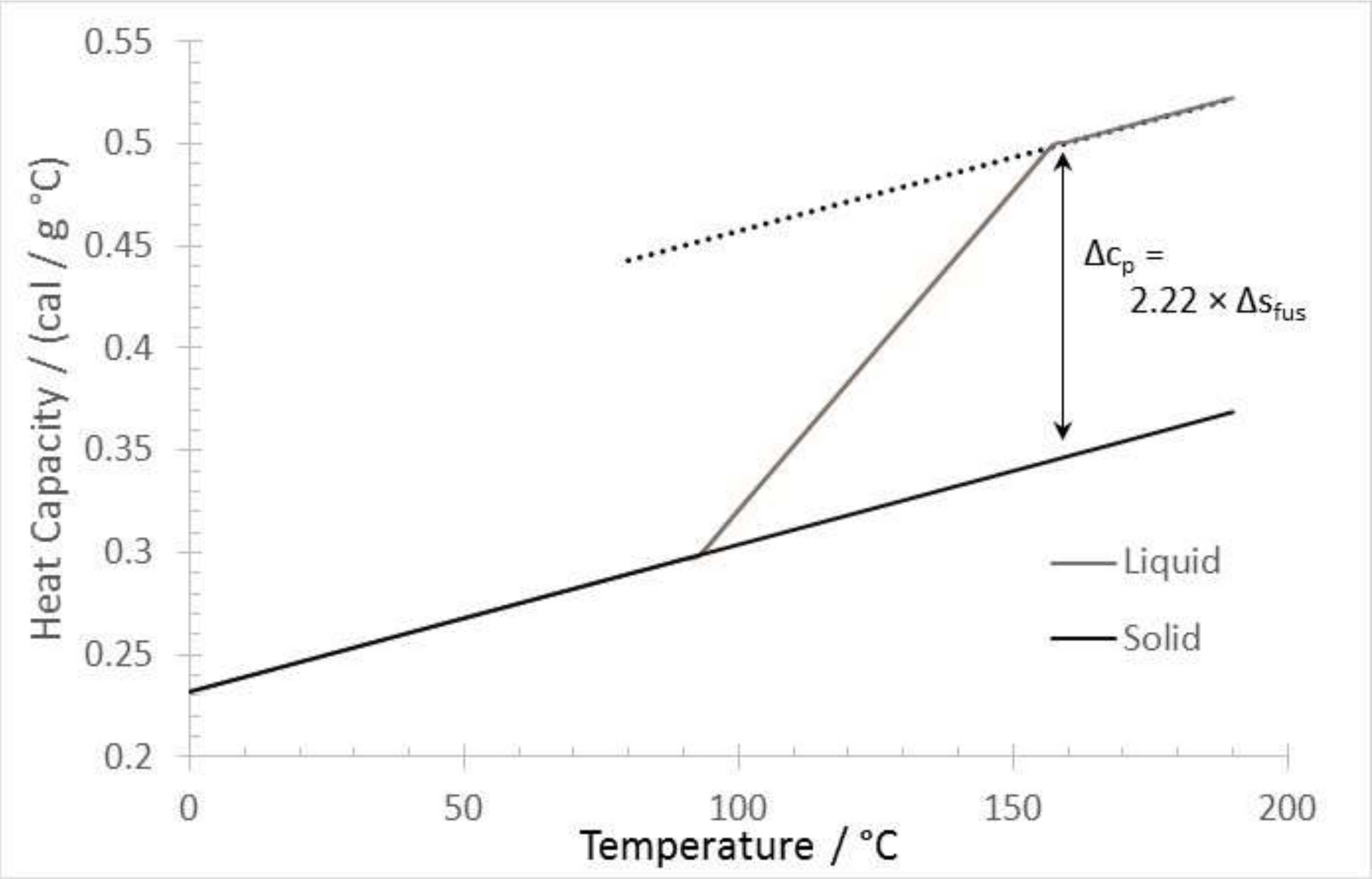
$$C_P^{solid} = 7.489 + 0.15992T \; and$$

$$C_P^{liquid} = C_P^{solid}, \; for \; T < 366K$$

$$C_P^{liquid} = -187.294 + 0.693T, \; for \; 366K < T < 430K$$

$$C_P^{liquid} = 42.011 + 0.15992T, \; for \; 430K < T$$

Pure Compound: RDX



Heat capacity of RDX solid and liquid as a function of temperature.

Pure Compound: HMX

- $T_m = 280.5°C\ (553.65\ K)$
- $T_{\beta \rightarrow \delta} = 157°C\ (430.15\ K)$
- $\Delta_{fus}h° = 9036\ cal\ mol^{-1}$
- $\Delta\ h°_{\beta \rightarrow \delta} = 2190\ cal\ mol^{-1}$
- Heat capacity:

$$C_P^{solid} = 23.916 + 0.1629T \ and$$

$$C_P^{liquid} = C_P^{solid}, for \ T < 415K$$

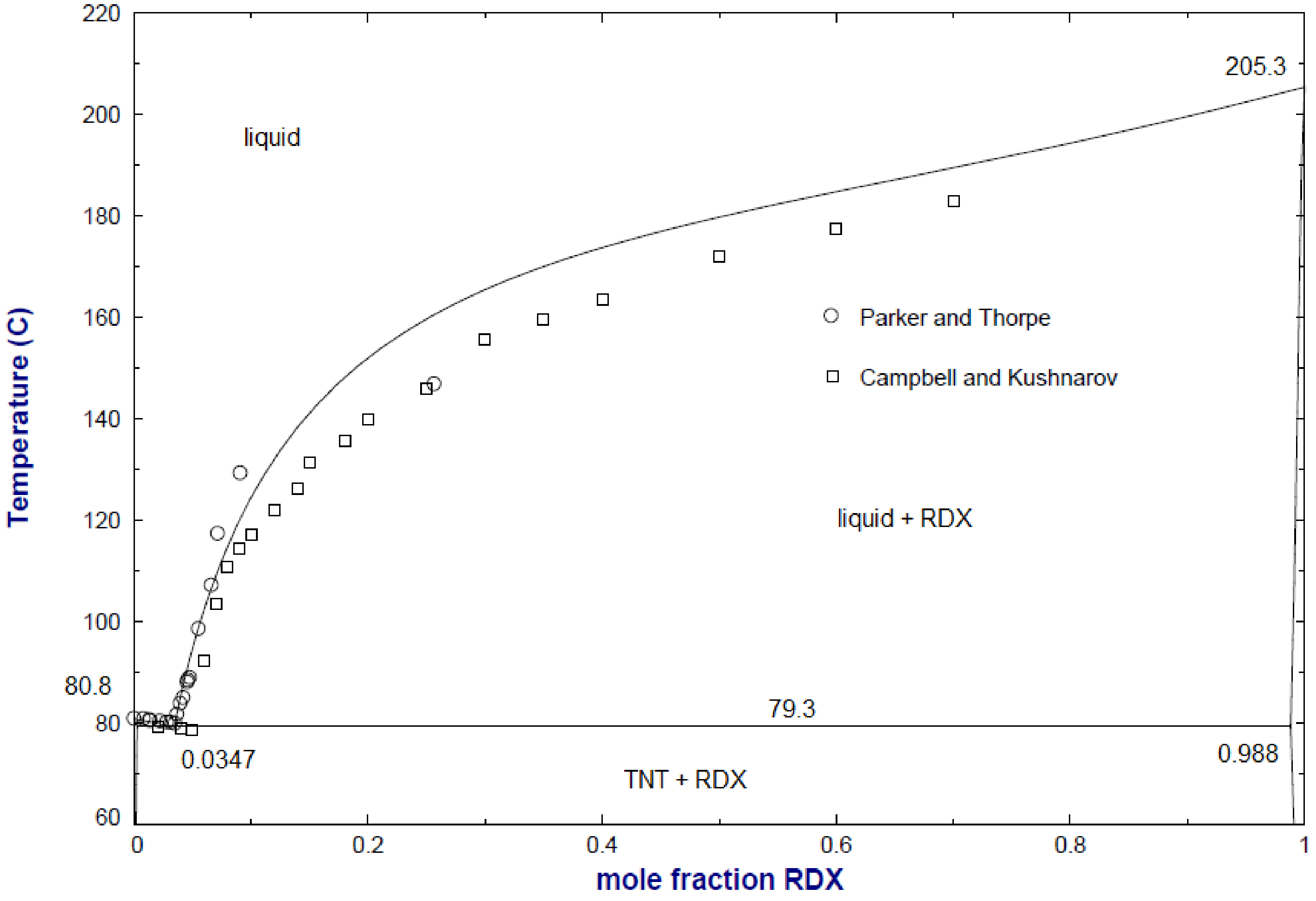
$$C_P^{liquid} = -157.419 + 0.600T, for \ 415K < T < 498K$$

$$C_P^{liquid} = 60.181 + 0.1629T, for \ 498K < T$$

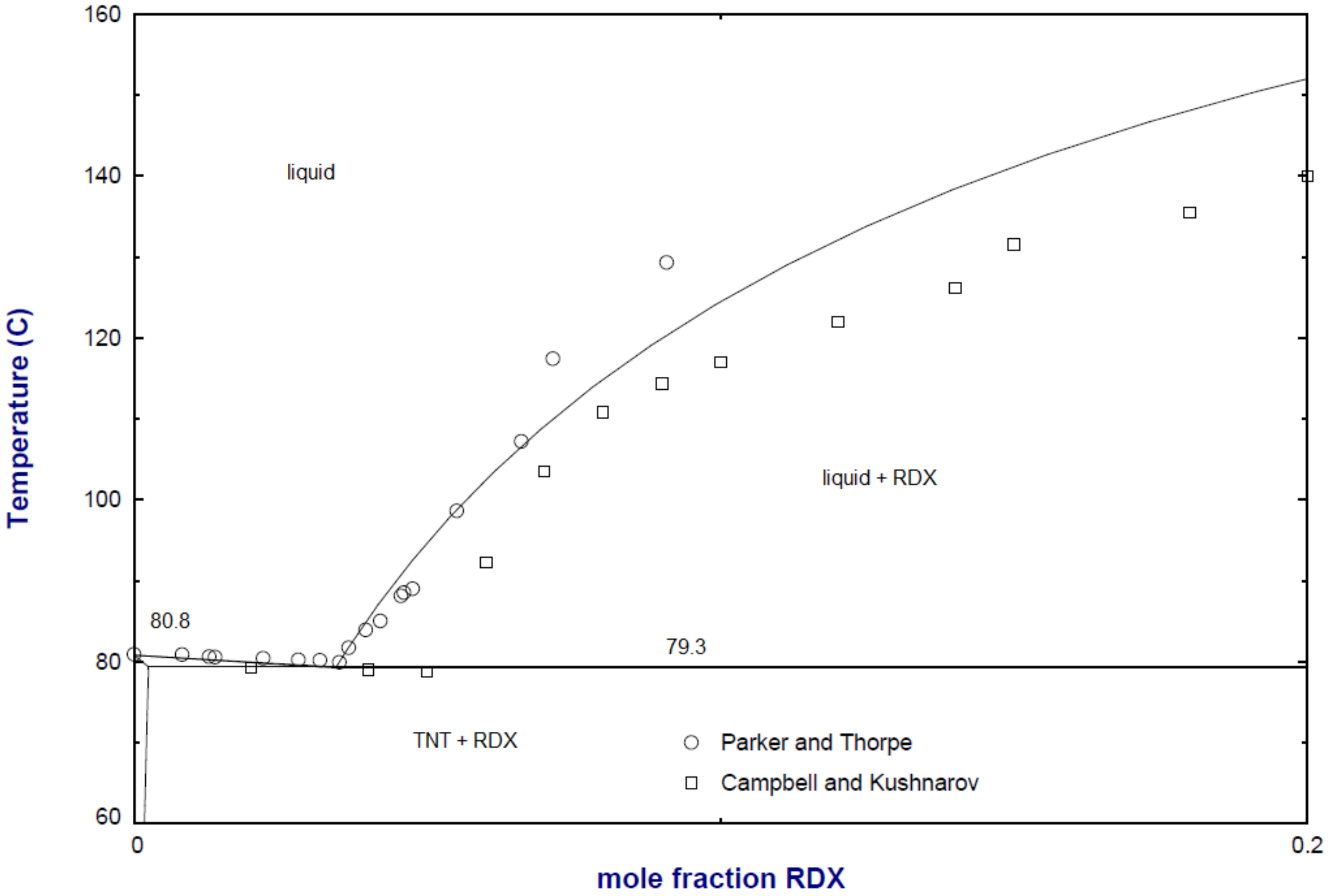
Binary Diagram: TNT – RDX

- RDX into TNT form: +3100 cal mol^{-1}
- TNT into RDX form: +3100 cal mol^{-1}
- Liquid: $G^{xs}=X_{TNT}X_{RDX}(1000\ \mathrm{cal\ mol}^{-1})$

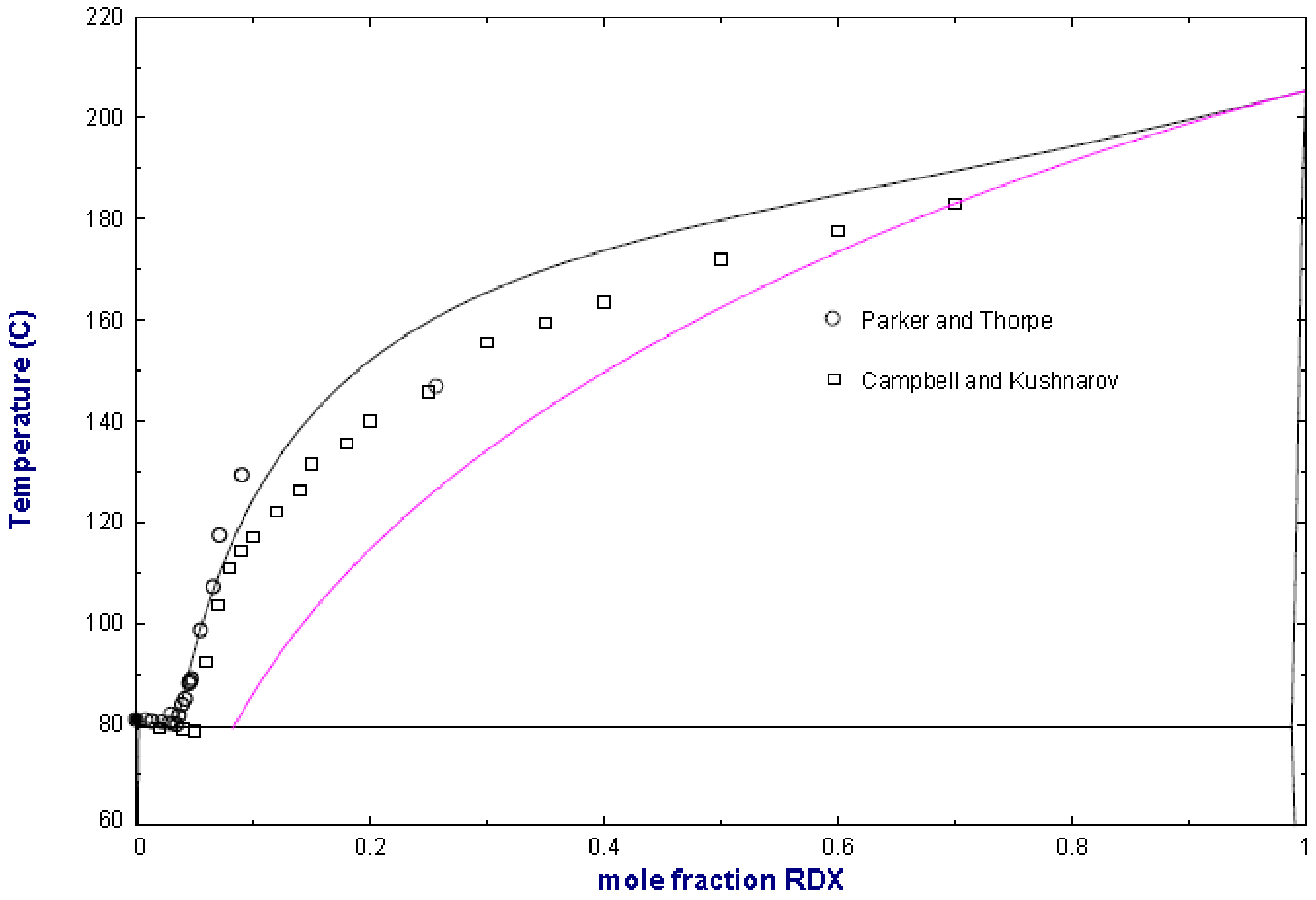
Binary Diagram: TNT – RDX



Binary Diagram: TNT – RDX



Binary Diagram: TNT – RDX



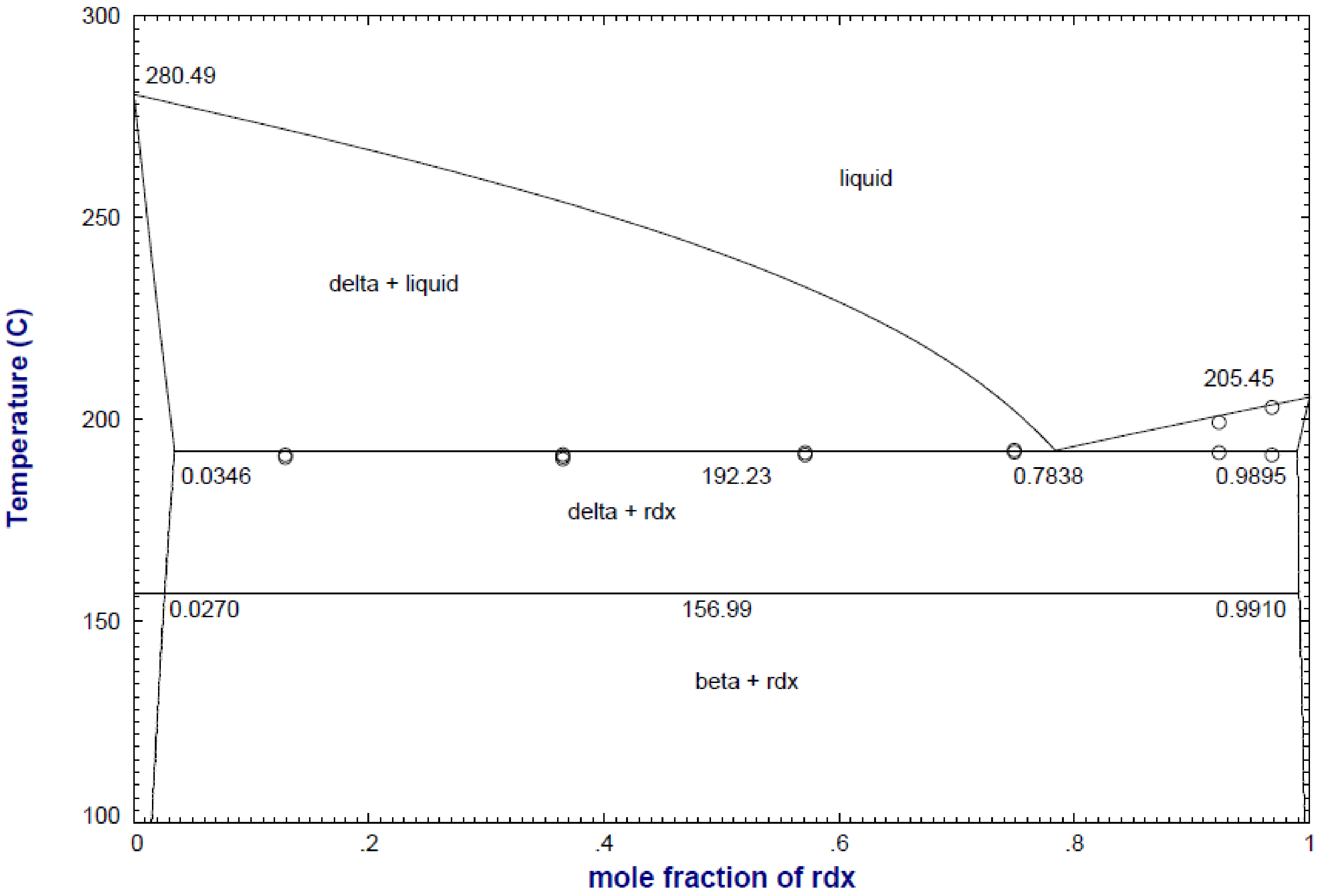
Change in Heat Capacity

- Magnitude of excess energy:
  - $G^{xs} = X_{TNT}X_{RDX}(1000 \text{ cal mol}^{-1})$
    $= 250 \text{ cal mol}^{-1}$ at $x=0.5$
- Magnitude of change in heat capacity:
  - $\Delta Cp \times \Delta T = (5 \text{ cal mol}^{-1}\text{K}^{-1}) \times 50 \text{ K}$
    $= 250 \text{ cal mol}^{-1}$
- Getting ΔCp information important

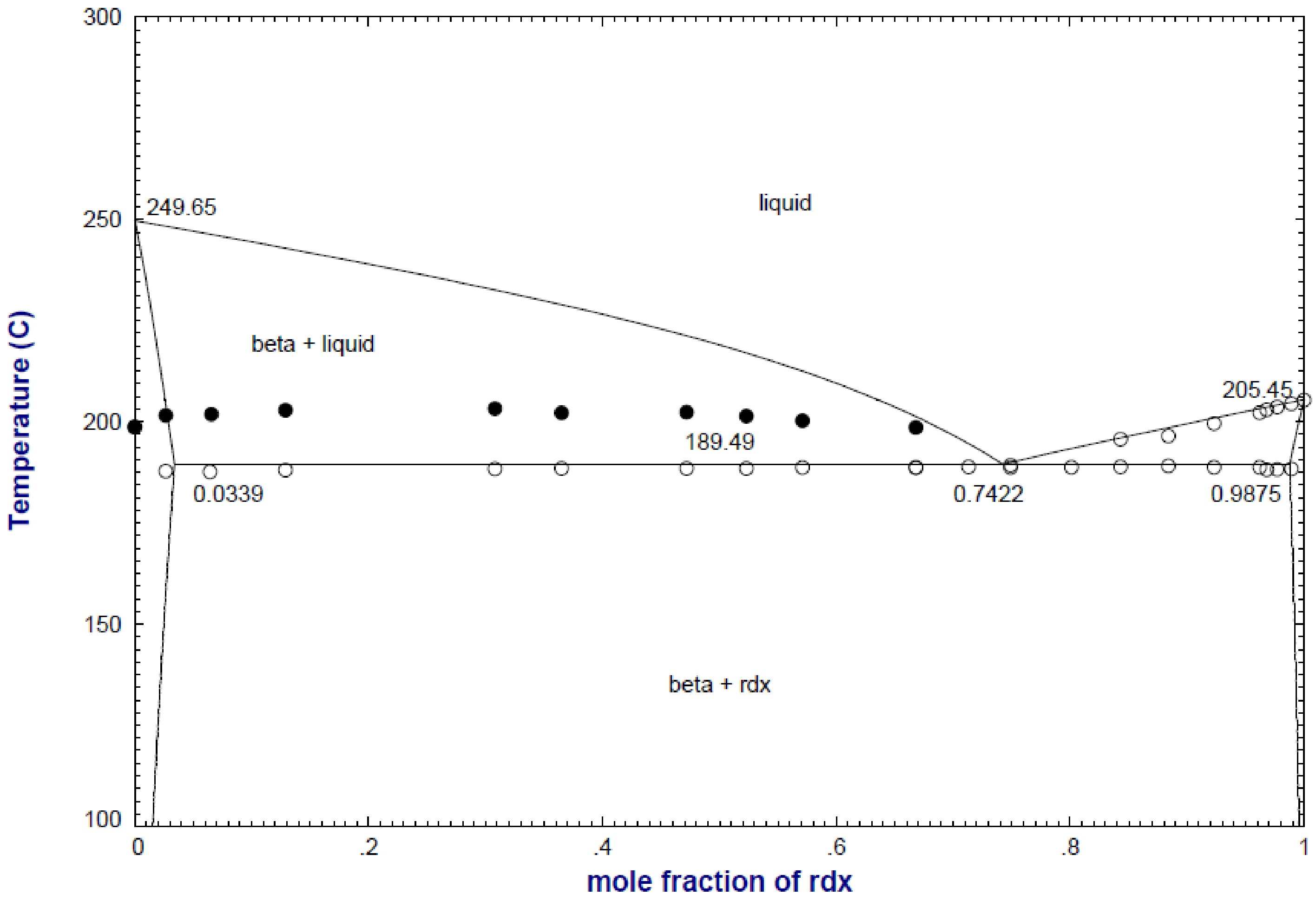
Binary Diagram: HMX – RDX

- RDX into HMX forms: +3100 cal mol^{-1}
- HMX into RDX form: +4000 cal mol^{-1}
- Liquid: $G^{xs}=X_{HMX}X_{RDX}(400\ \text{cal mol}^{-1})$

Binary Diagram: HMX – RDX



Binary Diagram: HMX – RDX



Energetics in HMX - RDX

- Energy expressions as a function of composition for the solutions
- Potential to investigate energy differences between phases
  - Nucleation Barrier
  - Mass Transfer

Summary

- Phase diagram features are
  - More dependent on the behavior of pure components
  - Less dependent on interactions in a (solid) solution
- Heat capacity is important
- Further work looking at better models and specific energetics of the transformation in HMX

Thank you for your attention

Questions?